MATHEMATICAL MODELLING FOR BIOLOGICAL WASTEWATER TREATMENT PLANTS, GAUTENG, SOUTH AFRICA

Report to the
WATER RESEARCH COMMISSION

by

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WRC Report No 2563/1/19
ISBN 978-0-6392-0114-6

February 2020

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EXECUTIVE SUMMARY

Emerging contaminants in the water bodies pose a health hazard to the environment and human health. Discharge of effluents from wastewater treatment plants (WWTPs) into water bodies contribute to water pollution. The WWTPs face challenges in removing contaminants in real-time due to the continuously changing process parameters, diversity and pollutant concentrations.

Conventional mathematical modelling and simulation, artificial intelligence/deep learning/machine learning/evolution computation/internet of things (IoT), blockchain, sensor and big data are becoming integral components and essential to describe, predict, forecast and control the complicated interaction of the wastewater treatment processes that are of revolutionized emerging technology breakthrough in the awareness and implementation of the fourth industrial revolution *(4IR)* era. This is due to complex biological reaction mechanisms, lack of reliable on-line instrumentation, unforeseen changes in microbes, organic and inorganic compounds, multivariable aspects of the real wastewater treatment plant *(WWTP)* and highly time-varying that create a need for the intelligent technique for analysis of multi-dimensional process data known as the 'big data' and diagnoses of inter-relationship of the process variables in the *WWTPs.* The physical, measured and performance parameters were analysed according to international standards.

Review on the existing models were taken into consideration to reach a consensus concerning the simplest models that possess the capability of realistic predictions of the performance of the activated sludge and biofilm wastewater treatment plant on the nitrification-denitrification, oxygen demand*, pH,* alkalinity, temperature, mixed liquor of the suspended solids*,* nitrogen, phosphorus, primary settling, sludge retention time, emerging micropollutants-parabens, chlorination, *COD* and trace metals in the course of diurnal variations. The database was analyzed to determine bio-kinetic models' parameters range by considering the specific parameters correlation.

Our study applied mass balance equations, activated sludge model *(ASM1)* and artificial neural network *(ANN)* using *MATLAB (neural network toolbox),* octave, python in prediction of the flow rates, organics *(substrate and biomass growth),* inorganics, micropollutants and trace metals speciation. This combined knowledge of the process dynamics with the prowess of mathematical methods for evaluation of the operation points, plant dimensions, biochemical parameters interaction with microbes, estimation and identification of the controller parameters had an excellent impact in addressing the challenges posed by the time-varying parameters.

Emphasis was put on the numerical solution's ability to approximate the analytical solution of the conservation law of mass balance. Calibration of the models was adjusted with the set of influent data in the process of modification of the input data until the simulation models results matched the dataset. Validation was identified to meet the modelling objectives with the level of confidence. The goodness of the prediction *(prediction performance)* was attained using the coefficient of determination *(R^2)* of 0.98-0.99, sum of square error *(SSE) 0.00029-0.1598,* room mean-square error *(RMSE) of 0.0049-0.8673* and mean squared error *(MSE) 2.7059e-14 to*

2.3175e-15. The models were found to be a robust tool for predicting *WWTP* performance. This revealed that the influent indices could be applied to the prediction of the effluent quality *(EQ)*. The overall models were used to detect the inconsistency within the *WWTP* datasets through identification and confirmation of the mass flow into and out of the systems. The modelling and computation of the speciation of compounds offered an extremely powerful tool for the process design, data handling, troubleshooting and optimization representing a multivariable system that cannot be effectively handled without appropriate modelling, computer-based techniques and procurement for the best compliance with international standards plant upgrades efficiency and diversification.

The approach can also be used to handle many other types of waste treatment systems, environmental management, carbon capture and emerging technologies so as to meet the cost-effectiveness, environmental, technical criteria and wide range of big data support in the implementation of the national and sustainable development goals *(SDGs).*

The above summary highlights work done by the main doctoral student, whose project is entitled *Mathematical modelling of biological wastewater treatment process and bioenergy production.*

In Appendices F and G, we present a summary of studies by two other students under the WRC project. These studies covered (i) Method development of analytical techniques for sample analysis and (ii) Degradation of organics in the WWTP, using nanotechnology.

Briefly, for analysis of contaminants in the wastewater samples, we investigated multivariate-based optimization techniques for sample preconcentration using solid phase extraction (SPE) and dispersive liquid-liquid microextraction (DLLME) followed by chromatography-mass spectrometry techniques for quantification of parabens and polyaromatic hydrocarbons in the wastewater treatment plant. We also investigated the performance of tungsten trioxide (WO_3) nanomaterials modified with various nanoparticles, to produce iron-doped WO_3, cadmium sulphide-doped-WO_3, and Z-scheme cobalt oxide-tungsten oxide (Co_3O_4/WO_3) nanocomposites for the photocatalytic degradation of parabens and methylene blue. The best photodegradation results were produced with Z-scheme Co_3O_4/WO_3 nanocomposite.

ACKNOWLEDGEMENTS

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Ms Sharene Janse van Rensburg – WaterLab

The following were supported by the WRC under the current project:

- Dr Anthony Njuguna Matheri — PhD student's project – Department of Chemical Engineering, University of Johannesburg
- Dr Geoffrey Bosire — Post Doc – Department of Chemical Science, University of Johannesburg
- Dr Eric Ngigi — PhD student's project – Department of Chemical Science, University of Johannesburg
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LIST OF ABBREVIATIONS

Abbreviation	Description
ACN	Acetonitrile
ASMs	Activated Sludge Models
ASP	Activated Sludge Process
ANFIS	Adaptive Neuro-Fuzzy Inference Systems
APHA	America Public Health Association
AWWA	American Water Works Association
AA	Amino Acid
NH_4*-N*	Ammonia Nitrogen
AD	Anaerobic Digestion
ADM	Anaerobic Digestion Model
AHP	Analytic Hierarchy Process
ANP	Analytical Network Process
AI	Artificial Intelligence
ANN	Artificial Neural Network
AMPTS 11	Automatic methane Potential Test System Machine
ANO	Autotrophic Nitrifier Organisms
ADWF	Average Dry Weather Flow
BAT	Best Available Technology
BMPs	Best Management Practices
BMP	Bio-chemical Methane Potential
BOD	Biochemical Oxygen Demand
BPR	Biological Phosphorus Removal
BPC	Bio-Process Control
CV	Calorific Value
CHP	Combine Heat and Power
CHNS	Carbon Hydrogen Nitrogen Sulphur
CODH	Carbon Monoxide Dehydrogenase
C/N	Carbon to Nitrogen Ratio
CNHS	Carbon, Nitrogen, Hydrogen and Sulphur
CNSP	Carbon, Nitrogen, Sulphur and Phosphorus
CBR	Case-Based Reasoning
COD	Chemical Oxygen Demand
CoJ	City of Johannesburg
CoT	City of Tshwane
CSOs	Combined Sewer Overflows
CMAS	Completely Mixed Activated Sludge
CFD	Computer Fluid Dynamics
CGI	Computer Generated Imagery
CI	Consistency Index
CR	Consistency Ration

CS	Cryogenic Separation
CW	Constructed Wetlands
CSTR	Continuous Stirred Tank Reactor
CRR	Cumulative Risk Rating
QDW	Daily Quantity of Waste
DMA	Decision Matrix Approach
DSS	Decision Support Systems
DESTA	Decision Support Tool for Aquaculture
TU Delft	Delft University of Technology
DNA	Deoxyribonucleic Acid
DWA	Department of Water Affairs
DCM	Dichloromethane
DE	Differential Equation
DCL	Digestion Chamber Loading
LDC	Digestion Chamber Loading *(kg of TS or VS/m^3 of digestion chamber volume. day)*
DRB 200	Digital Digester
DR 3900	Digital Programmable Analyzer
DMU	Discharge of Pumping and Mixing Unit
DBPs	Disinfection By-Products
DO	Dissolved Solids
DAI	Distributed Artificial Intelligent
DS	Dry Solids
E	Efficiency
EC	Electrical Conductivity
EP	Emerging Pollutant
EDSS	Environmental Decision Support Systems
EPA	Environmental Protection Agency
ES	Expert System
EA	External Aeration
FM/AM	Facilities Management/Automated Mapping
FSIEG	Financial Stability, Innovation and Economic Growth
FAAS	Flame Atomic Absorption Spectrometry
F/M	food and microorganism ratio
HCHO	Formaldehydes
FIR	Fourth Industrial Revolution
FSA	Free and Saline Ammonia
FIS	Fuzzy Inference System
FL	Fuzzy Logic
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectrometer
GA	Genetic Algorithms
GIS	Geographical Information Systems
GP	Goal Programming
GFAAS	Graphite Furnace Atomic Absorption Spectrometry

GHG	Greenhouse Gas
GUA	Growing Up Africa
HSE	Health, Safety and Environment
HP-LC	High-Performance Liquid Chromatograph
HRT	Hydraulic Retention Time
Hydroponic	hydroculture
IPP	Independent Power Producer
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
IWC	Influent Waste Concentration
CIW	Influent Waste Concentration *(kg of TS or VS/m^3 of digestion chamber volume)*
IH	Innovation Hub
ITSS	Inorganic Total Suspended Solids
ICA	Instrumentation, Control and Automation
IMSW-MS	Integrated Municipal Solid Waste Management Systems
IWM	Integrated Waste Management
IAEA	International Atomic Energy Agency
IBM	International Business Machines Corporation
IWA	International Water Association
KBS	Knowledge-Based System
KSOFM	Kohonen Self-Organization Feature Maps
LCMS	Liquid Chromatography-Mass Spectrometer
LCFA	Long Chain Fatty Acids
MAB	Microalgae Biofixation
MCLs	Maximum Contaminants Level
MBR	Membrane Bioreactor
MeOH	Methanol
MLSS	Mixed Liquor Suspended Solids
MLVSS	Mixed Liquor Volatile Suspended Solids
MC	Moisture Content
MS	Monosaccharaides
MCSM	Monte Carlos Simulation Model
MADM	Multi-Attributes Decision Making
MAPE	Mean Absolute Percentage Error
MCDA	Multi-Criteria Decision Analysis
MAIS	Multi-Layered Artificial Immune Systems
MODSS	Multiple Objective Decision Support Systems
MT	Membrane Technology
MSW	Municipal Solid Waste
MSE	Mean Squared Error
NOM	Natural Organic Matter
NNOs	Nitrite to Nitrate
nbVSS	Nonbiodegradable Volatile Suspended Solids
NGO	Non-Government Organization

OLI	Open Learning Initiatives
OASIS	Operation Assistant and Simulated Intelligent System
OFMSW	Organic Fraction of Municipal Solid Waste
OLD	Organic Loading Rate
PSA	Pressure Swing Adsorption
PPE	Personal Protection Equipment
PO_4^{3-}	Phosphates
PFR	Plug Flow Reactor
PAHs	Polycyclic Aromatic Hydrocarbon
PS	Pond System
PEI	Potential Environmental Impact
PR	Probabilistic Reasoning
PEETS	Process Energy Environmental Technology Station
PFD	Process Flow Diagram
R&D	Research and Development
RI	Random Index
RDBMSs	Relational Database Management Systems
RAMS+CH	Reliability, Availability, Maintainability, Safety and Plus Cost, Human Resource
RS	Remote Sensing
REIPPPP	Renewable Energy Independent Power Producer Procurement Programme
RNG	Renewable Natural Gas
RTD	Residence Time Distributions
RNA	Ribonucleic Acid
RAC	Risk Assessment Codes
RBC	Rotating Biological Contractors
RMSE	Root Mean Square Error
RST	Rough Set Theory
RBS	Rule-Based Reasoning
SDWA	Safe Drinking Water Act
SSOs	Sanitary Sewer Overflows
SBR	Sequencing Batch Reactors
SMART	Simple Multi-Attribute Rating Technique
SRT	Sludge Retention Time
SCT	Soft Computing Techniques
SPE	Solid Phase Extraction
SABIA	South Africa Biogas Industry Association
SANS	South Africa National Standards
SMA	Specific Methanogenic Activity
SSE	Sum of Square Error
SVM	Support Vector Machine
SDG	Sustainable Development Goal
TUT	Technical University of Tshwane
TOPSIS	Technique for Order Preference by Similarities to Ideal Solution
TCD	Thermal Conductivity Detector

TDS	Total Dissolved Solids
TAC	Total inorganic acids
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
TN	Total Solids
TS	Total Solids
TSC	Total Solids Concentration in digester
TSW	Total Solids Concentration of waste
TSS	Total Suspended Solids
TF	Trickling Filter
THMs	Trihalomethanes
UV	Ultraviolet Radiation
UNEP	United Nation Environmental Programme
UNICEF	United Nations Children Funds
UNDP	United Nations Development Programme
UNIDO	United Nations Industrial Development organization
UCT	University of Cape Town
UJ	University of Johannesburg
UP	University of Pretoria
Wits	University of Witwatersrand
UASB	Up-flow Anaerobic Sludge Blanket Reactor
VUT	Vaal University of Technology
VBA	Visual Basic Applications
VFA	Volatile Fatty Acid
VOC	Volatile organic acids
VS	Volatile Solids
VSS	Volatile Suspended Solids
VDC	Volume of Digestion Chamber
WAR	Waste Reduction Algorithms
WWTP	Wastewater Treatment Plant
WPCF	Water Pollution Control Federation
WRC	Water Research Commission
WRRFs	Water Resource Recovery Facilities
WSM	Weighted-Sum Method
WBG	World Bank Group
WHO	World Health Organization

LIST OF COMPUTATIONAL TOOLS

AI	Artificial Intelligence *(AI)* or machine intelligence *(MI)* in the Fourth Industrial Revolution *(FIR)* with machine learning *(deep learning and predictive analytics)*
AQUASIM	WWTP modelling and simulation software
ArcGIS	WWTP modelling and simulation software
ASIM	WWTP modelling and simulation software
ASPEN PLUS	WWTP modelling and simulation software
BALAS	WWTP modelling and simulation software
BIOWIN	WWTP modelling and simulation software
CapdetWorks	WWTP modelling and simulation software
CDF-Computer Fluid Dynamics	WWTP modelling and simulation software
CGI	Application for computer graphics
CHEMCAD	WWTP modelling and simulation software
Deep Learning Softwares	Tensorflow, Theano, Torch, Wolfram mathematical, Keras, Matlab-neural network toolbox, Neural designer, Intel Math Kernel Library, Deeplearning4j, Pytouch and Caffe.
DTD Pro	WWTP modelling and simulation software
DYNOCHEM	WWTP modelling and simulation software
GPSX	WWTP modelling and simulation software
IWA/COST benchmark	Benchmark for wastewater treatment models
JASS	WWTP modelling and simulation software
MATLAB Deep Learning	Anova function and train function as Trainlm and using levenberg-marquardt algorithms
MATLAB SIMULINK	WWTP modelling and simulation software
Microsoft, MacOS, Linux	Deep learning used platforms and other computing office applications
Monte Carlos Simulation Model	WWTP modelling and simulation software
MS EXCEL	Window version support program for visual basic application *(VBA)* and support charts, graphs and histograms
PRO2	WWTP modelling and simulation software
SIMBA	WWTP modelling and simulation software
SPSS	IBM Statistical Package for Social Scientists
STOAT	WWTP modelling and simulation software
STOWA	WWTP modelling and simulation software
SUMO	WWTP modelling and simulation software
Tensorflow	Main library as Cuda *(Nvidia), Torch, Caffe, Neo, Keras,* and *ISK* intel
WERF	*WWTP* modelling and simulation software
WEST	WWTP modelling and simulation software

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CHAPTER 1: INTRODUCTION

1.1 Background

The population growth, economic development, urbanization, improvement in living-standards, awareness and in the implementation of the fourth industrial revolution *(FIR)* has increased waste generation and introduced emerging contaminants into waste streams that may pose sanitary and environmental risks (Al-Khatib, Monou, Zahra, Shaheen & Kassinos, 2010; Amin, 2009; Matheri *et al.,* 2018). These contaminants have increased the demand for specialized emerging pollutants *(EPs)* removal techniques in wastewater. The emerging contaminants of concern include *(trace metals, personal care products, endocrine disruption chemicals, flame retardants, pesticides, pharmaceutical, plasticizers, various fluorinated compounds, nanomaterial, etc.)* that has led to more stringent regulations on wastewater discharge quality parameters (Stamou & Antizar-Ladislao, 2016). These contaminants end up in water bodies and landfills, leading to pollution of the environment thus putting a strain on health, economic and social sectors (Lemoine *et al.,* 2013; Stamou & Antizar-Ladislao, 2016). The rapid increase in the quantities of waste generated demand a wider coverage of existing waste management system that provides sustainable standards for innovative technologies for treatment. Achieving these standards requires the quantitative characterization of given waste streams, implementation of innovative integrated waste management systems and reliable waste management data which provides an all-inclusive resource for a comprehensive, critical and informative evaluation of waste management options in all waste management programmes (N.-B. Chang & Davila, 2008; Miezah, Obiri-Danso, Kádár, Fei-Baffoe & Mensah, 2015; Ojeda-Benítez, Armijo-de Vega & Marquez-Montenegro, 2008).

In the Gauteng Province of South Africa, wastewater management and treatment services are performed by twelve *(12)* Water Services Authorities via an infrastructure network comprising of *56* wastewater collectors and treatment systems. Figure **1.1** shows the distribution of wastewater treatment plants *(WWTPs)* in Gauteng Province (Department of Water Affairs, Accessed 2016).

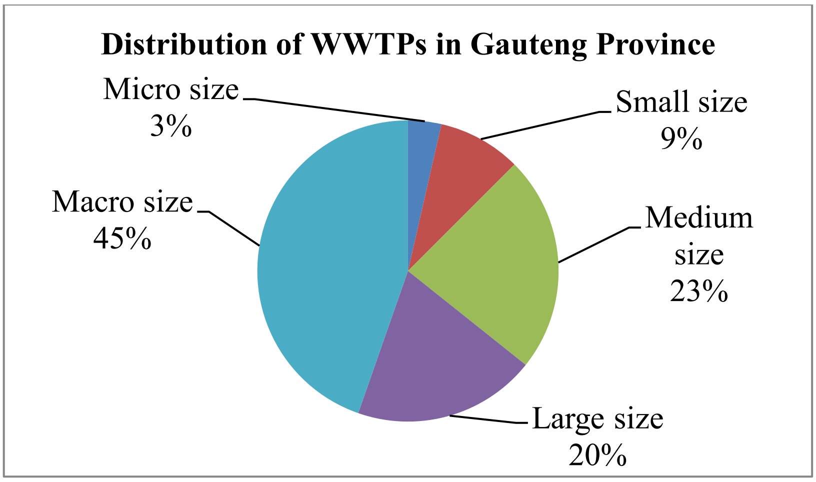

Figure 1.1: *Distribution of WWTPs in Gauteng Province, South Africa (Department of Water Affairs, Accessed 2016).*

A total flow of *2579 ML/day* is received at the *56* treatment facilities, which has a collective hydraulic design capacity of *2595 ML/day (an average dry weather flow, ADWF).* Gauteng Province has some of the best wastewater practitioners' and plants in South Africa and are operated with non-renewable energy. These plants consistently produce high-quality effluent, but organic and hydraulic loads exceed the theoretical design capacities (WWTPs.). To maintain this achievement in effluent quality requires highly qualified plant managers, adequate resources, operational adjustments and swift turnaround in scientific data collection and analysis. **Table 1.1** shows the number of *WWTPs* distribution in Gauteng Province, their total design capacity in *(ML/day)* and total daily inflows *(ML/day)* (Department of Water Affairs, Accessed 2016).

Table 1.1: *Wastewater treatment plants distribution in Gauteng Province (Department of Water Affairs, Accessed 2016).*

	Micro Size *< 0.5 Ml/day*	Small Size *0.5-2 Ml/day*	Medium Size *2-10. Ml/day*	Large Size *10-25. Ml/day*	Macro Size *>25 Ml/day*	Undetermined	Total *Ml/day*
No. of *WWTPs*	2	5	13	11	25	0	56
Total design capacity *(Ml/day)*	0.70	4.75	73.10	182	2334.50	0	2595.10
Total daily inflows *(Ml/day)*	0.71	3.40	59.60	131.60	2383.70	5	2576

South Africa adopted incentive-based regulations as a means to identify, ensure, reward, and encourage excellence in the wastewater management (Stack, Huang, Wang & Hodge, 2011). It is within this strategy that the Green Drop regulation programme was conceived within the Department of Water Affairs *(DWA)* on the *11th September 2008,* which is now referred to as Department of Water and Sanitation (DWS). In parallel, the *DWA* commenced with a full-scale assessment of all municipal *WWTPs* across South Africa and used this baseline to develop the risk-based regulatory approach. This two-pronged approach by the water sector partners has been widely acknowledged. The green drop certification incentive-based regulation seeks to identify and develop the core competencies required for the water sector that if strengthened, will gradually and sustainably improve the level of wastewater management in South Africa. The risk-based regulation seeks to establish scientific baseline comprising of the critical risk areas within the wastewater services production and to use continuous risk measurement and reporting to ensure that corrective measures are taken to abate these high and critical risk areas (Stack *et al.,* 2011).

The green drop requirements are used to identify and assess the entire value chain involved in the delivery of municipal wastewater services, whilst the risk analyses focused on the treatment function specifically (WWTPs.). According to green drop *2009* and *2011* assessments used to evaluate the various treatment processes applied by municipalities across the nine provinces in South Africa, simplification of the *WWTPs* technology was done by grouping them into three generic groups: *(i)* trickling biofilters *(ii)* activated sludge processes and variations and *(iii)* pond and lagoon systems (Rudi & Marlene, 2013).

Gauteng Province has the leading numbers of wastewater treatment plants with a provincial green drop score of *78.8%.* **Figure 1.2** shows the map of South Africa and Gauteng province that serves as our research study case.

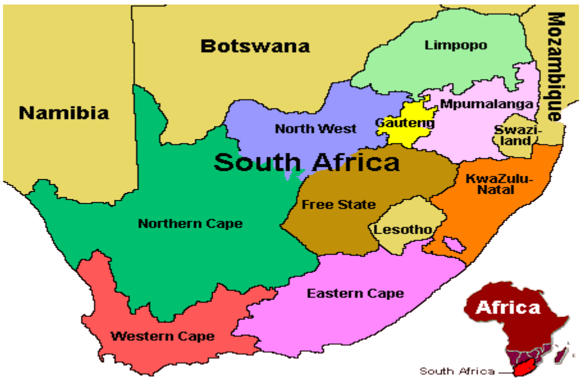

Figure 1.2: *Gauteng province among other South African Provinces with a Provincial green drop score of 78.8%*

The emerging contaminants of concern included trace metals, organics, inorganics and micropollutants that have led to more stringent regulations on wastewater discharge quality parameters. Wastewater treatment is inherently dynamic because of the large variation in the influent concentration, flowrates and composition. The pollutants have attracted much attention in recent years due to their bioaccumulation, toxicity and wide range of sources and persistence. The presence of these pollutants is brought about by industrial activities that generate numerous chemical elements. This creates a research gap on the construction of historical records of contamination, quantification of the intensity of pollution based on enrichment factor, risk assessment codes *(RAC)* and excess flux, and investigation of the sources by assessing inter-elements relationships and through component analysis (Wang *et al.,* 2015).

The automation of the wastewater treatment processes instrumentation, control and automation *(ICA)* is the best approach in enhancing the efficiency of wastewater treatment process. Developing countries still use elementary control that often fed with off-line data where the on-line sensors that are both robust and accurate, either in-line *(operating in a side stream*) or ex-situ *(operating within the process),* still pose major drawback and is still minimal up to date. The is due to lack of understanding of the treatment processes and proper understanding of mathematical models; plant constraints in flexibility to manipulate the process; lack of fundamental knowledge concerning benefits versus costs of the automated treatment processes; inadequate instrumentation and reliable technology; unsatisfactory communication in designing of the plants among the designers, operators, researcher, government regulatory agents, equipment manufacturers and suppliers and lastly lack of proper training to the operators on how to operate the advanced sensor and control equipment (Jeppsson, 1996). Designing and constructions of any *WWTPs* and selection of optimal *WWTPs* alternatives are important issues and depends on the capital and operation cost *(economic)*. It is provided in the feasibility report on *WWTPs* project as to cut capital and operation cost (Zeng, Jiang, Huang, Xu & Li, 2007). The development of conventional mathematical models, artificial intelligence *(AI)* and optimization models in decision making has been of considerable concern over past decade in the network design and complex interaction among various uncertain parameters (Vahdani & Naderi-Beni, 2014). Selection of best method of treatment processes is important before designing and implementation of programmable sampling for the cumulative risk rating *(CRR)* assessment of wastewater treatment plants (Karimi, Mehrdadi, Hashemian, Bidhendi & Moghaddam, 2011). Mathematical modelling and simulation become essential to describe, forecast, predict and control the complicated interaction of the wastewater treatment processes (Jeppsson, 1996). The models provide an idealized representation of an actual physical system of the wastewater treatment system (WEF, 2011). Primary modelling allows determining optimal working conditions which are theoretically possible to analyse and estimate the variety of different process possibilities. This reduces additional costs for continuous and repeated experiments. There are several computer programs that are used in the simulation modelling of wastewater treatment processes; they include DYNOCHEM, WEST, CHEMCAD, MATLAB, BIOWIN, WATERCAD, WEAP, STROAT, SIMBA Microsoft Excel, AI-based *WWTPs* design tool and knowledge representation tool *(e.g. deep learning/machine learning)* in *WWTP* domain among others. These programs are intended for the determination of the mass and energy balance, and the modelling of chemical processes (Porubova, Bazbauers & Markova, 2011). Simulations by an adequate mathematical model is a novel tool for this purpose and implementation of the mass balance models and Activated Sludge Models *(ASMs)* originally proposed by the International Water Association *(IWA)* Task Group for mathematical modelling of wastewater treatment processes and *AI*-based models are employed. The models are validated by comparing the simulations with the laboratory experimental results and historical big data (Henze, Gujer, Takashi & Van Loosdrecht, 2002; Parawira, 2004).

1.2 Aims and Objectives

1.2.1 Aims of the study

The proposed study focused on carrying out mass balance and AI-based models of the organics, inorganics, emerging micropollutants and trace metals on *WWTPs* in Gauteng province, South Africa. The pollutants studied include trace metals *(Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn)*, total *COD*, filtered *COD*, soluble *COD*, *(after flocculation and filtration)*, total nitrogen *(N)*, total kjeldahl nitrogen *(TKN)*, ammonia nitrogen *(NH_4-N)*, nitrate/nitrite nitrogen, total phosphorus *(TP),* phosphates *(PO_4^{3-}),* volatile fatty acids *(VFA),* total suspended solids *(TSS),* chlorine *(Cl),* micropollutants and trace metals.

1.2.2 Objectives of the study

The objectives of the study were:

i. To carry out site reconnaissance and dimension of the *WWTPs* process unit. This was to assist in getting the complete picture *(mass balance)* about the occurrence, concentration, fate and transport of trace metals, organic and inorganic compounds.
ii. To carry out in-depth sampling at different intervals *(process units)* based on retention time from the liquid, mixed sludge, dewatered sludge and analyze organics, inorganics, trace metals and emerging micropollutants.
iii. To analyse thermodynamic and reaction bio-kinetics models that will be used to gain a better understanding of the variable dependency in the wastewater treatment process, biosolids utilization.
iv. To carry out mathematical modelling and simulation of the trace metals, organic, inorganic, micropollutant compounds, physically measured data *(operation variables),* performance variables in the *WWTPs.* This will enable a better understanding of each treatment unit and henceforth improved analytical strategies for the pollutant's removal.
v. To optimize parameters and validate empirical results through goodness of the prediction *(prediction performance)* to ascertain comparability of satisfactory results.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This section outlines an overview of wastewater treatment plants (WWTPs in South Africa in general and Gauteng Province in particular.

2.2 Wastewater Treatment Plants in Gauteng Province, South Africa

South Africa has built a substantial wastewater management industry that comprises of approximately 970 treatment plants, extensive pipe networks (sewers), pumping stations and transportation systems that treat on average 7 589 000 kilolitres of wastewater on a daily basis (DWS, 2016). Gauteng, being a capital city in terms of gross domestic product (GDP), owns and operates 51 smalls, medium, large and macro-sized wastewater treatment plants (WWTPs) and represents the highest overall treatment capacity which deploys mostly high-end technologies in the country (DWS, 2016). Wastewater is by definition a byproduct of human settlements; the type of wastewater generated is determined by the human activities in the areas under consideration. Normally if there are no industrial activities then only domestic wastewater is generated. With regards to domestic wastewater, demographics of an area are indicative of the type and amount of wastewater being generated. **Figure 1.2** shows the map of South Africa showing Gauteng province, which was selected for the study.

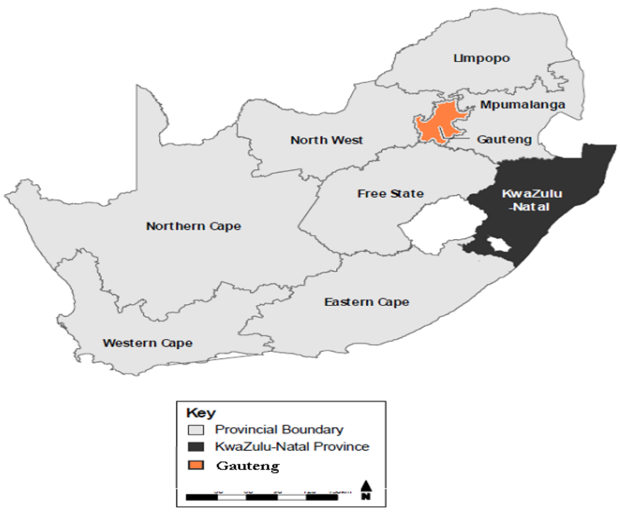

***Figure 2.1**: The map gives the geographic location of the Gauteng Province in relation to the other provinces in the country*

The proper functioning of wastewater treatment works lies primarily with Water Service Authorities (WSAs) and their providers (WSPs) who operate and maintain the physical infrastructure, the chemical and biological processes. Generally, wastewater treatment plants can be categorized according to the following sizes based on the wastewater volumes handled (flow volume/time): micro size plants <0.5 Mℓ/day; small size plants 0.5-2 Mℓ/day; medium size plants 2-10 Mℓ/day; large size plants 10-25 Mℓ/day; and macro size plants >25 Mℓ/day. The distribution of WWTPs in the whole of South Africa is given in **Figure 2.2.**

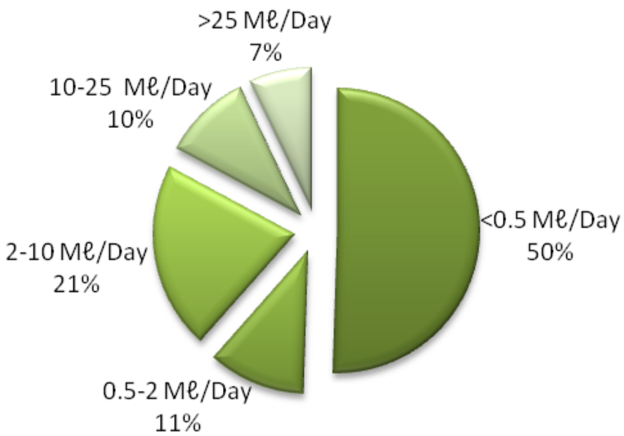

Figure 2.2*: Size distribution of wastewater treatment plants in South Africa*

The distribution of wastewater treatment plants (WWTPs) shows that 50% of all the WWTPs fall in the micro size category, with 20% comprising of large size WWTPs while macro size takes 7%.

2.2.1 Description of Distribution of WWTPs

i. Micro size plants (50%), treating less than 0.5 Mℓ per day, constitute approximately half of all treatment plant facilities in South Africa. This can be explained by the fact that the largest population in South Africa lives in small towns and the treatment plants are small and only cater for the needs of that community.

ii. Small plants (11%) in the size range of 0.5-2 Mℓ per day are the third highest

iii. Medium size plants (21%) category is the second highest and constitute nearly a quarter of all the WWTPs

iv. Large plants (10%) category is the fourth largest of the wastewater treatment facilities in South Africa.

v. Macro size (7%) plants >25 Mℓ/day category constitutes the smallest fraction of all the categories of wastewater treatment facilities in South Africa. This can be understood on the basis of the fact that the macro WWTPs are expensive to construct and maintain, therefore can only be done in major cities like Johannesburg, Durban, Pretoria and Cape Town.

2.2.2 The distribution of wastewater treatment works in Gauteng province

In order to confirm this observation, **Figure 2.3** presents the distribution of WWTPs in Gauteng province (GP). The GP distribution of WWTPs shows a reverse trend to the distribution in the country where half (50%) of all the WWTPs are macro size, whereas the micro size fraction constitutes the lowest (2%) unlike the overall distribution in the entire country.

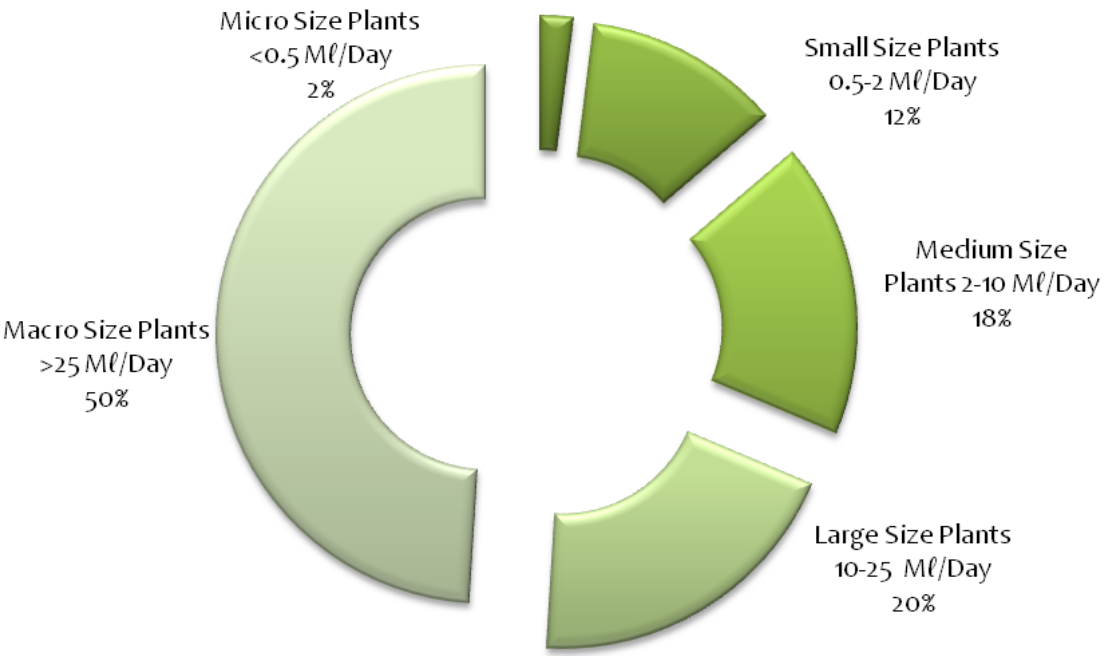

Figure 2.3*: The status and distribution of wastewater treatment works in Gauteng linked to density, economies of scale and centralization engineering philosophy*

Generally, aboutt 90% of the WWTPs in Gauteng province are categorized as ranging from medium to macro sized plants. This can be attributed to the fact that about 80% of the population of Gauteng province reside in the city of Johannesburg or Tshwane. **Table 2.1** shows the locations of the 51 WWTPs and the size categories.

***Table 2.1**: The breakdown of municipal-owned WWTPs in Gauteng in terms of size and location*

Works Size	**Micro Size Plants <0.5 Mℓ/Day;**	**Small Size Plants 0.5-2 Mℓ/Day;**	**Medium Size Plants 2-10 Mℓ/Day;**	**Large Size Plants 10-25 Mℓ/Day;**	**Macro Size Plants >25 Mℓ/Day.**
No of WWTW	1	6	9	10	25
% of works	2	12	18	20	50
WWTW Names	Esther Park	Magalies	Ennerdale	Herbert Bickley	Driefontein
		Oheni Muri	Babalegi	Jan Smuts	Bushkoppies
		Ekangala	Carl Grundling	Themba	Goudkoppies
		Rethabiseng	Rynfield	Sandspruit	Olifantsvlei
		Refilwe	Heidelberg	Tsakane	Baviaanspoort
		Rayton	Ratanda	Benoni	Sunderland Ridge
			Meyerton	Daveyton	Rooiwal
			Vaal Marina	J.P. Marais	Daspoort
			Godrich	Leeukuil	Klipgat
				Randfontein	Rietgat
					Zeekoegat
					Olifantsfontein
					Hartebeesfontein
					Dekama
					Vlakplaas
					Rondebult
					Waterval
					Ancor
					Welgedacht
					Rietspruit
					Sebokeng
					Hannes van Niekerk
					Flip Human
					Percy Stewart
					Northern Works

Table 2.2 shows the levels at which the WWTPs in Gauteng are operating based on the 100% treatment capacity and those exceeding 100% (average flow as a percentage of the design flow) (DWS, 2016).

***Table 2.2**: List of WWTPs in Gauteng with names of the plants, responsible authority, Municipality and the operating capacity – whether 100% performance or exceeding the design flow:*

Priority Order Of Problem Works I.T.O. Capacity Reached and Exceeded /Volume Flow Exceeded						
Priority Order Of WWTW	**Name Of WWTW**	**Responsible Authority**	**Responsible Municipality/ Organization**	**Design Capacity Of Plant** (Ml/D)	**Flow Amount Exceeding Capacity** (Ml/D)	**Average Flow As % Of Design Capacity**
1	Percy Stewart	Mogale City	Mogale City	18	12	250.0%
2	Meyerton	Midvaal	Midvaal	5	10	200.0%
3	Rietspruit	Emfuleni	Emfuleni	25	18	172.0%
4	Welgedacht	Ekurhuleni Metro	ERWAT	35	24	168.6%
5	Sebokeng	Emfuleni	Emfuleni	100	50	150.0%
6	J.P. Marais	Ekurhuleni Metro	ERWAT	15	7	146.7%
7	Heidelberg	Lesedi	ERWAT	5	2	140.0%
8	Olifantsvlei	City of Johannesburg	Johannesburg Water	180	80	144.4%
9	Waterval Farm	Ekurhuleni Metro	ERWAT	105	35	133.3%
10	Zeekoegat	City of Tshwane	City of Tshwane	30	9	130.0%
11	Vlakplaas	Ekurhuleni Metro	ERWAT	83	24	128.9%
12	Sunderland Ridge	City of Tshwane	City of Tshwane	45	10	122.2%
13	Driefontein	City of Johannesburg	Johannesburg Water	25	5	120.0%
14	Hartebeesfontein	ERWAT	ERWAT	45	8.4	118.7%
15	Bushkoppies	City of Johannesburg	Johannesburg Water	200	5	102.5%
16	Ekangala	Kungwini	Kungwini	2	0.5	110.00%
17	Northern Works	City of Johannesburg	Johannesburg Water	410	0	100.0%
18	Temba	City of Tshwane	City of Tshwane	12.5	0	100.0%
19	Rooiwal (3 works)	City of Tshwane	City of Tshwane	245	0	100.0%
20	Daspoort	City of Tshwane	City of Tshwane	60	0	100.0%
21	Jan Smuts	Ekurhuleni Metro	Ekurhuleni Metro	10	0	100.0%
22	Esther Park	Ekurhuleni Metro	Ekurhuleni Metro	0.4	0	100.00%
23	Rayton	Nogenk tsa Taemane	Nogenk tsa Taemane	0.6	0	100.00%
24	Randfontein	Randfontein	Randfontein	20	0	100.0%

*The information extracted from **Table 2.2** based on the level at which the WWTPs in Gauteng are operating, indicate that one third (33%) of the treatment plants in the cities are not under workload stress. However, the two-thirds (67%) of the plants that are under stress, ought to be investigated for their dissolved pollutant outflow. If the WWTP is under stress the BOD level* *will be high and this might pose a challenge in the mobilization of heavy metals bound on humic and fulvic acids.*

Table 2.3 is an overview of the Standards NOT being met by the various WWTPs in Gauteng, as captured by the Department of Water and Sanitation (DWS, 2016) Regional Office (now known as Department of Water & Sanitation*).*

***Table 2.3**: A quick overview of the Standards NOT being met by the various WWTPs in Gauteng, as captured at the Department of Water Affairs and Forestry (DWAF, 2008) Regional Office. NB.*

a) WWTPs

Name of WWTPs	Responsible Authority	River into which Effluent is Discharged	WMA	Technology being used	Standards Not Met Pollutants
Ancor	Ekurhuleni Metro	Suikerbosrant	Upper Vaal	Bio-filtration	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Babalegi	City of Tshwane	Apies	Crocodile - Marico	Deactivated sludge process	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Baviaanspoort	City of Tshwane	Pienaars River	Crocodile - Marico	Activated Sludge	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Benoni	Ekurhuleni Metro	Lake ~Blesbok Spruit	Upper Vaal	Bio-filtration	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Bushkoppies	City of Johannesburg	Harrington Spruit ~ Klip River	Upper Vaal	Activated Sludge	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Carl Grundling	Ekurhuleni Metro	Suikerbosrant	Upper Vaal	Activated Sludge	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Daspoort	City of Tshwane	Apies	Crocodile - Marico	Activated Sludge and Bio-filters	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Daveyton	Ekurhuleni Metro	Daveyton Spruit ~Blesbok Spruit	Upper Vaal	Bio-filtration	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Dekama	Ekurhuleni Metro	Natal Spruit	Upper Vaal	Bio-filtration	E.coli, NH_4^+ ,NO3- ; NO_2-; PO_4^{2-};COD; SS
Driefontein	City of Johannesburg	Crocodile	Crocodile - Marico	BNR	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Ekangala	Kungwini	Bronkhorstspruit	Olifants	Stabilization Ponds	E.coli, FC; COD; N
Ennerdale	City of Johannesburg	Rietspruit	Upper Vaal	Phosphate BNR	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Ester Park	Ekurhuleni Metro		Crocodile - Marico		E.coli; FC; pH; SS; N
Flip Human	Mogale City	Wonderfontein Spruit	Upper Vaal		E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Godrich	Kungwini	Bronkhorstspruit	Olifants	Activated Sludge	E.coli; FC; PO_4;
Goudkoppies	City of Johannesburg	Harrington Spruit ~ Klip River	Upper Vaal	Activated Sludge	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS

Hannes van Niekerk	Westonaria	Wonderfontein Spruit	Upper Vaal	Activated Sludge and Biofiltration	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Hartebeesfontein	Ekurhuleni Metro	Rietvlei	Crocodile - Marico	Activated Sludge	E.coli, EC
Heidelberg	Lesedi	Suikerbosrant	Upper Vaal	Activated Sludge	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Herbert Bickley	Ekurhuleni Metro	Suikerbosrant	Upper Vaal	Activated Sludge	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
J.P. Marais	Ekurhuleni Metro	Blesbok Spruit	Upper Vaal	Activated Sludge	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Jan Smuts	Ekurhuleni Metro	Jan Smuts Dam ~ Blesbok Spruit	Upper Vaal	Bio-filtration	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Klipgat	City of Tshwane	Tolwane	Crocodile - Marico	Activated Sludge and Bio-filters	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Leeukuil	Emfuleni	Vaal River	Upper Vaal	BNR	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Magalies	Mogale City	Magalies	Crocodile - Marico		E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS

b) Continued….WWTPs

Name of WWTPs	Responsible Authority	River Into Which Effluent Is Discharged	WMA	Technology Being Used	Standards Not Met
Meyerton	Midvaal	Louis Fourie Spruit ~ Klip River	Upper Vaal	Activated Sludge	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Northern Work	City of Johannesburg		Crocodile - Marico		
Oheni Muri	Midvaal	Louis Fourie	Upper Vaal	Activated Sludge	E.coli; FC; pH; SS; N
Olifantsfon-tein	Ekurhuleni Metro	Kaal Spruit	Crocodile - Marico	Activated Sludge and Bio-filters	E.coli NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Olifantsvlei	City of Johannesburg	Klip River	Upper Vaal	BNR	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Percy Stewart	Mogale City	Blougat Spruit-Hartbeespoort Dam	Crocodile - Marico	BNR and Biofiltration	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Randfon-tein	Randfontein	Elandsvlei-Hartbeespoort Dam	Crocodile - Marico	BNR and Biofiltration	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS

Ratanda	Lesedi	Suikerbosrant	Upper Vaal	Activated Sludge	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Rayton	Nokeng tsa Taemane	Bronkhorstspruit	Olifants	Activated Sludge	E.coli, PO_4;COD; SS; Nitrates
Rethabiseng	Kungwini	n/a	Olifants	Oxidation Ponds	E.coli; FC; NH_4^+ ,NO_3^- ; NO_2
Rietgat	City of Tshwane	Sout Spruit	Crocodile - Marico	Activated Sludge	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Rietspruit	Emfuleni	Rietspruit	Upper Vaal	BNR	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Refilwe	Nokeng tsa Taemane	Elands River	Olifants	Activated Sludge	E.coli, COD; PO_4
Rondebult	Ekurhuleni Metro	Elsbrong Spruit	Upper Vaal	Bio-filtration	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Rooiwal	City of Tshwane	Apies	Crocodile - Marico	Activated Sludge and Bio-filters	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Rynfield	Ekurhuleni Metro	Rynfield Dam ~ Blesbok Spruit	Upper Vaal	Biofiltration	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Sandspruit	City of Tshwane	Sun Spruit	Crocodile - Marico	Activated Sludge	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Sebokeng	Emfuleni	Rietspruit	Upper Vaal	BNR and Biofiltration	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Sunderland Ridge	City of Tshwane	Hennops	Crocodile - Marico	Activated Sludge and Bio-filters	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Temba	City of Tshwane	Apies	Crocodile - Marico	Activated Sludge and Bio-filters	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Tsakane	Ekurhuleni Metro	Suikerbosrant	Upper Vaal	Activated Sludge	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Vaal Marina	Midvaal	Louis Fourie	Upper Vaal	Activated Sludge	E.coli; NH_4^+ ,NO_3^- ; NO_2^-; PO_4; SS
Vlakplaas	Ekurhuleni Metro	Natal Spruit	Upper Vaal	Bio-filtration	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS
Waterval	Ekurhuleni Metro	Klip River	Upper Vaal	BNR	E.coli, NH_4^+ ,NO_3^- ; NO_2^-; PO_4^{2-};COD; SS

2.3 Wastewater Treatment Processes

Wastewater collected from cities and towns must ultimately be returned to receiving water or to the land. The complex question that seeks to be answered relate to the nature and the extent to which contaminants in wastewater must be removed to protect the environment. These questions must be answered specifically for each case. This requires analyses of local conditions and terms of reference, together with application of scientific knowledge, engineering judgment consideration of the South Africa National Standards (SANS) or World Health Organization (WHO) (Health.).

2.3.1 Components of wastewater treatment plants

The components that make up the wastewater flow from any community depends on the following factors (E. Metcalf).

- Domestics (sanitary) wastewater, this is the wastewater discharged from residential, commercial and institutional facilities.
- Industrial wastewater, this is wastewater discharge from the industry.
- Infiltration/inflow, this is the storm water that enters the sewer either indirectly or directly. Infiltration is water that enters the sewer system through leaking joints, cracks and breaks, or porous walls. Inflow is storm water that enters the sewer system from storm drain connections (catch basins), roof leaders, foundation and basement drains, or through manhole covers.
- Storm water, rainwater and snowmelt runoff.

2.3.2 Classification of treatment methods

The principal methods used for the treatment of wastewater and sludge are identified in **Figure 2.4** where unit operations and processes are grouped together to provide various levels of treatments. The term "preliminary" or "primary", refers to physical unit operations, "secondary" refers to chemical and biological unit processes, and "advanced" or "tertiary" refers to combination of all three. The major stages in wastewater treatment plants and the unit operations, processes or methods applicable to the removal of these contaminants, are shown in **Figure 2.4** (E. Metcalf).

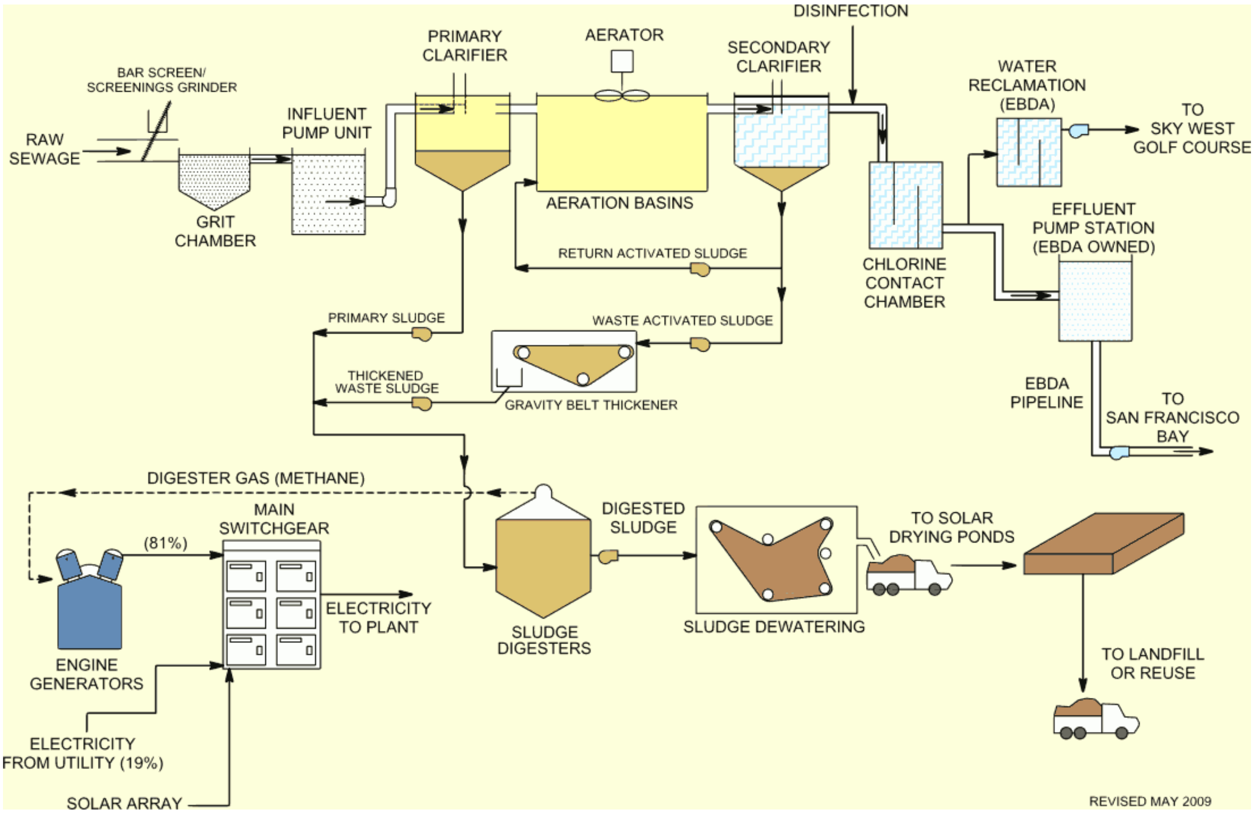

Figure 2.4*: General wastewater treatment process units operation (E. Metcalf).*

The treatment of wastewater takes places by application of physical forces known as unit operations, and chemical or biological reactions that are called unit processes. The Unit operation and unit processes are grouped in various levels of treatment known as; preliminary, primary, secondary and tertiary. Their activities includes (Crites & Tchobanoglous, 1998; Metcalf, 1979).

2.3.2.1 Primary wastewater treatment

In the primary treatment, physical operations like sedimentation are applied. This is used to remove portion of the suspended solids and organic compounds found in the wastewater. Advanced primary treatment involves the use of chemicals to enhance the removal of suspended solids and dissolved solids. It is accomplished by chemical addition and filtration.

2.3.2.2 Secondary wastewater treatment

In secondary treatment, biological and chemical processes are used to remove most of the organic compounds. This enhances removal of biodegradable organics matters and suspended solids. Disinfection is also typical in convectional secondary treatment. In the industrial wastewater, activated sludge process is used. It is a biological treatment process using air and biological floc composed of bacteria and protozoa.

Secondary treatment with units for nutrients removal like biological nutrients removal (BNR) in the wastewater treatment, aeration tanks, settling ponds, trickling filters or rotating biological contractors (RBC) are used for biodegradable organics, suspended solids and nutrients (phosphorus and nitrogen) removal. Activated sludge process is applied to oxidised nitrogenous matter, carbonaceous biological matters and removing nutrients (nitrogen and phosphorus). **Figure 2.5** shows the generalized schematic diagram of an activated sludge process in the WWTPs. In case of phosphate and nitrogenous matter, additional steps are added where mixed liquor is left in anoxic condition, i.e. there is no residence dissolved oxygen.

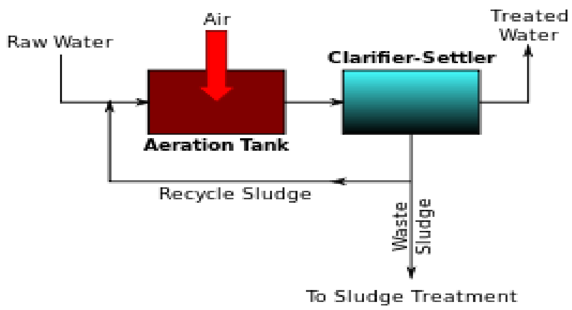

Figure 2.5*: General schematic diagram of an activated sludge process*

2.3.2.3 Tertiary Wastewater Treatment

Tertiary treatment enhances the removal of residual suspended solids after secondary treatment by granular medium filtration or micro screens. Disinfection by chlorine or ultraviolet rays enhances the killing of the pathogens.

In advanced treatment, unit operation and unit processes are used in the removal of dissolved and suspended materials remaining after normal biological treatment when required for various water reuses applications. **Figure 2.6** shows the flow diagram for unit operations and processes in physical, chemical and biological processes used in wastewater treatment [3].

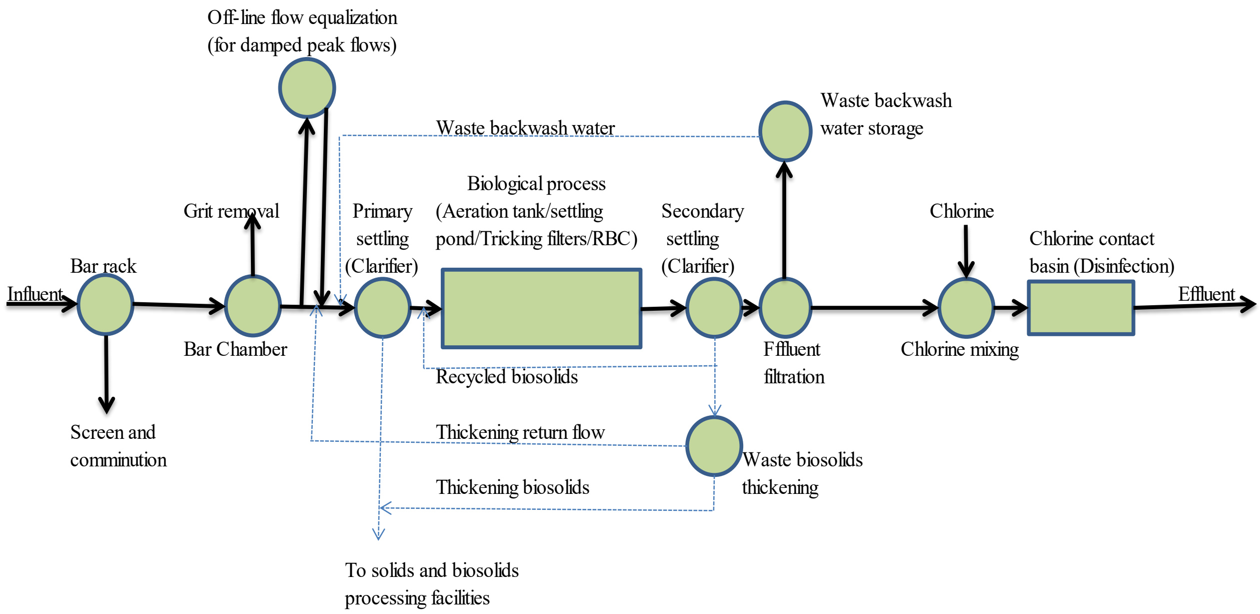

Figure 2.6: *Flow diagram for unit operation and processes in physical, chemical and biological processes used in wastewater treatment (E. Metcalf).*

2.3.3 Physical, chemical and biological characteristics of wastewater and their source.

The main physical properties, chemical and biological constituents of wastewater and their sources are reported in **Table 2.4**. Many of these parameters listed have similar chemical properties. For example, temperature, physical property, affects both the biological activity in the wastewater and the amounts of gases dissolved in the wastewater.

***Table 2.4**: Important contaminants of concern in wastewater treatment (Henze & Comeau, 2008; Metcalf, 1979)*

Contaminants	Reason for importance
Suspended solids	Suspended solids can lead to the development of sludge deposits and anaerobic conditions when untreated wastewater is discharged in the aquatic environment
Biodegradable organics	Composed principally of proteins, carbohydrates and fats, biodegradable organics are measured most commonly in terms of BOD (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand). If untreated and discharged to the environment, their biological stabilization can lead to the depletion of the natural oxygen resources and to the development of septic condition.
Pathogens	Communicable diseases can be transmitted but the pathogenic organisms in wastewater
Nutrients	Both nitrogen and phosphorus, along with carbon are essential nutrients for growth. When discharged to the aquatic environment, these nutrients can lead to the growth of undesirable aquatics life thus leading to pollution of groundwater
Priority pollutants	Organics and inorganics compounds selected on the basis on their known or suspected carcinogenicity, mutagenicity, teratogenicity, or high acute toxicity.
Refractory organics	These organics tends to resist conventional methods of wastewater treatment. Typical examples include surfactants, phenols and agricultural pesticides
Heavy metals	Heavy metals are usually added to wastewater from commercial and industrial activities and may have to be removed if the wastewater is to be reused
Dissolved inorganics	Inorganics constituents such as calcium, sodium and sulphate are added to the original domestic's water supply as a results of water use and may have to be removed if the wastewater is to be reused.

2.3.3.1 The quantitative methods of analysis: gravimetric, volumetric or physicochemical.

Analysis of the contaminants listed in **Table 2.4** required different analytical methods depending on the nature of the contaminant, the availability of the technique and the information required.

- Physiochemical methods of analysis include; turbidity, calorimetry, potentiometry, polarography, fluorometry, spectroscopy and nuclear radiation.
- Volumetric methods are based on; analysis volumes, e.g. flow rate of the wastewater.
- Gravimetric methods are based on; analysis mass of mass, e.g. methods to determine suspended solids (E. Metcalf).

2.4 Mechanisms of the Treatment Processes

Different mechanisms or pollutant removal methods are available. These discussed below.

2.4.1 Sedimentation

Sedimentation is more or less effective for the removal of suspended matter, depending upon the size and the density of the particles to be removed and time available for the process. Heavy and large particles are removed in a relatively short time, while much light or finely divided material takes longer period, e.g. clay soils. If the concentration of such "non-settleable" particles is excessive, then sedimentation alone is not an adequate method of treatment, and other means are employed (Metcalf, 1979).

2.4.2 Coagulation

This is a technique of treating water with certain chemicals for the purpose of collecting non-settleable particles into larger or heavier aggregates which are more readily removed. The resulting clumps of solids material, termed "floc" are removed by sedimentation, filtration, or both. Optimum amount of chemicals are used in coagulation processes (Metcalf, 1979).

2.4.3 Filtration

This process in capable of removing particulate matters too light or too finely divided to be removed by sedimentation. That is, sand, anthracite, diatomite and other fine-grained materials. Filtration always follows sedimentation units, so that the larger quantity of relatively coarse material is removed by sedimentation, to avoid rapid clogging of the filter, which in turn remove the particles for which sedimentation is not effective. Fine screens or micro-strainers are sometimes used prior to sand filtration (Metcalf, 1979).

2.4.4 Disinfection

Disinfection is conducted in order to destroy pathogenic organisms. It is usually accomplished by the application of chlorine or certain chlorine compounds. Other methods using ultra violet rays and ozonation are also currently in use. Disinfection is the only step which is intended specifically for control of the bacteriological quality (Metcalf, 1979).

2.4.5 Softening

The removal of the elements which contribute to hardness of a water, primarily calcium and magnesium, is called softening. When domestic supplies are softened, usually the lime-soda process or the ion-exchange process, is used. Chemicals are added to precipitate calcium carbonate, and if further softening is required, magnesium is precipitated as magnesium hydroxide. Usually, the process results in a reduction of the total quantity of dissolved solids in the water. In ion-exchange process, calcium and magnesium salts are converted to sodium salts, and little change in the total dissolved solids result (Metcalf, 1979).

2.4.6 Aeration

Aeration is sometimes employed in connection with taste and odor control. Excessive carbon dioxide can also be removed in this way, and the corrosive effect of some water can be reduced. The removal of carbon dioxide by aeration sometimes also reduces the dosages of chemicals required in subsequent treatment processes. By supplying dissolved oxygen, aeration is often helpful in the removal of iron. Some microorganisms require oxygen to survive. This microorganism consume and accumulate heavy metals thus reducing metals in wastewater discharge (Metcalf, 1979).

2.4.7 Trace elements removal

Specific processes to remove heavy metals are employed only in water which contains sufficient concentration of these substances to cause persistent problems. A number of different techniques exist such as; adsorption, membrane filtration, electro dialysis and photo catalysis. The choice depends upon the concentration and the chemical nature of the trace element present (Metcalf, 1979).

2.4.8 Anaerobic digestion

Anaerobic digestion (AD) is biological breakdown of organic matters in the absence of oxygen. This process takes place by a series of four fundamental steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Sreekrishnan, Kohli & Rana, 2004). The degradation steps of anaerobic digestion process are outlined in **Figure 2.7**. Hydrolysis is a process where large organic polymers such as proteins, fats and carbohydrates are broken down into fatty acids, amino acids and simple sugars. The products of hydrolysis go through an acidogenetic process where organic acids and low alcohols are produced. Hydrogen, carbon dioxide and acetic acid are produced in the acetogenic process which is required for the methanogetic process. Methanogenes converts the simple acids and the hydrogen produced by fermentative bacteria species, to methane gas and carbon dioxide (Sundararajan, Jayanthi & Elango, 1997).

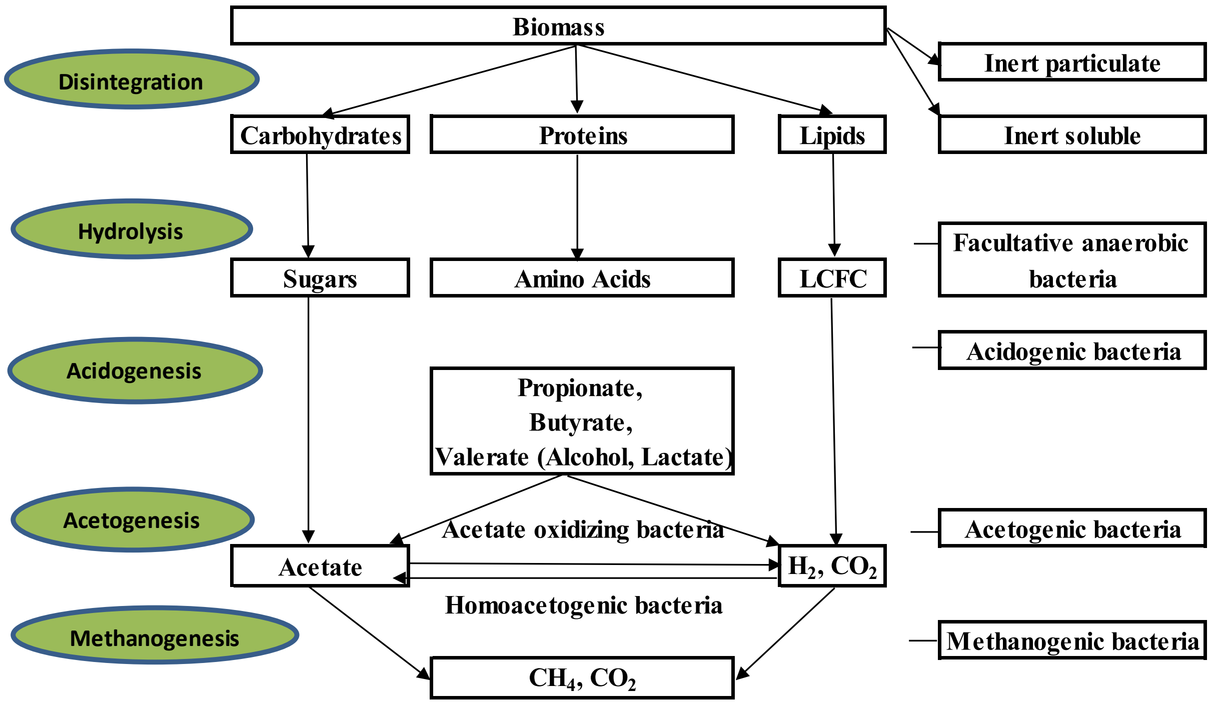

Figure 2.7*: Degradation steps of anaerobic digestion process (Angelidaki et al., 1996).*

The rate of AD processes depends on a number of parameters that include: temperature, pH, partial pressure, nature of substrate, retention time, carbon/nitrogen ratio (C/N), pressure, volatile fatty acids, microbes balance, trace metals and concentration of substrate, agitation, grinding, chemical oxygen demand, loading rate, particle size, co-digestion, digester constructions designs and size (Sreekrishnan *et al.,* 2004).

Table 2.5 shows the summarized unit operations and unit processes that are used in the removal of the major and minor constituents that are found in the wastewater.

Table 2.5: *Unit operation and processes in wastewater treatment plants (E. Metcalf)*

Constituent	Unit operation or process
Suspended solids	Screening
	Grit removal
	Sedimentation
	High-rate clarification
	Flotation
	Chemical precipitation
	Depth filtration
	Surface filtration
Biodegradable organics	Aerobic attached growth variation
	Aerobic suspended growth variation
	Anaerobic suspended growth variation
	Anaerobic attached growth variation
	Lagoon variation
	Physical-chemical systems
	Chemical oxidation
	Membrane filtration
Phosphorus	Chemical treatment
	Biological phosphorus removal
Nitrogen	Chemical oxidation (breakpoint chlorination)
	Suspended-growth/Fixed-film nitrification and denitrification variation
	Air stripping
	Ion exchange
Nitrogen and Phosphorus	Biological nutrients removal variations
Pathogens	Chlorine dioxide
	Chlorine compounds
	Ozone
	Ultraviolet (UV) radiation
Colloidal and dissolved solids	Membranes
	Carbon adsorption
	Ion exchange
	Chemical treatment
Volatile organic compounds	Air stripping
	Carbon adsorption
	Advanced oxidation
Odors	Carbon adsorption
	Chemical scrubbers
	Bio-filters
	Compost filters

2.5 Technique used in Selecting Plants to Sample

Several methods have been developed to give unbiased results when it comes to decision making on a choice of technology. In principle, all methods are based on the steps summarized below (Kigozi, Aboyade & Muzenda, 2014);

- Identification of the problem
- Identification of stakeholders
- Seeking the unbiased opinions of the stakeholders in the form of solutions to the identified problem. The identified solutions are treated as alternatives and the key performance indicators of the chosen options become the selection criteria
- Modelling the obtained solutions so as to obtain impartial results through detailed analyses. At the modelling stage is when the decision maker decides on which particular selection method to employ basing on the nature of the problem at hand.

In modern times, technologies are probabilistic in nature and the evaluation criterion are multi-dimensional. This calls for complex tools that can capture all the dimensions of a decision problem. The existing technology selection methods include;

2.5.1 Multi-criteria decision analysis (MCDA)

Multi-criteria decision analysis (MCDA) is an approach employed by decision makers to make recommendations from a set of finite seemingly similar options based on how well they score against a pre-defined set of criteria. MCDA techniques aim to achieve a decision goal from a set of alternatives using pre-set selection factors herein referred to as the criteria (Chai, Liu & Ngai, 2013). The selection criteria are assigned weights by the decision maker basing on their level of importance. Then using appropriate techniques, the alternatives are awarded scores depending on how well they perform with regard to particular criteria. Finally ranks of alternatives are computed as an aggregate sum of products of the alternatives with corresponding criteria. From the ranking, a decision is then made (Dodgson, Spackman, Pearman & Phillips, 2009).

There are several variations in MCDA techniques used currently employing mathematics and psychology. These include; analytic hierarchy process (AHP), Simple multi-attribute rating technique (SMART) and case-based reasoning (CBR).

AHP aims at organizing and analyzing complex decisions basing on their relative importance independent of each other (Pohekar & Ramachandran, 2004; Saaty, 2004). Saaty (2004) developed a scale of 1-9 to score alternatives basing on their relative importance as shown in **Table 2.6.** However, the major drawback of the AHP is the alteration of ranks in cases where new alternatives are introduced into an already analyzed problem (Pohekar & Ramachandran, 2004; Saaty, 2004).

Table 2.6*: Saaty's scale intensity 1-9 (Saaty, 2004)*

Scale Intensity	Definition	Explanation
1	Equal Importance	Two elements equally contribute to the intended objective
3	Moderate importance	Basing on judgement and experience one element is favoured over the other
5	Strong Importance	Basing on judgement and experience one element is strongly favoured over the other
7	Very Strong Importance	One element is very strongly favoured over the other and its dominance can be demonstrated in practice
9	Extreme Importance	The evidence favouring one element over another is of the highest order of affirmation

By applying the SMART technique, alternatives are ranked basing on ratings that are assigned directly from their natural scales (Barron & Barrett, 1996; Belton, 1986). The advantage of the SMART technique over AHP is the fact that the decision-making model is developed independent of the alternatives. Therefore the scoring of the alternatives is not relative and therefore introduction of new alternatives doesn't affect the ratings of the original ones making it a more flexible and simpler technique (Belton, 1986). In CBR, problem solving is done basing judgement on similar past problems and experiences. Basically, the decision is made basing on what has happened before (Leake, 1996).

2.6 Designs to be considered in selecting a WWTP

The fundamental prerequisite to begin the design of wastewater facilities is the determination of the design capacity that is the function of the wastewater flow rate. The determination of WWTPs flow rate consists of (Mackenzie, 2011):

- Selection of a design period (hydraulic retention time/residence time distribution)
- Estimation and projection of the population, commercial and industrial growth.
- Estimation and projection of wastewater flows
- Estimation of inflow and infiltration
- Estimation of parameters/variables that affects the wastewater treatment process

2.6.1 Establishment of design criteria

The design criteria for the construction of wastewater treatment consists of performance. This establishes the functional performance of the plant. The design criterion is the combination of the two. Performance criteria defines the desired objective but eliminates means of achieving this (Mackenzie, 2011).

The factors to be considered in establishing the design criteria for the water and wastewater treatment systems include:

- Environmental and regulatory standards
- Wastewater characteristics
- Site limits
- System reliability
- Design life
- Cost

2.6.2 Environmental and regulatory

The standards are prescribed by the regulating agency under the Law. This provides the basis for elimination of treatment technologies that are not appropriate. The standards require that WWTPs meets performance standards/numerical requirements for organic compounds and trace elements concentration. Modeling can assist WWTPs in meeting the required standards. The Agency do not prescribe the technology that is to be used in meeting the standards but set goals to be achieved by the engineers when selecting the appropriate treatment processes (Mackenzie, 2011).

2.6.3 Wastewater characteristics

Wastewater characteristics include the flow rate of the wastewater and its composition. The wastewater characteristics include (Mackenzie, 2011):

- Contribution from commercial and industrial activity.
- Composition and strength of the wastewater
- Hourly, daily, weekly, monthly, and seasonal variations in flows and strength of the wastewater
- Rainfall/runoff intrusion

2.6.4 System reliability

System reliability refers to the ability of a component or system to perform its designated function without failure.

2.6.5 Site limitation

The area and location available for the treatment plant, sewer systems, and water distribution system availability of roads, power, and a connection to the raw water supply define the site limits.

2.6.6 Design life

Design life is the economic comparison of alternatives (components of processes with different designs).

2.6.7 Cost

Design criteria for the process units and manpower depend on the economics evaluation. This cost estimates consist of capital costs (construction, engineering, land, legal, and administrative) and operating cost (personal, power, chemical, miscellaneous utilities). The economic analysis includes; present worth, annual cash flow, rate of return, benefits-cost and breakeven analysis.

2.7 Classification of WWTPs according to nature of influent

Wastewater is classified into the following categories (Mackenzie, 2011):

2.7.1 Domestic or sanitary wastewater

This is the wastewater discharged from residences, institutions, and commercial facilities. Conversion of total wastewater flow to a per capita allows for the separation of population growth from the growth in unit production of wastewater.

2.7.2 Industrial wastewater

This is the wastewater discharged from industries. It comprises of organic and inorganic compounds. If the industrial water requirement is known, an estimate of wastewater flow may be made by assuming about 85-90% of the water used becomes wastewater when internal plant recycling is not practised.

2.7.3 Infiltration and inflow

Infiltration is water that enters the sewer system from sewer service connections and the ground through foundation defective pipes, drains, pipe joints, connections, and manholes. In inflow, water enters the sewer system from roof downspouts (leaders), area drains, cooling water discharges, basements, swampy areas, catch basins, surface runoff, street water, manhole storm water, and drainage.

2.7.4 Storm water

Storm water is the runoff from rainfall.

2.8 Tracer Techniques and their Utilization in Wastewater Treatment Plants

A tracer is any substance whose chemical, biological and physical properties provides observation, identification and study of the behavior of chemical, biological and physical processes that occur either in a given lapse of time or instantaneously (IAEA, 2011a).

The residence time distribution (RTD) is determined experimentally by injecting an inert tracer into the reactor at an inlet and measuring the tracer concentration, *C* in the effluent stream over time. The tracer must be (de Souza Jr & Lorenz):

- Easily detectable
- Should have physical properties close to the reacting mixture
- Nonreactive species
- Should be soluble in the system

The efficiency of an installation depends on the gas, liquid and solid phase flow structure and their residence time distributions (RTDs) (Farooq, Khan, Gul, Palige & Dobrowolski, 2003; IAEA, 2011a). In 1953, Danckwerts (Danckwerts, 1953) introduced the concept of residence time distribution (RTD) which since then have become important tool in the analysis of industrial units. Danckwerts showed that the RTD could be obtained by tracer methods if a tracer behaves identically with all other fluid molecules. Generally, these methods rely on tracer input in the inflow of the system under investigation and on interpreting the monitored outlet tracer response of the system. Levenspiel (Levenspiel, 1972) thoroughly explained the RTD approach showing how it may legitimately be used, how to use it, and when it is not applicable what alternatives to turn to. Chmielewski *et al.,* 1998 performed radiotracer investigations of industrial wastewater equalizer-clarifiers and proposed a flow model for the system. The fluid dynamics is still under study by researchers and not yet fully understood, making it difficult for the theoretical prediction of important processes parameters such as phase distribution, mixing, flow rate and sedimentation characteristics of trace elements and organic compounds (IAEA, 2011a).

Trace techniques are useful tools to investigate the WWTPs purification efficiency that aid in both their performance optimization and design. There are many tracers, for example radioactive tracers (or a radioactive tracer) that have extremely high detection sensitivity and strong resistance against severe process parameters. They are used for on-line diagnosis of various parameters in WWTPs. The information necessary for the preservation of knowledge and transfer of technology to developing countries has not yet been established by the international tracer community where IAEA plays a major role in facilitating the transfer of radiotracer technology to developing member States (IAEA, 2011a).

2.8.1 The success of radiotracer application depend on (IAEA, 2011a):

- The possibility of on-line measurement under operating conditions (parameters) without disruption of the processes in the plant' units (without sampling).
- The strong resistance of radiotracers against the process conditions of WWTPs.
- The possibility to perform radiotracer experiments using small amount of radioactive material that labelled wastewater may be handled as non-radioactive waste.
- The extremely high detection sensitive of radiotracers facilitates their use in large scale WWTP treating millions of litres of effluents.
- Multi-tracer simultaneous test for the solids and liquid phases.

For the manual sampling, residence time distribution (RTD) is applicable with any type of tracer for any detection system. The tracing process consists of; injection of a tracer at the inlet (upstream) of a system and recording the concentration-time curve, *C(t),* at the outlet as shown in **Figure 2.8**. The inlet marks time zero. A second detector located at the outlet records the passage of the tracer from the vessel (IAEA, 2011a).

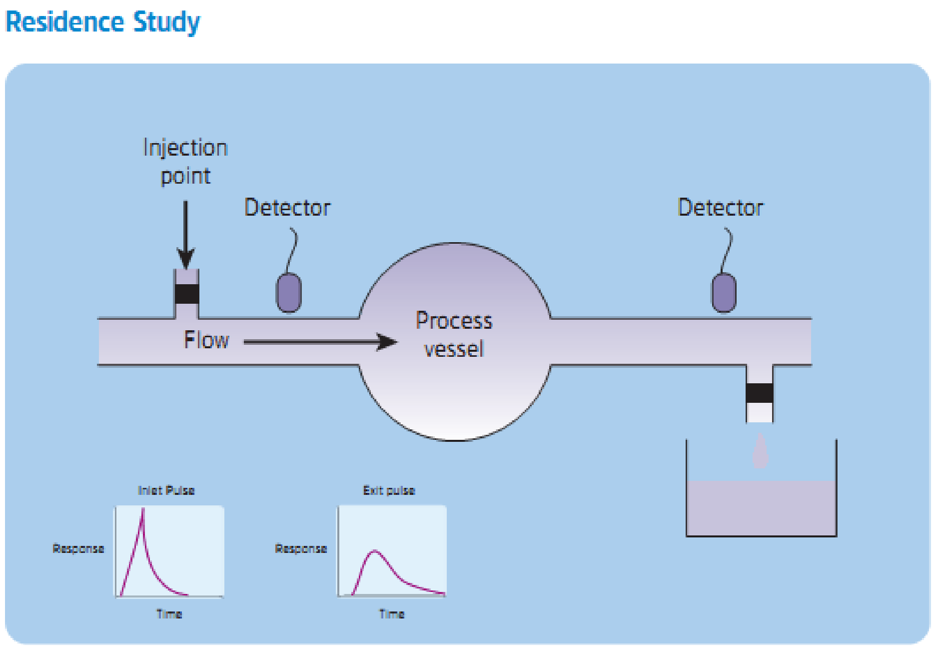

Figure 2.8 *Principle of tracer residence time distribution (RTD) (de Souza Jr & Lorenz; IAEA, 2011a).*

The answers provided in the WWTPs and investigated using radiotracer techniques includes:

- How the inlet flow into the tank is distributed?
- Are there any dead areas or stagnant zones in the tanks?
- Are there short circuits between inlet and outlet?
- At what distance are mixtures effective?
- How long is the retention time in the tank?
- Is the retention time suitable for the sanitation and ideal distribution?
- How quick is the sedimentation?
- Are the sludge scrappers effective?

2.8.2 Residence time distribution calculation using a tracer

Residence time distribution (RTD) is the distribution function that describes the amount of time a hydraulic take inside the digester/reactor. It is used to characterize the mixing and flow within reactors for non-ideal and to compare the behavior of real reactor to ideal models. It is useful in designing future reactors, estimating the yield of a given reactor and troubleshooting existing reactors.

The non-ideality of industrial processes leads researchers to develop corrections to the ideal models with less restriction. RTD is a function that describes the evolution of the average instantaneous concentration against the elapsed time and expressed as normalized (Stenstrom, 2003).

At the tracer injection the concentration C_0 is always low at the beginning, however it increases with time due to flux in the reactor. If C_o is the concentration of the tracer at the inlet of the reactor, The fraction of tracer remaining in the reactor *(F)* of the tracer at the outlet of the reactor will be given by the following **Equations 2.1-2.4** (de Souza Jr & Lorenz):

$$F(t) = \frac{(C(t)}{C_0} \text{...} \text{Eq. 2.1}$$

The tracer concentration in the reactor outlet is given by:

$$C(t) = C_0 \int_0^t E(t)\, dt \text{...} \text{Eq. 2.2}$$

Combining equation 2.1 and 2.2 gives

$$F(t) = \int_0^t E(t) dt \text{...} \text{Eq. 2.3}$$

$$E\ (t) = \frac{dF(t)}{dt} \text{...} \text{Eq. 2.4}$$

The residence time distribution curve is shown in **Figure 2.9.** The curves can be analyzed quantitatively and the behaviour of the flow inside the reactor can be outlined and observed.

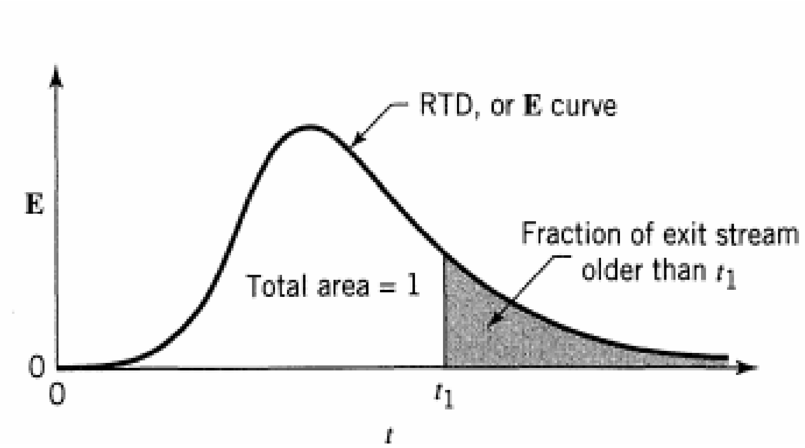

***Figure 2.9**: Residence time distribution curve behavior*

The E curve is the distribution needed to account for non-ideal flow (Stenstrom, 2003). Residence time *(τ)* is another important parameter that needs to be determined. It is the time that certain number of molecules has remained within a unit volume. For a fixed volume *(V)* and flow rate *(Q),* the mean residence time ideal is given by **Equation 2.5** (de Souza Jr & Lorenz):

$$\tau = \frac{V}{Q} \qquad \text{Eq. 2.5}$$

Residence time distribution in the biochemical processes is related to hydraulic residence time and bacteria residence time.

2.9 Economic Benefits of the Tracer Utilization in Wastewater Treatment Plant

Tracer technology allows movement of organic compounds and trace elements to be measured in a range of wastewater application technologies. The tracer benefits includes (IAEA, 2011a):

- Cost effective monitoring technique
- Insight into many areas of water quality
- Sludge behaviour
- Plant processes:
    - ✓ WWTP flow balancing
    - ✓ Determination of effective volume in anaerobic digesters
    - ✓ Retention efficiency of storm tanks
    - ✓ Sediments dynamic studies
    - ✓ Location and quantification of sewage network infiltration.
- Enable clients to identify areas where substantial savings in both capital and operational expenditure can be made.
- It reduces environmental impact of waste discharge.
- Provides data for the design of future plants
- Validation or/and provision of empirical data for computer fluid dynamics (CFD) models

The experiment design consist in selection of tracer injection points, position of detectors, radioisotopes transportation, radiological safety consideration, tracer injection, data acquisition, treatment and interpretation (Rivera *et al.,* 2012).

2.10 Conventional Tracer for WWTPs

The major non-radioactive tracers used for investigation of WWTPs units are optical and chemical tracers.

2.10.1 Chemical tracer

Chemical tracer is easily detectable substance measurable off-line (by sampling) at very low concentration by instrumental analytical techniques such as, gas chromatography (GC), high performance liquid chromatography, neuron activation analysis, inductive coupled plasma spectroscopy (ICP), etc. (IAEA, 2011a).

Sodium dichromate, sodium chloride, sodium iodide, sodium nitrite, potassium chloride, manganese sulphate, sodium pertechnetate and lithium chloride are actively used for water tracing in hydrology although they are not suitable and convenient to be used in WWTPs units according to IAEA (IAEA, 2011a; Rivera *et al.,* 2012). However, lithium chloride solution as tracer was reported to be of use in WWTPs as reported by IAEA (IAEA, 2011a).

The advantages of lithium chloride include:

- It has no toxicity
- It does not react or degrade in wastewater
- It has a low detection and measurement limits (atomic absorption spectrometry)

2.10.2 Optical tracers

Optical tracer is divided into two categories (IAEA, 2011a):

- Colour tracer
- Fluorescent tracer

In colour tracers, the detected parameter is the colour of tracer which is measured through a light or laser beam where a wavelength has to be adapted to fluid in order not to be absorbed in it.

The fluorescent tracer is excited by a laser beam or light that mainly operates in the ultraviolet (UV) region. The fluorescent tracer using Rhodamine WT and a fluorometer are reported for online investigation of water phase dynamics in some WWTP units (designs, Accessed 2016; IAEA, 2011a).

2.11 Radioactive versus Conventional Tracer Techniques, Applied to WWTPs (IAEA, 2011a).

The field of application of a gas tracer are aeration tanks, biological filters, disinfection units, anaerobic digesters. **Table 2.7** gives the gas tracer used for radioactive and conventional tracer technique, advantages and disadvantages of the application to the WWTPs in determining the residence time distribution.

***Table 2.7**: Comparison of radioactive and conventional tracer techniques using gas tracers in the WWTPs (IAEA, 2011a).*

	Radioactive tracer	Conventional tracer
Tracer used	^{41}Ar, ^{79}Kr, $CH_3{}^{82}$, Br	Cl_2, SO_2, NO_2, SF_6, etc.
Advantages	High selectivity	Simple analysis
	Low detection limit	Easy analysis
	In-situ/On-line measurement (no sampling)	
Disadvantages	Poor availability	Poor selectivity
	High costs	Poor detection threshold
	Strict radiation safety regulation	Difficult to get statistically
		Representative sample

The field of application of liquid tracers are in equalization tanks, central collection networks, flash mixers, clarifier, aeration vessels, anaerobic digester, and dispersion of discharge in water. **Table 2.8** gives the liquid tracer used for radioactive and conventional tracer technique, advantages and disadvantages of the application to the WWTPs in determining the residence time distribution.

***Table 2.8**: Comparison of radioactive and conventional tracer techniques using liquid tracers in the WWTP (IAEA, 2011a).*

	Radioactive tracers	**Conventional tracers**
Tracers used	$K^{82}Br$, $NH_3{}^{82}Br$, $Na^{99m}Tc_2O_4$, ^{113m}In-EDTA, ^{46}Sc-EDTA, $Na^{131}I^-$, $^{24}Na_2CO_3$, etc.	Electrolytes (NaCl solution): conductivity Dyes (Rhodamine, Fluorescence): Colour Acids & Alkali: pH
Advantages	No interaction with WWTPs treatment Low detection threshold Online measurement No limitations due pH, conductivity and colour Some radiotracers are readily available and inexpensive	Easily available and cheap
Disadvantages	Strict radiation safety regulations relatively expensive detection equipment	Not suitable for colour, conducting liquids Stratification due to density difference Large threshold detection concentration Possible interference with WWTPs treatment operations

The field of application of solid tracers are in sand and grit removal, collection networks, clarifiers, biological reactors (aerobic and anaerobic), discharge networks. **Table 2.9** gives the solid tracer used for radioactive and conventional tracer technique, advantages and disadvantages of the application to the WWTPs in determining the residence time distribution.

Table 2.9 *Comparison of radioactive and conventional tracer techniques using solid tracers in the WWTP (IAEA, 2011a).*

	Radioactive Tracers	**Conventional Tracers**
Tracers used	^{113m}In, ^{99m}Tc, ^{198}Au, ^{140}La, etc.	No known solid tracers Current methods; sampling, filtering, drying, weighing
Advantages	No interaction with WWTPs treatment Low detection threshold Online measurement No limitations due pH, conductivity and colour Some radiotracers are readily available and inexpensive Independent detection without interference with gas and liquid detection	
Disadvantages	Strict radiation safety regulations Relatively expensive detection equipment	Tedious Difficult to get statistically Representative sample

2.12 Modelling and Simulation of Wastewater Treatment Process

2.12.1 Models

For nearly 40 years, scientists have developed and improved on the biological models of organic substances. For the complete process to be developed, an appropriate model is required.

Models are classified into two forms:

- Dynamic model
- Static model

Numerical modelling investigates the dynamic and static behaviour of a system without doing or by performing a reduced number of practical experiments. Most experimental approaches are time-consuming if all variables are investigated, to obtain the optimum conditions. Few experimental results enable modelling, simulation, proper calibration and validation (Dipl-lng.M & Schon, 2009).

Dynamic models consider time as a variable while static models do not. Numerical modelling investigates the dynamic and static behaviour of a system without doing or by performing a reduced number of practical experiments. Most experimental approaches are time-consuming if all variables are investigated to obtain the optimum conditions. Few experimental results enable modelling, simulation, proper calibration and validation (Dipl-lng.M & Schon, 2009). **Figure 2.10** shows generic steps followed in generating the model.

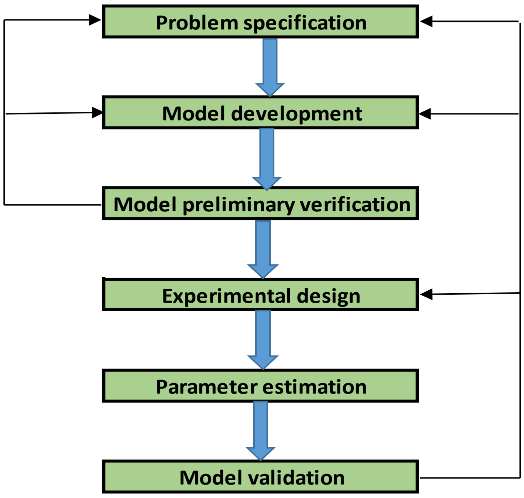

Figure 2.10*: Generic steps followed in generating the model (Eva, 2010; Sanders, Veeken, Zeeman & Van Lier, 2003).*

The step followed in modelling include (Eva, 2010; Sanders *et al.,* 2003):

- Problem specification: the following questions are addressed; intention of the research, aim of the model, operation and control of the design and lastly degree of accuracy required.
- Model development: this is where questions about the model are established.
- Preliminary verification: in this stage the analysis of the identifiability of model and parameters are set. If the model does not match intended objective, then the development returns to the second or first step.
- Experimental design: optimum set of experimental analysis that will used to produce best data for best model fitting and validation are chosen.
- Parameters estimation: model is fitted to experimental data by adjusting model parameters.
- Model validation: predictions made by the model and actual experimental data are compared to evaluate the accuracy.

2.12.2 Advantage of modelling in wastewater treatment processes

The most prominent advantages of using the models in wastewater treatment process, are (Henze, 2008):

- Evaluating possible scenarios for upgrading
- Evaluating new plant design
- Supporting management decisions
- Developing new control schemes
- Providing operator training
- Saving time and money in the process of technology/process selection.
- Comparison of the system performance in a quantitative instead of a qualitative way allows in many cases for easier decision-making and rapid comparison of options (Henze, 2008).

The second main reason for using model is the possibility of saving time and money in the process of technology/process selection. Comparison of the system performance in a quantitative instead of a qualitative way allows in many cases, for easier decision-making and rapid comparison of options (Henze, 2008).

Another strong reason for using model is the possibility of minimizing risks. By using model, 'what if' scenarios can be examined in a quantitative way in respect of what the effects of potential risks are. Furthermore, application of models improves knowledge transfer and decision-making (Henze, 2008).

2.12.3 Mass balance analysis

Mass balance is the fundamental approach used to study the hydraulic flow characteristic of reactors/digesters and to delineate the changes that takes place when a reaction takes place. It defines what occurs in the treatment reactors as a function of hydraulic retention time. It is based on the principle of mass conservation or law of conservation of mass, where mass is neither created or destroyed but may transformed from one form to another (e.g. solid to liquid to gases) (E. Metcalf). Mass balance for the heavy metals in primary, secondary and the whole WWTPs process shows good closures for all metals species (Karvelas, Katsoyiannis & Samara, 2003).

The general steps used in preparing the mass balance analyses includes (E. Metcalf) :

- Preparing a flow diagram or a simplified schematic of the system or the process for which mass balance is to be prepared.
- Drawing a system or control volume boundary to define the limits over which the mass balance is to be applied.
- List all of the assumptions and pertinent data that will be used in the preparation of the material balance on the schematics of flow diagram.
- Select a convenient basis on which the numerical calculation will be used.

To apply a mass-balance analysis to the liquid contents of the reactor in WWTPs, it will be assumed that (E. Metcalf):

- The volumetric flowrates into and out of the container is constant.
- The liquid within the reactor is not subject to evaporation (isothermal conditions)
- The liquid within the container is mixed completely
- A chemical reaction involving the reactant *C* is occurring within the reactor
- The rate of change in the concentration of the reactant *C* occurring within the reactor is governed by a first-order reaction ($r_c = -kC$-decrease in the reactant while $r_c = +kC$-increase in the reactant).

The general mass balance equation is given by.

Rate of accumulation	=	Rate of flow the	-	Rate of flow	+	Rate of generation (utilization)
of reactant within		of reactant into		of reactant out of		of reactant within
the system boundary		system boundary		the system boundary		the system boundary

The corresponding simplified word statement is given by **Equation 2.6:**

Accumulation = Inflow – Outflow + Generation Eq. 2.6

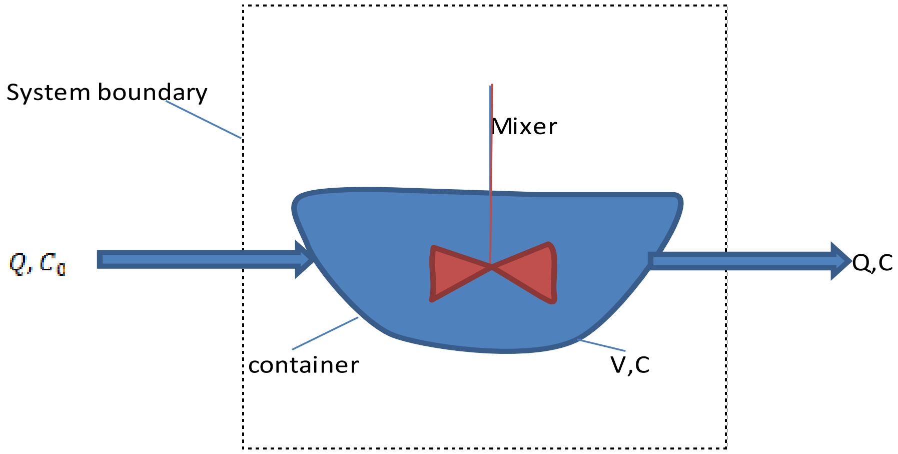

***Figure 2.11**: Mass balance on its associate inputs and outputs*

Symbolic representation by **Equations 2.7, 2.8:**

$V\frac{dC}{dt} = QC_o - QC + V(rate\ of\ reaction, r_c)$ ………………………………... Eq. 2.7

Substituting $-kC$ for r_c yields;

$V\frac{dC}{dt} = QC_o - QC + V(-kC)$……......……………………………………Eq. 2.8

Where:

V = Volume of reactor (m^3), L^3

$\frac{dC}{dt}$ = Rate of change of reactant concentration within the reactor ($g/m^3.s$), $ML^{-3}T^{-1}$

Q = Volumetric rate of flow into and out of the container (m^3/s), L^3T^{-1}

C_0 = Concentration of reactant in the influent (g/m^3), ML^{-3}

C = Concentration of reactant in the reactor and effluent (g/m^3), ML^{-3}

K = First-order reaction-rate constant (1/s), T^{-1}

2.12.4 Different types of models

Several mathematical models are available to describe the biochemical transformation and degradation processes in WWTPs. The most popular is the IWA (International Water Association) Activated Sludge Model (ASM) and Anaerobic Digestion Model 1 (ADM1) family (Henze *et al.*, 2000). ASM1 and ADM1 are very extensively used in the wastewater community and has become the standard model for dynamic simulation of activated sludge plants (Langergraber *et al.,* 2004a).

Other types of the model for WWTPs include:

- DTS Pro-Modelling of gas, liquid and solid flows at a steady theoretical interpretation framework for tracer.
- ASM2/2d are able to describe enhanced biological and chemical removal (Langergraber *et al.,* 2004a).
- ASM3 introduced a new set of processes to describe the COD flow (Langergraber *et al.,* 2004a).
- ASAL models for BOD removal (Langergraber *et al.,* 2004a).
- Lawrence and McCarty model for COD and nutrients removal (H.).
- ADM1 as proposed by the International Water Association (IWA) group deals with mathematical modelling of anaerobic digestion processes by Batstone *et al.,* 2002a (Eelke, 2014).
- Biosorption equilibrium models for metal removal.

2.12.5 Bio-chemical kinetics models

The theory of biological processes has been previously represented mathematically to represent process kinetics (Porubova *et al.,* 2011). Most of the models allow biological treatment process calculations. This allows monitoring parameters and enhancing plant efficiency. The following are some common kinetic expressions describing biological treatment (Gerber & Span, 2008):

- Biosorption equilibrium models
- First order kinetic model
- Monod kinetic model
- Chen and Hashimoto kinetic model
- Contois kinetic model

- Modified Gompertz kinetic model
- Michaelis-Menten kinetic model
- Anaerobic Digestion Model (ADM1)
- Activated Sludge Models (ASM)
- Biosorption equilibrium models

2.12.6 Identification of constraints for the modelling scenarios:

The constraints include equipment constraints such as lower capacities, pump limits, potential unit out of service. And the operating constraint that includes solids retention time for nitrification, anaerobic digester HRT, maximum allowable mixed liquor concentration, dewatering facility operating shift length.

2.12.6.1 Establish key performance indicators (KPIs)

This involves which parameters should be tracked and it serves as a model output.

2.12.6.2 Establish modelling scenarios

This identifies temperature, flow and load pattern to apply in conjunction with estimated future daily average flows and whether a plant can accommodate an additional input from a nearby plant.

2.12.6.3 Run modelling scenarios

It is important to run model iteratively, particularly if the objective is to determine the ultimate plant capacity with existing infrastructure.

2.13 Standards of Organics and Inorganics in Wastewater

Table 2.13 shows the water standards enacted by-law in various Government and Non-Government institution Worldwide. It summarizes different substances/parameters concentration. The American National Safe Drinking Water Act (SDWA) signed in 1974 and enacted by the Environmental Protection Agency (EPA) shows the contaminants; organics, inorganics, radionuclides and microbial, maximum contaminants level (MCLs) for the public water quality standards, best available technology (BAT) and potential health effects.

Table 2.10 shows the metals of importance in the wastewater treatment plants. It comprises nutrients necessary for biological growth, concentration thresholds of inhibitory effects on heterotrophic organisms, land application of effluent and used to determine if biosolids are suitable for land application.

***Table 2.10**: The metals of importance in the wastewater managements*

Metals	Symbol	Nutrients Necessary for Biological growth		Concentration thresholds of inhibitory effect on heterotrophic organisms,	Used to determine SAR for land application	Used to determine bio solids are suitable for land Application
		Macro	Micro	mg/L	of effluent	
Arsenic	As			0.05		×
Cadmium	Cd			1		×
Calcium	Ca	×			×	
Chlomium	Cr		×	1		
Cobalts	Co		×			
Copper	Cu		×	0.1		×
Iron	Fe	×				×
Lead	Pb		×			
Magnesium	Mg	×	×		×	
Manganese	Mn		×			
Mercury	Hg			0.1		×
Molybdenum	Mo		×			×
Nickel	Ni		×	1		×
Potassium	K	×				
Selenium	Se		×			×
Sodium	Na	×			×	
Tungsten	W		×			
Vanadium	V		×			
Zinc	Zn		×	1		×

2.14 Sources of Trace Metals in Wastewater Treatment Plant

Trace elements pollution has attracted much attention in recent years due to its bioaccumulation, toxicity and wide range of sources and persistence (Wang *et al.,* 2015). Besides the toxicity caused by inorganic metals, the latter also affect the ecosystems of the receiving water (Berkun & Onal, 2004). The presence of these metals (e.g. Pb, Cd, Cr, Cu, Zn, As, Mn, Al, etc.) are brought about by industrial activities that generate numerous chemical elements (Wang *et al.,* 2015). The metals concentrations could be analyzed by the use of inductively coupled plasma-optical emission spectroscopy (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FAAS), and graphite furnace atomic absorption spectrometry (GFAAS) (Mogolodi, Ngila & Mabuba, 2015; Shamuyarira & Gumbo, 2014). Several methods have been developed for the removal of heavy metal in the wastewater such as evaporation, precipitation, electroplating, membrane processes, ion exchange, etc. These methods have several demerits such as high reagent requirement, unpredictable metal ion removal, etc. (Das, Vimala & Karthika, 2008).

Metals are involved in metabolism and microbial growth in WWTPs. Essential metals like Ca, Cu, Co, Fe, K, Mg, Mn and those with non-essential biological functions such as Al, Cd, Cs, Hg, Pb, and Hg can be accumulated by microorganisms through non-specific physio-chemical interactions as well as specific mechanisms of sequential transport (Barakat, 2011; Karvelas *et al.,* 2003; Van Wyk, 2011). Thus, research studies should be undertaken in order to construct historical records of contamination and quantification of the intensity of heavy metal pollution based on enrichment factor, risk assessment codes (RAC) and excess flux. Investigation of the sources of heavy metals by assessing speciation relationships through component analysis, is crucial (Wang *et al.,* 2015).

2.15 Levels of Metals in WWTPs in Gauteng

In seven of the nine provinces of South Africa, more than half the water is provided by inter-basin transfers (DWS, 2016). This demonstrates the intensity with which the country's available resources are already being used. The current status of water quality varies substantially, with the most contaminated water resources being the Vaal River, Crocodile West (Limpopo), Umgeni and Olifants River systems. Radionuclide and heavy metal contamination in South Africa are the legacy of more than a century of unregulated gold mining, coupled with high-density populations living in daily close contact with dust and sediment arising from mine tailings dams (Van der Merwe-Botha, 2009). Parts of Soweto and

East and West Rand residential complexes are located on land that would be classified as "contaminated sites" in developed countries. The degree of pollution also impacts on the local water resources (Van Eeden & Schoonbee, 1996).

Effluents from WWTPs and sanitation systems should be audited in terms of the current functionality of these systems. For instance, WWTP systems function according to the license agreement specifications. A question that we asked while compiling this data was, do the WWTPs have appropriate technology and the planned expansions? A plan of action or programme should be agreed with local municipalities and its implementation monitored. Repeated audits should be based on a predetermined schedule, while keeping compliance monitoring in place. Thus, there is need to develop policies, standards, parameters, criteria and guidelines for water quality compliance. These should consider factors such as people's needs, drinking water standards, agriculture, industry, mining and the natural environment. The treatment capacity of all wastewater treatment works needs to be established so as to ensure that the overflow influent does not contaminate the treated effluent. This way any effluent that is discharged into the environment does not impact negatively on the ecosystem. The existing monitoring programmes may not necessarily provide this information and therefore expanded sampling and monitoring processes may be required (Van Eeden & Schoonbee, 1996).

According to the National Water Act, waste discharge standards in accordance with DWS 2016 guidelines (DWS, 2016), wastewater limit values applicable to the discharge of wastewater, into environmental resource are stipulated in **Table 2.11.** The data given in **Tables 2.12-2.14** have been compiled to reflect the established or measured levels of metals in selected WWTPs in Gauteng for raw wastewater (**Table 2.12**) and treated effluent (**Table 2.13).** The data in these tables indicate that, point and non-point sources are the main pathways through which heavy metals enter the environment. Point source pollution is that which originates from a known source, e.g. discharge from an electroplating industry. Wastewater conveys the pollutant to and from the WWTPs that enter the receiving environment. In some cases, the influent is not stripped off the heavy metals as non-point sources have a diffuse source of origin, such as storm water. This type of pollution is insidious because of its diverse and variable nature (DWS, 2016). Studies have revealed that the groundwater in the mining district of Johannesburg, South Africa, is heavily contaminated and acidified as a result of oxidation of pyrite contained in the mine tailings dumps and has elevated concentrations of heavy metals.

Sludge from WWTPs could be a good source of information on the levels of metals in raw wastewater. This is because if the treatment process manages to remove all the metals, these are likely to be transferred from the liquid into the sludge. **Table 2.11** shows the level of metal ions in sludge.

***Table 2.11**: Discharge Standards Guidelines*

Variables and substances	Existing General Standards	New Standards
Chemical oxygen demand	75 mg/l	65 mg/l
Colour, odour or taste	No substance capable of producing the variables listed	No substance capable of producing the variables listed
Ionised and unionised ammonia*	3,0 mg/l	1,0 mg/l
Nitrate (as N)	15	15 mg/l
pH	Between 5,5 and 9,5	Between 5,5 and 7,5
Phenol index	0,1 mg/l	0,01 mg/l
Residual chlorine (as Cl)	0.25 mg/l	0,014 mg/l
Suspended solids	25 mg/l	18 mg/l
Total aluminium (as Al)	-	0,03 mg/l
Total cyanide (as Cn)	0,02 mg/l	0,006 mg/l
Total arsenic (as As)	0,02 mg/l	0,01 mg/l
Total boron (as B)	1,0 mg/l	0,5 mg/l
Total cadmium (as Cd)	0,005 mg/l	0,001 mg/l
Total chromium III (as CrIII)	-	0,11 mg/l
Total chromium VI (as CrVI)	0,05 mg/l	0,02 mg/l
Total copper (as Cu)	0.01 mg/l	0,002 mg/l
Total iron (as Fe)	0.3 mg/l	0,3 mg/l
Total lead (as Pb)	0,01 mg/l	0,009 mg/l
Total mercury (as Hg)	0,005 mg/l	0,001 mg/l
Total selenium (as Se)	0,02 mg/l	0,008 mg/l
Total zinc (as Zn)	0.1 mg/l	0,05 mg/l
Faecal coliforms per 100 ml	1000 mg/l	1000 mg/l

*Ionised and unionised ammonia free and saline ammonia (as N)

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Table 2.12*: Metal content (mg L^{-1}) <u>raw influent</u> from selected Gauteng WWTPs (City of Tshwane Data from 2011-2013))*

Metal	Temba	Godrich	Zeekoegat	Babalegi	Rayton	Sandspruit	Rietgat
Al	1066±78	10689±45035	791±297	6.40±5.43	807±302	1587±1125	1249±715
As	12.0±32.1	13.6±30.4	16.9±26.9	10.0±20.0	14.5±30.9	26.1±41.7	14.4±25.3
Cd	3.97±13.8	2.85±8.70	435±45.2	10.1±31.2	3.91±11.5	3.70±11.1	4.05±10.7
Cr	2.51±5.76	2.63±5.85	26.3±27.2	70.8±81.3	3.77±6.27	5.39±8.64	8.65±10.7
Cu	49.7±54.3	82.8±115.7	97.9±38.6	150±130	88.6±30.7	52.5±28.6	65.9±69.2
Fe	1281±773	954±821	2965±4972	3230±644	737±163	2432±2583	4300±4546
Mn	218±73.2	116±65.1	138±55.9	350±340	95.9±103	101.7±65.9	140±45.3
Ni	13.9±11.6	6.27±7.00	27.3±17.4	80±170	8.11±7.49	8.57±9.18	8.58±7.25
Pb	80.6±81.4	75.8±59.6	62.8±60.8	450±320	86.9±63.5	63.9±67.7	51.1±50.0
Zn	185±90.7	201±293	991±617	2870±2560	247±89.0	181±120	229±269

Table 2.13: *Metal content (µg L^{-1}) in* *<u>treated effluent</u>* *from selected Gauteng WWTPs (City of Tshwane Data from 2011-2013))*

Metal	Temba	Godrich	Zeekoegat	Babalegi	Rayton	Sandspruit	Rietgat
Al	131±162	115±237	264±218	184±181	289±225	127±102	116±106
As	8.67±24.7	9.09±22.8	7.25±18.8	2.56±7.31	10.1±28.4	2.85±7.42	7.85±28.2
Cd	4.04±13.4	3.00±9.41	3.07±8.84	9.12±26.3	3.75±10.1	4.93±13.7	20.0±40.6
Cr	1.21±3.07	1.61±3.99	4.22±7.99	18.5±74.0	6.20±15.0	2.98±5.95	34.8±45.1
Cu	15.2±10.3	11.9±8.88	22.1±20.0	15.3±8.12	29.8±11.3	15.5±12.4	109±443
Fe	185±83.0	102±70.2	453±462	242±126	293±178	217±187	959±1614
Mn	56.7±67.9	44.2±48.4	106±54.1	169±115	48.4±69.8	67.5±42.5	85.2±62.4
Ni	9.40±6.78	5.77±5.28	19.5±10.0	21.1±18.0	7.1±5.81	7.59±10.4	68.5±88.6
Pb	70.6±76.4	64.3±53.0	44.7±51.9	90.5±93.0	89.5±60.9	49.5±53.2	58.1±94.3
Zn	100±204	39.7±43.0	352±383	342±568	72.931.9	88.82±255	73.9±69.7

Sludge from WWTPs is known to be a good agricultural resource which could be a significant source of income if the quality is well managed through elimination and mitigation of heavy metals present in the influent received by the treatment works (Jaganyi *et al.,* 2005; Moeletsi *et al.,* 2004). In certain cases, the sludge has residual heavy metals making it unsuitable for agricultural use. Secondary treatment with lime is done to immobilise these metals and reduce the possibility of being leached into underground water and disposed into landfills.

Table 2.14: *Levels of Metals (mg L^{-1}) in* *<u>sludge</u>* *from Selected Gauteng WWTPs (City of Tshwane Data from 2011-2013))*

Metal	Zeekoegat	Rietgat	Baviaanspoort	Daspoort	Rooiwal
Al	5621±5251	5539±6452	3451±2426	NI	NI
As	2.84±10.5	NI	4.78±19	NI	Ni
Cd	7.72±20.2	9.49±27.9	7.61±19	7.42±21.9	11.4±8.91
Cr	218±48.8	43.2±19.3	72.8±150	48.3±50.6	426±237
Cu	555±144	159±102	179±112	179±70.1	477±247
Fe	17563±8191	105640±124917	18303±39550	17081±18633	8499±5963
Mn	362±117	492±148	211±144	155±64.3	287±125
Ni	92.2±22.0	28.3±18.7	65.9±84	15.2±10.8	121±47.2
Pb	69.3±23.5	48.3±80.7	48.6±86	NI	NI
Zn	15298±35026	954±	1516±3452	748.5209	3625±1961

NI = not included

2.16 Organic Compounds in Water and Sludge in WWTPs, Gauteng Province

Most of the organic contaminants in wastewater originates from products that are used in everyday life and in very large quantities such as pharmaceuticals, personal care products, pesticides, PAHs among others. Numerous previous studies have indicated that these compounds undergo partial or no removal during treatment processes and are therefore detected in the effluent water and in aquatic environments. These emerging compounds were also not included in the relevant legislation for monitoring and hence there were no limit values set for treated wastewater (Thomaidi, Stasinakis, Borova & Thomaidis, 2015).

Within the water treatment plants, there is secondary contamination which occurs from the different processes within the plant used in treating the water. A well-known example is the disinfection by-products (DBPS) which occur as a result of disinfection with, chlorine, chloramine, ozone, chlorine dioxide with natural organic matter (NOM) and iodide or bromide (Richardson & Ternes, 2011). These by-products include trihalomethanes (THMs) and haloacetic acids, both of which are suspected human carcinogens and are now regulated by the EPA for DBPs with the maximum contaminant levels of 80 and 60 µg/L, respectively (Zazouli *et al.,* 2007). Other DBPs include nitrosamines, bromonitromethanes iodo-trihalomethanes, haloaldehydes, and halonitromethanes (Richardson & Ternes, 2011).

Emerging pollutants are defined as compounds that are not currently covered by existing water-quality regulations. They are usually present in surface waters at trace levels and cause known or suspected adverse ecological and/or human health effects (Boleda, Galceran & Ventura, 2011; Farré, Pérez, Kantiani & Barceló, 2008; Geissen *et al.,* 2015). Modern society depends on a large range of organic chemicals and compounds which ultimately enter urban wastewater, posing potential environmental threats to the living (Bolong, Ismail, Salim & Matsuura, 2009; Clarke & Smith, 2011). The examples of emerging pollutants found in wastewater include endocrine disruptors compounds (EDCs), pharmaceuticals, drugs of abuse, personal-care products, steroids and hormones, surfactants, perfluorinated compounds, flame retardants, industrial additives and agents, gasoline additives,1,4-dioxane and swimming pool disinfection by-products (Farré *et al.,* 2008).

2.16.1 Polyaromatic hydrocarbons (PAHs)

PAHs are a class of diverse organic compounds with two or more aromatic rings of carbon and hydrogen atoms. They are reported to be among the widespread organic contaminants in aquatic environments including WWTP. PAHs do not degrade easily and are persistent to the environment with an increase in molecular weight. They bioaccumulate in food chains, rendering them harmful and toxic to humans and living organisms, via their carcinogenic, mutagenic, and endocrine disruption effects (Ferretto *et al.,* 2014). Sources of PAHs include but not limited to forest and rangeland fires, oil seeps while their anthropogenic sources are mostly combustion of fossil fuel, coal tar, used lubricating oil, municipal incineration and petroleum spills and discharge. They are introduced into the aquatic life via discharge of oil in transit from oil tankers during sea activities, industrial and urban wastes as a result of surface runoff, wastewater effluent as well as atmospheric particles (Ferretto *et al.,* 2014; Haritash & Kaushik, 2009). PAHs up to now have always been on the priority list of regulated contaminants by the European union (EU) and the USEPA (Ferretto *et al.,* 2014). Due to their constant introduction into aquatic life, it is of high importance that they are monitored for effective removal in the WWTP.

2.16.2 Pesticides

Pesticides comprise a collective group of organic chemical compounds used for different purposes such fungicides, herbicides, insecticides, rodenticides among other uses. They are mostly used in agriculture for enhanced food production worldwide. Surface run-off from agriculturally related use has been the most predominant source of entry pesticide contamination into the environment. However, WWTP represents one of the main sources of contamination in urban areas mostly attributed to non-agricultural uses (Köck-Schulmeyer *et al.,* 2013).

Pesticides can undergo environmental degradation to from transformation products (TPs) through various mechanisms such as biological or chemical which occur through hydrolysis,photolysis, and/or redox reactions. TPs are on the increase as recent detailed reports by Vidal et al., [49] indicate that they could be more persistent and toxic than the parent compound, e.g. carbamates, organophosphorus (Zhao & Hwang, 2009) DDE which is more persistent that DDT. The presence of natural organic matter, as well as the disinfection process present in WWTPs, play a role in the transformation of pesticides to their metabolites. A report by Bavcon *et al.* (2003) [50], investigated the formation of transformation products of two organophosphorus, i.e malathion and diazinon under different environmental conditions (Bavcon, Trebše & Zupančič-Kralj, 2003). There is, therefore, a need to monitor pesticides and their TPs in the wastewaters as most previous methods only focused on the parent compound (Martínez Vidal, Plaza-Bolaños, Romero-González & Garrido Frenich, 2009).

Recent work by Dabrowski *et at*. (2014) [52] shows a wide use of pesticides in South Africa,with reports of atrazine, simazine and terbuthylazine being frequently reported in ground and surface water at relatively high concentrations, in areas where there is high maize production. Atrazine application in maize crops which is the most widely produced crop in SA, is in the tune of 1014.42×10^3 kg. This is a huge volume of pesticides and if not well monitored for effective removal in wastewaters will ultimately be recycled throughout body systems via various means of exposure aforementioned (Dabrowski, Shadung & Wepener, 2014). Hence in this study, we shall use advanced chromatographic techniques coupled with mass spectrometers in addition to modeling, as these instruments possess high sensitivity to ng/L levels for developing a robust method for detecting a vast number of priority pesticides compounds in South African wastewaters.

2.16.3 Disinfection by-products

Disinfectants are chemicals used in disinfection processes, pre-oxidation and for the removal of taste and bad odour. Disinfection can thus be described as removal, deactivation or killing of pathogenic microorganisms. Microorganisms are destroyed or deactivated, resulting in termination of growth and reproduction (Peter & Freese, 2009). Disinfection in normally carried out in the final stages of water treatment processes. Disinfection by-products (DBPs) are toxic chemical substances formed as a result of the interaction between natural organic matter, anthropogenic contaminants, bromide or iodide with disinfection agents such as chlorine, chloramine, chlorine dioxide and ozone that are used in water treatment plants (Fischer, Fries, Korner, Schmalz & Zwiener, 2012; Richardson, Plewa, Wagner, Schoeny & DeMarini, 2007).

An intensive report was done by Richardson *et al.* (2007) [55], categorized the different classes of DBPs as regulated and non-regulated (Richardson *et al.,* 2007). The regulated ones include trihalomethanes chloroform, bromodichloromethane, chlorodibromomethane, and bromoform), haloacetic acid (chloroacetic acid, bromoacetic acid, chloroacetic acid, dibromo acetic acid and trichloroacetic acid) and Oxyhalides (bromate and chlorite) (Acero, Benítez, Real & González, 2008; Bond, Huang, Graham & Templeton, 2014). THMs were the first reported DBPs and together with haloacetic acids (HAA), they are the most prevalent of all DBPs, most of which are regulated by the EPA (Richardson *et al.,* 2007). The contact pathways of the THMs to humans have been reported to be via inhalation, ingestion, and dermal pathways (Chowdhury, 2012). It has also been reported that use of UV and advanced oxidation (UV/H_2O_2) increases the formation of DBPs in water treatment processes (Richardson & Ternes, 2011). In another study, it was shown that ozonation followed by post chlorination led to the formation of the highest number of halo nitromethanes. However, when ozone is used in water treatment, it lowers the formation of THMs and HAAs, but the only challenge is the presence of natural bromide at elevated levels which leads to the formation of dibromo acetic acid, a high occurrence trans-species carcinogen (Richardson *et al.,* 2007). Ozonation followed by post chlorination is normally done as ozone has a short residual lifetime and hence giving more chances for bacterial regrowth if not followed with chemical disinfection (Peter & Freese, 2009).

Halo-aldehydes, according to Richardson's report [55], are the 3rd most prevalent DBPs after THMs and HAAs. An example is trichloroacetaldehyde (chlorate hydrate CH), the most common in this class. Its formation depends more on the type of NOM and increases in chlorine dosage. Other groups of DBP include halonitromethanes, iodo-acids, halo-acids, iodo-THMs, MX compounds, haloamides, halo acetonitriles, halopyrroles, nitrosamines, and aldehydes (Richardson *et al.,* 2007). In light of all of the above, it is imperative to assess the occurrence of different classes of DBPs in South African wastewaters be conducted and hence make an informed decision on how effectively to treat our waters with minimal risk of exposure to environmental and human health.

2.16.4 Personal care products

The number of organic chemicals that comprise personal care products (PCPs) are in thousands. These products are used daily and in large quantities by multitudes of individuals. They include items such as shampoo, soaps, lotions fragrances and cosmetic products, dental care products among others (Lubliner, Redding & Ragsdale, 2010). The organic compounds of concern present in these products include but not limited to UV filter (e.g. benzophenone), preservative (e.g. parabens), antimicrobials (e.g. triclosan (TCS) and triclocarban (TCC)) musk fragrances (e.g. galaxolide), insect repellants (e.g. DEET), plasticizers (e.g. phthalates) among others (Brausch & Rand, 2011). Unlike pharmaceuticals which are intended for internal use and have been extensively studied unlike, PCPs are dermally applied and only enter the wastewater mostly through wash off of the human body, improper disposal in toilets, sinks or trash as they go down the drain. They may also be absorbed into the body and released through urine or in other cases excreta (Pedrouzo, Borrull, Marcé & Pocurull, 2011). Due to their frequent usage and continuous introduction into the wastewater systems, they become ubiquitous to the environment. A review was done by Brausch *et al.* [60] who reported PCPs as commonly detected in surface waters worldwide, but little research has been done on them regarding their occurrence, toxicity and potential risk to the environment. The authors reported that TCS and TCC are among the top most frequently detected PCPs in WWTP effluent with TCS being detected with its methyl derivative M-TCS after biological methylation (Bedoux, Roig, Thomas, Dupont & Le Bot, 2012; Brausch & Rand, 2011). A study by Bedoux *et al.* [62], also indicated that TCS is partially eliminated in sewage treatment plants and has been detected in μg/L level in influents, effluents, and sludge's, natural waters as well as drinking water (Bedoux *et al.,* 2012). In another study, it was reported that benzophenone was detected in approximately 50% of the treated and untreated. Benzophenone is a UV filter used as an enhancer in fragrances and is also used in the manufacture of insecticide, agrochemicals, and pharmaceuticals (Pitarch *et al.,* 2010). This clearly indicates high detection rate in wastewater. Benzophenone has been listed as one of the chemicals having endocrine disrupting effects (Hernández, Portolés, Pitarch & López, 2007).

There are over 10,000 different chemicals used in PCPs are and only 11% have been tested for human health and safety in the USA. In spite of this, the health effects associated with the continuous exposure of these contaminants cannot be ignored (Russ, 2009). Organic chemicals such as phthalates, triclosan paraben, and nitrosamines have been listed as endocrine disruptors and human carcinogens. Phthalates and parabens mimic estrogen in the body, creating a potential breast cancer risk (Russ, 2009).

2.16.5 Parabens

Among the emerging pollutants are personal-care products (PCPs) which are synthetic organic compounds derived from the usage by individuals in soaps, lotions, toothpaste, cosmetics and other PCPs (Pietrogrande & Basaglia, 2007). The latter are a major contaminant in water bodies (Soni, Carabin & Burdock, 2005) due to continuous release through recreational waters, domestic, urban and industrial wastewaters (Blanco, Casais, Mejuto & Cela, 2009). A sub-group of these PCPs are parabens which are widely used as antimicrobial agents due to their low toxicity, inertness and low cost (Boleda *et al.,* 2011) used in cosmetic products and food (Perlovich, Rodionov & Bauer-Brandl, 2005). These are homologous series of ρ-hydroxybenzoic acid esterified at the C-4 in the chemical structure, and may be used as singly or mixed to exert antimicrobial effect (Soni *et al.,* 2005).

Parabens are considered safe preservatives have been in use for over 50 years (Sasi, Rayaroth, Devadasan, Aravind & Aravindakumar, 2015; Steter, Rocha, Dionísio, Lanza & Motheo, 2014) and have a long shelf life. The use of parabens as preservatives have been in existence for a longer time and their continuous release into the environment and aquatic media through domestic wastewater, is of concern as they give rise to long-term effects on wildlife (Canosa, Rodríguez, Rubí, Negreira & Cela, 2006). Different authors explored the effects of parabens on the environment and human health (Błędzka, Gromadzińska & Wąsowicz, 2014) with antifungal effects on treatment of paper bio-deterioration (Neves, Schäfer, Phillips, Canejo & Macedo, 2009) as they mimic oestrogen (Oishi, 2002; Prusakiewicz, Harville, Zhang, Ackermann & Voorman, 2007) and are thus labelled as weak endocrine disruptor and allegedly causing breast cancer (Shanmugam, Ramaswamy, Radhakrishnan & Tao, 2010). According to the legislation laid out by the European Union, the overall content of parabens in cosmetics should be 0.4% (w/w) for single treatment and 0.8% (w/w) for mixtures. In Japan most of the cosmetic products contain 1% (w/w) (Terasaki, Yasuda, Makino & Shimoi, 2015) while in Africa, especially South Africa, there is no legislation adopted on these pollutants.

Thus, parabens have been in existence for a long period of time and therefore urban wastewater systems have contributed to the release of household chemicals that contain these pollutants in the aquatic environment. Conventional methods mainly used in wastewater treatment plants (WWTPs) have been reported with efficiency higher than 90% (Andersen, Lundsbye, Wedel, Eriksson & Ledin, 2007; Haman, Dauchy, Rosin & Munoz, 2015; Trenholm, Vanderford, Drewes & Snyder, 2008; Yu *et al.,* 2011), thus reducing the concentrations of the inlet of WWTPs. High removal efficiency of benzylparaben, butylparaben, and isobutyl paraben have been found to be removed by batch-activated sludge treatment (Yamamoto, 2007a). However, the high instability with the main by-product as ρ-hydroxybenzoic acid, have been detected in high concentrations in both raw wastewater and effluents (Blanco *et al.,* 2009). The drawbacks of the conventional methods are that they partially remove the pollutants where the residuals still register concentrations at ng l^{-1} levels as well as concentrations of the derivatives formed by transformation of the parent compounds (Haman *et al.,* 2015; Lee, Peart & Svoboda, 2005; Trenholm *et al.,* 2008).

Various researchers have reported methods of paraben detection in pharmaceuticals using different techniques after extraction and separation MERC (Driouich, Takayanagi, Oshima & Motomizu, 2000; Huang, Lai, Chiu & Yeh, 2003) and SPE (M.-R. Lee, Lin, Li & Tsai, 2006) techniques with great ease due to their simplicity and effectiveness (Márquez-Sillero, Aguilera-Herrador, Cárdenas & Valcárcel, 2010) using chromatography techniques HPLC (Belgaied & Trabelsi, 2003) hyphenated to mass spectrometer GC-MS (Shanmugam *et al.,* 2010) through a derivatization step to determine the parabens in cosmetics, drugs, etc.

2.17 Production of Organic Compounds in Wastewater Sludge (WWS)

Sludge is the waste residue that is generated from the wastewater treatment processes that involve the primary (physical and chemical), the secondary (biological) and tertiary processes. The primary stage involves removal of solid particulates such as sand, debris, fats, mineral oils, grease, surfactants and other particulate matter (Anjum, Al-Makishah & Barakat, 2016; Yang *et al.,* 2016). This step produces the primary sludge. The secondary process involves removal of dissolved and colloidal constituents in the secondary settling tank leading to the generation of secondary sludge. The combination of the primary and secondary processes constitute what is referred to as activated sludge system (Anjum *et al.,* 2016). Depending on the source of solids inherent in the incoming influent and the type of the wastewater treatment plant (WWTP), this leads to the production of large volumes of wastewater sludge (WWS) (Fytili & Zabaniotou, 2008; Yang *et al.,* 2016). The WWS is removed for further treatment before final disposal, to the environment. The common disposal routes described by Verlicchi *et al.* [69] are landfilling incineration, land application, ocean dumping and composting (Verlicchi & Zambello, 2015). Some of these disposal methods such as ocean-disposal have been banned by the EU (Fytili & Zabaniotou, 2008).

The WWS contains nutrients and other substances which can be beneficial for improving soil properties and fertility such as phosphorus and nitrogen, which are vital for plants growth. However, it has been widely reported that WWS contains harmful organic contaminants which come as a result of sorption of organic chemicals onto the organic chemical substances in the sludge matrix due to their lipophilicity or hydrophobicity which contain particles, charge and functional groups (Semblante *et al.,* 2015; Shaw, 2010). The concentration ranges as reported in a review by Clarke *et al.*, 2011 (Clarke & Smith, 2011), may be in the range of ng/kg to percentages (%). This makes WWS potentially hazardous to human health (Clarke & Smith, 2011). Some of these organic contaminants include pesticides, polyaromatic hydrocarbons

(PAHs), pharmaceuticals, hormones, polychlorinated biphenyls (PCBs), among others. Continuous application of wastewater sludge on farmland leads to the buildup of persistent compounds in the soil, creating a possible threat to the soil ecosystem, especially for the soil living organism. The organic compounds can also be up taken by the plant material and end up in the human body system through the food chain (Verlicchi & Zambello, 2015).

2.17.1 Occurrence of organic contaminants in wastewater sludge

Hydrophobic organic contaminants are more prone to partition on the organic portion of the WWS. This is largely dependent on the chemical structure of the compounds. Organic compounds also sorb onto sludge via electrostatic attraction. Those that exist in their neutral or positively charged form, have been reported to have high sorption capacity in primary and secondary sludge, whereas those that are negatively charged do not significantly sorb onto the (WWS). This is because of electrostatic repulsion (Stevens-Garmon, Drewes, Khan, McDonald & Dickenson, 2011). The combination of hydrophobic, electrostatic as well as Van der Waals forces, can, therefore, govern the behaviors and fate of these organic contaminants in wastewater sludge (Hyland, Dickenson, Drewes & Higgins, 2012).

Compounds which are persistent in WWS include to polyaromatic hydrocarbons (PAHs), Di (2-ethylhexyl) phthalate (DEHP), pesticides, polychlorinated by-phenyls (PCBs),personal care products of different classes such as antimicrobials (triclosan (TCS) and triclocarban (TCC)) ,nonylphenol ethoxylates, bisphenol A, to name a few (Barnabé, Brar, Tyagi, Beauchesne & Surampalli, 2009). All these organic compounds are toxic, carcinogenic, mutagenic and teratogenic, as well as their metabolites such as of Di (2-ethylhexyl) phthalate and bisphenol A. Researchers such as Nalli *et al.* (Nalli, Cooper & Nicell, 2006; Nalli, Horn, Grochowalski, Cooper,& Nicell, 2006) reported the toxicity of microbial metabolites of DEHP, 2-ethylhexanol, 2-ehtylhexanal and 2-ethylhexanoic acid, compared to the parent compounds. Triclosan and triclocarban found in personal care products such as shampoos, soaps, and detergents, are been widely reported to partition into (WWS) during wastewater treatment (Ying & Kookana, 2007). A mass balance in WWTPs was reported to show that 75% of TCC and TCS was recovered in sludge (Heidler & Halden, 2007). Concentrations of di (2-ethylhexyl) phthalate (DEHP) have also been reported to adsorb onto suspended organic matter and consequently amassing in sewage sludge in the WWTP. Their concentrations have also been reported to range between 1.8 to 1340 mg/kg d.w. (Chang, Wang & Yuan, 2007; Meng *et al.,* 2014). A recent review by Ramos *et al.* [82] on UV-filters showed that compounds like benzophenone and benzotriazoles were detected in WWS in Spain, Australia and Norway, with maximum concentrations peaks during the summer period with concentration ranging between 150-3303 ng/g-dw (Ramos, Homem, Alves & Santos, 2016). Liu *et al.* (Liu, Ying, Shareef & Kookana, 2012) reported on the distribution of UV-filters in sludge in three different treatment stages (anaerobic digestion, sludge retention (7 days) and sludge stabilization) in which the highest concentrations were found in digested sludge. However, the final biosolids had lower concentrations than the raw sludge. Concentrations of organic contaminants vary from one treatment plant to another. It also depends on the physiochemical properties of the compound such as molecular weight, hydrophobicity, water solubility and lipophilicity, resistance to biodegradation, sludge characteristics, and operational procedures of the treatment plant.

2.17.2 Removal/biodegradation of organic contaminants in wastewater sludge (WWS)

Being a highly hazardous wastewater treatment by-product, WWS has to be stabilized and treated for detoxification in order to attain a certain class of solids (class A), that complies with the environmental regulation of international standards, prior to final disposal (Chang, You, Damodar & Chen, 2011). There are a number of techniques used in treatment and dewatering of WWS. They are biological processes, chemical degradation, and volatilization, the most notable one is being biological processes. Biological processes that are being widely integrated into WWTPs involve aerobic and anaerobic digestion for removal of toxic compounds and pathogenic microorganism and to stabilize the waste activated sludge (Semblante *et al.,* 2015). A review by Kang *et al.* (Kang, Katayama & Kondo, 2006) revealed on the on the biodegradation of BPA by bacteria, fungi, planktons, plants and animals and highlighted that BPA degradation products could enhance estrogenicity or toxicity. Reports on BPA presence are widely reported, however, no data is available on their toxic intermediates (Barnabé *et al.,* 2009). Due to the limitations that biological processes incur, the sludge has to be pre-treated first prior to biological digestion. Various methods of sludge pretreatment include thermal hydrolysis, photo-catalysis, ozonation, ultrasound, enzymatic lysis acidification, alkaline hydrolysis, among others. This enhances the preceding biological treatment of the sludge and lowers the solid retention time (SRT) needed during digestion (Chang *et al.,* 2011; Zhang, Chen, Zhao & Zhu, 2010). Anaerobic processes are more favorably accepted in comparison to aerobic and composting methodologies due to the low energy footprint and reduced costs. Membrane bioreactors (MBR) together with SRT have also been reported to aid in the removal of some of these organic contaminants via adsorption onto sludge, with subsequent biodegradation. Longer SRT results in the MBR to yield higher biodegradation rates as it was the case with benzophenone in a study reported by Wijekoon *et al.*, 2013.

Compounds that rapidly biodegrade enhance reaction with extracellular enzymes, however, the organic compounds that biodegrade gradually, lower their bioavailability and aggravate accumulation in sludge (Semblante *et al.,* 2015). PAHS have been reported to biodegrade more efficiently during aerobic processes. In addition, thermophilic composting also aids in the removal of PAHs via intense microbial activity and volatilization owing to the temperature favoring the movement of the PAHs and their solubility in water, and causing them to be available to microorganisms (Stamatelatou, Pakou & Lyberatos, 2011).

2.18 Environmental and health impacts of organic contaminants in wastewater and wastewater sludge (WWS)

There are various entry points in which organic contaminants can be introduced or re-introduced into the environment. One of the ways is via disposal of final effluent and wastewater sludge (WW) application that is loaded with toxic organics on terrestrial environment. WWS is a potential threat to the environment. It has been mostly used in the land application as fertilizer or soil conditioner for decades (Wijekoon *et al.,* 2013). This maybe is beneficial for agricultural use, however, exceeding concentrations of these organic contaminants render them detrimental for agricultural purposes (Barnabé *et al.,* 2009). The organic contaminants that accrue in the sludge have a potential to enter the environment as not all is removed during sludge treatment, and subsequently, accumulates in the agricultural soil and finally end up in the food chain via uptake by crops (Zolfaghari *et al.,* 2014). Human and animal exposure to these organic contaminants leads to a vast array of health effects including endocrine disruption, the problem with reproduction and immune system disorders, cancer and consequently death. Aquatic life is also affected as effluent water that has traces of these organic contaminants can decrease fish production by either reducing or eliminating the fish population rendering them unsafe for human consumption. Poor water quality, impacts on the water quantities required for drinking, industry, agriculture in a given area. Communities that live nearby waterways such as rivers, in which the partially treated water is discharged, are also greatly affected as their livelihood depend on these water sources (Meena *et al.,* 2010).

CHAPTER 3:
MATHEMATICAL MODELLING AND MASS BALANCE FOR THE ORGANIC AND INORGANIC COMPOUNDS IN THE WASTEWATER TREATMENT PROCESSES

3.1 Summary

This section deals with the methodology used to collect data from **Plant A** wastewater treatment plant in South Africa. The methodology covered the procedures which were used to collect and analyse the design, operation and management data, process performance data, in process and effluent quality data from wastewater treatment plants. Technology selection tools as part of the questionnaire were developed and reviewed in collaboration with some of the participating managers at the target sites. Pre-testing of the methodology was carried out and comments from participating subjects were in cooperated into the final methodology which was used in this study. Wastewater quality parameters which were measured in-situ were identified and the initial analytical procedures amended from those which were described during the project proposal stages. The sample selection and analysis procedures were revised to be in line with the requirements of the mass balance modelling procedures. Procedures for carrying out the bio-kinetic selection, mass balance, mathematical modelling *(Activated Sludge Model No.1)* for wastewater quality parameters *(i.e. emerging micro pollutants, organic and inorganic compounds*) were developed. Simulation modelling was undertaken and lastly, calibration and validation was initiated. Conclusions were drawn with suggestions for follow up studies, offered.

3.2 Modelling Framework for Wastewater Treatment Processes

Figure 3.1 shows a framework on how modelling of micro pollutants, organic and inorganic compounds, nutrients were developed.

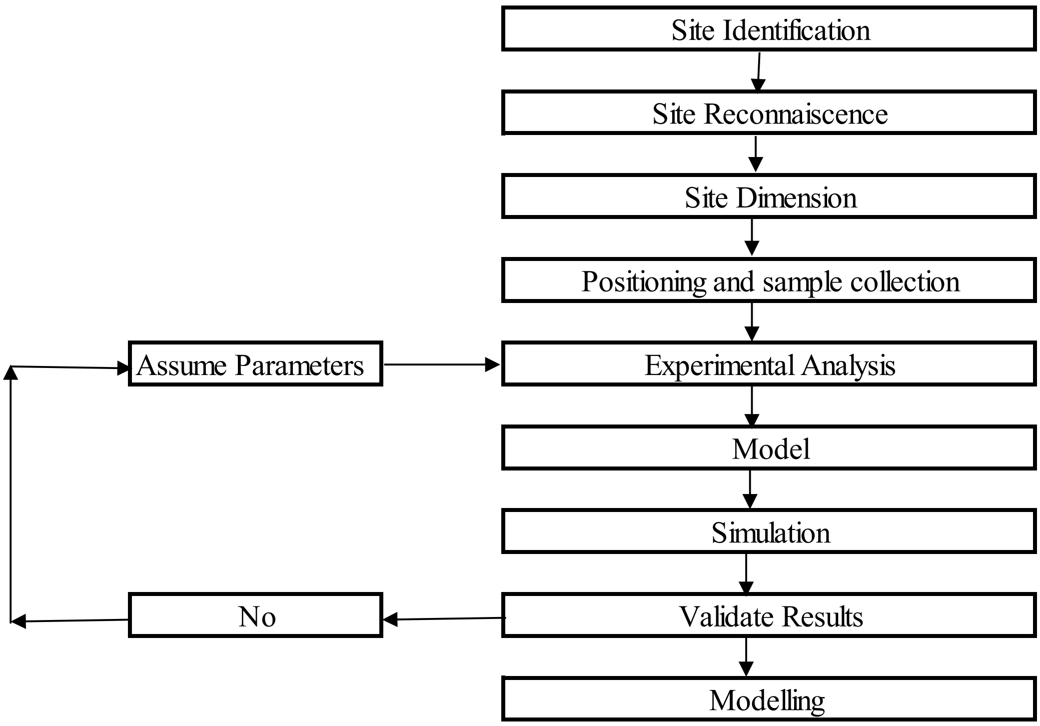


Figure 3.1: *Modelling framework for wastewater treatment process*

Primary modelling allowed estimate *(prediction)* and analysis of a variety of different process possibilities, and to determine optimal working conditions which are theoretically possible. Thus, the additional costs that might appear in continuous and repeated experiments were avoided. Simulation models using *Microsoft Excel 2016* with the application of the *ASM1* were used to run the simulation modelling.

3.3 Wastewater Treatment Plant's Selection and Sampling Positions

Figure 3.2 shows the framework from questionnaire development to identification of sampling positions.

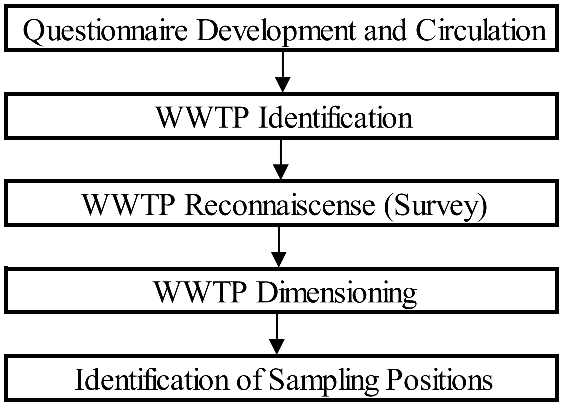


Figure 3.2: *Framework for the wastewater treatment process plant selection and the sampling positions*

3.3.1 Questionnaire development and site identification

The first step was to develop a questionnaire *(Appendix B),* to get information on the identification of the site locations of *WWTPs* and request for the permission to visit the sampling sites and collect data. The questionnaire was developed and applied to both domestic and industrial wastewater treatment plants in Gauteng Province, South Africa. The results obtained from the questionnaire distributed to the *WWTPs* management and those from the feasibility study was analysed by the multi-criteria decision analysis *(MCDA).* The *MCDA* was used in this study to identify sampling plants, obtain information as to why certain technologies were selected and to determine the performance of existing *WWTPs*. The sampling sites to be selected for this study were based on the cumulative risk rate *(CRR),* plant capacity, human population, industrialisation, relying on the experience and judgement of the historical sampling data from the plant. These alternatives accounted for the economic, environmental, social and technological aspects of the plants as indicated in ***Figure 3.3*** (Anagnostopoulos, Gratziou & Vavatsikos, 2007; Bottero, Comino & Riggio, 2011; Karimi *et al.,* 2011). The *IBM* statistical package for social scientists *(SPSS)* was to analyse the data on the plant selection process (George & Mallery, 2016; SPSS., 2016).

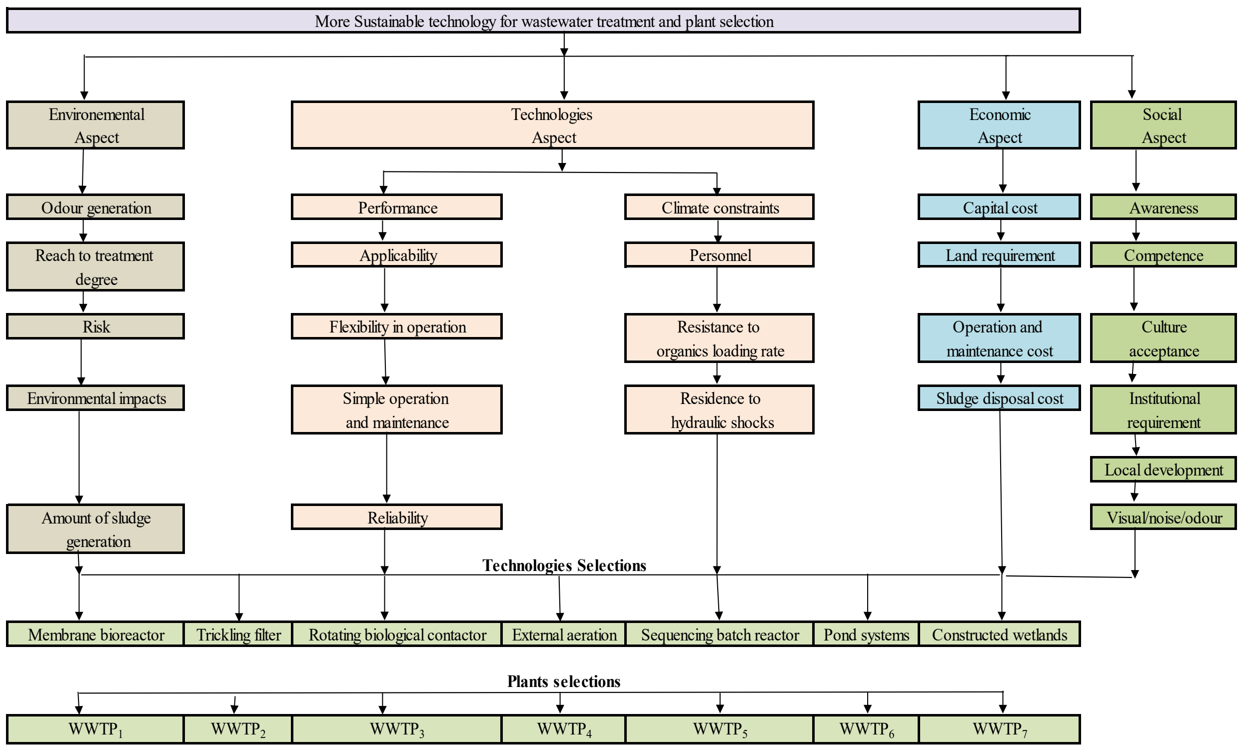


Figure 3.3: *Multi-criteria decision analysis (MCDA) on the wastewater treatment process*

3.3.2 Site reconnaissance *(surveying)*

Site reconnaissance was undertaken by surveying the wastewater treatment plant operations, occupational health risk and to familiarizing the research team with the efficient routine sampling program and instrumentations.

3.3.3 Site dimension

Process flow diagrams *(PFD)* of the plant design was used to locate sampling points based on hydraulic retention time *(HRT)* of the wastewater. This included taking actual dimensions of the process units to ascertain hydraulic retention time of the emerging micro-pollutant, organic and inorganic compounds. Controller parameters calculation was carried out. This was in accordance to the design of the plant, *Appendix D* and *E.*

3.3.4 Identification of the sampling positions

Manual and automated sampling was employed to collect wastewater samples. Sample collection took place on every process unit based on the hydraulic retention time *(HRT),* solid retention time *(SRT)* calculated and by use of a wastewater treatment plant design and tracer *(LiCl and* Li_2CO_3*)*, fluorescein sodium salt *(*$C_{20}H_{10}O_5Na_2$*:376.27)* application *(using stop watch on tracer appearance).* The tracer was dosed into influent of the plant section under evaluation. Sampling was done in two phases (IAEA, 2011b). The objective of the first phase was to build an understanding of the variation of the effluent quality over a shift and thus provided data for the statistical design of the sampling programme. The second phase was to establish pollution trends and monthly means of major pollutant parameters and confirm the results of the first phase of monitoring. Seasonal operational data were acquired for the year *2015-2017.* Sampling location, sampling time, sample storage, systematic flowrates, time weighting was observed to prevent sample deterioration. The accessibility, health, safety and environment *(HSE)* aspects was taken into consideration because wastewater mixed might be contaminated with sanitary wastewater in case of a disease outbreak.

3.4 Experimental Procedures

The experimental data used were made up of wastewater quality parameters measured in-situ and micro-pollutants, organic and inorganics compound analysed at the Departments of Chemical Engineering, Applied Chemistry, Process Energy and Environmental Technology Station *(PEETS)* all based at the University of Johannesburg and other results acquired from the Daspoort wastewater treatment plants, City of Tshwane, Pretoria, South Africa. The data were used to develop the mass balance models. ***Figure 3.4*** shows the development of the samplings programme, sample analysis and mass balance model development (Mackenzie, 2011; Metcalf, Eddy & Tchobanoglous, 2010).

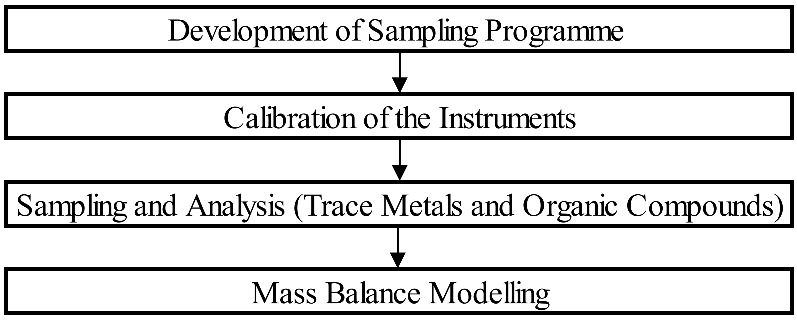


Figure 3.4: *Framework for the development of the samplings programme, sample analysis and mass balance model*

The measured influent organic and inorganic input data (influent wastewater characteristics) were (American Public Health Association, 2005); total *COD*, filtered *COD,* soluble *COD,* (after flocculation and filtration), total nitrogen *(N),* total kjeldahl nitrogen (TKN), ammonia nitrogen *(NH_4-N),* nitrate/nitrite nitrogen, free and saline ammonia *(FSA),* total phosphorus (*TP),* phosphates *(PO_4^{3-}),* volatile fatty acids *(VFA),* total suspended solids *(TSS),* chlorine *(Cl)* and trace metals. The micro-pollutant analysed were; methylparabens, ethylparabens and propylparabens. The physical measured data *(operation variables)* were tank volume, depth and layouts, flow connections and hydraulic behaviours and flow rates. The performance measured data were effluent organics, effluent nutrients, mixed liquor *(MLSS and MLVSS),* dissolved solids *(DO),* temperature, *pH,* alkalinity, ortho phosphate. Second phase objective was to establish pollution trends and monthly means of major pollutant parameters and confirm the results of the first phase of monitoring. The accessibility, health, safety and environment *(HSE)* aspects was taken into consideration because sometime wastewater is mixed with sanitary wastewater before discharge to sewer.

3.4.1 Material, chemical and apparatus

3.4.1.1 Material, chemical and apparatus used for the trace metal analysis

Nitric acid was used to adjust the *pH* of the wastewater before analysis. Fluorescein Sodium Salt *($C_{20}H_{10}O_5Na_2$:376.27),* Lithium carbonate *(Li_2CO_3)* and lithium chloride *(LiCl)* was used as a tracer in the wastewater treatment process. Argon was used as carrier gas for the inductively coupled plasma optical emission spectrometry *(ICP-OES)* analysis. Multi-element standards for trace elements in *100 ppm* and *1000 ppm* was used for *ICP-OES* calibration. Nitric acid and hydrogen peroxide was used for the digestion of the samples prior to trace elements analysis. The acrodiscs *(0.22, 0.45 μm)* syringe filters was used to filter the wastewater samples prior to trace metals analysis.

3.4.1.2 Reagents and materials used in micro pollutant-organic compounds analysis

The reagents used in the study to derivatize organics in wastewater and for reconstitution of the final extract included; dichloromethane *(DCM),* methanol *(MeOH),* acetonitrile *(ACN),* n-hexane formic acid, sodium sulphate and ammonium formate, were all purchased from Sigma-Aldrich. Solid phase extraction *(SPE)* cartridges used for extraction of organic compounds in this study were oasis *HLB 500 mg* and *ENVI-18 500 mg.* The acrodiscs *(0.22 µm)* syringe filters was used to filter the wastewater samples prior to chromatographic analysis. Reference analytical standards of the organics, all purchased from Sigma Aldrich for the measurements of concentrations of analytes in sample solutions included the polycyclic aromatic hydrocarbon *(PAHs);* benz[a]antracene, chrysene, acenaphthene, anthracene, naphthalene, pyrene, organochlorines and organophosphorus, triclosan, disinfection-by-product organics that included chloroacetic acid, dichloroacetic acid, trichloroacetic acid, and bromoacetic acid. Deionized water *(18 MΩ)* was used in making aqueous solutions and standard preparations.

3.4.2 Equipment used for the wastewater analysis

Plastic sample bottles of *500 mL* capacity were used to collect samples. Tracer detectors *(LiCl and* Li_2CO_3*)*, fluorescein sodium salt *(*$C_{20}H_{10}O_5Na_2$*:376.27),* and injector was used to establish the residence time distribution for the fluid and sludge. A microwave and hotplate were used in the digestion of the samples. A membrane filter *(pore diameter 0.22 µm)* was used to filter the samples before analysis. Inductively coupled plasma optical emission spectrometry *(ICP-OES)* was used for trace metals analysis. Organic compounds-micro pollutants were analysed using gas/liquid chromatograph coupled to various detectors such as the mass spectrometer *(GC-MS and LC-MS)* and with high-performance liquid chromatograph *(HP-LC)* with a *UV* detector. Chemical Oxygen Demand *(COD)* were analysed using spectrophotometer from Hach. Vials were used to hold liquid samples for analysis. Digital *pH* meter with electrodes for measuring temperature and electrical conductivity *(EC)* were used to analyse *pH,* temperature and *EC* respectively of wastewater treatment on-site.

3.4.3 Computation tools used in simulation modelling

The statistical analysis software package *(SPSS)* was used to analyse data collected from the questionnaire for plants selection. *Microsoft Excel 2016* was used to run the simulation models, carry out the mass balance of the wastewater treatment process and preparing graphical presentations.

3.5 Wastewater Sample Preparation and Analysis

3.5.1 Sample source

The samples were sourced from Daspoort Wastewater Treatment Plant at City of Tshwane *(CoT)* Metro, South Africa, according to the methodology proposed in this study.

3.5.2 Sampling procedure

The samples were collected in *500 mL* plastic containers, in duplicate, with no headspace volume to minimise aerobic biodegradation of organics substrates. They were marked with the indication of time, date and location of collection.

3.5.3 Sample storage

The samples were preserved by refrigeration without chemical addition for all the parameters measured except for trace metals sample to be analysed, where dilute nitric acid was used to lower the *pH* to *2* before refrigeration at *4°C*. This was to protect trace metals from precipitation and sorption losses to the container walls (Mackenzie, 2011; Metcalf *et al.,* 2010).

3.5.4 Sample analysis

This constitutes sample collection, instrumentation for trace metal and organic compound analysis.

3.5.4.1 On-site analysis

Wastewater electrical conductivity *(EC), pH* and temperature were measured on-site after sample collection.

3.5.4.2 Instrumentation for the trace metals analysis

Sample preparation methods for trace metals analysis involved using nitric acid *(12 mL)* and hydrogen peroxide *(4 mL)* for digestion of the sample *(10 mL)* by hot plate digestion at *120°C* for *2 hours*. Deionized water was added to dilute the sample to make *100 mL* after digestion. The sample was then filtered using cellulose acetate membrane filter *(0.22 µm).* The classes of metals were: suspended metals, metals present in unacidified samples that are retained on the *0.45 µm* membrane filter; dissolved metals, present in unacidified samples that pass through a *0.45 µm* membrane filter; total metals, the total of the dissolved and suspended metals or the concentration of metals determined on an unfiltered sample after digestion, and lastly acid extractable metals, metals in solution after an unfiltered sample is treated with a hot dilute mineral acids according to the standard method (Beamish, 2012; Biller & Bruland, 2012). Calibration standards was prepared using multi-element calibration solutions prepared using-*100 mg/L* nitric acid and deionized water. The sample was then analysed using inductively coupled plasma optical emission *spectrometry (ICP-OES-model ICAP 6500 Duo) – (165 Spetro Arcos equipped with autosampler (Cetac ASX-520)* technique. The parameters for operating the *ICP-OES* was set as follows: instrument power *1400 W,* the flow rate of the auxiliary argon *2 L/min,* argon gas flow rate *13 L/min,* the flow rate of the argon nebuliser *0.95 L/min* and *iTEVA* software was used. Based on the optical metals wavelength *(lower determination 166.250 nm and extending to 847.000 nm),* the most prominent analytical lines were chosen as follows*: Al-396.152 nm, Cd-228.616.502 nm, Co-228.616 nm, Cr-283.565 nm, Cu-324.754 nm, Fe-259.933 nm, Mn-257.610 nm, Ni-221.647 nm, Pb-220.353 nm, Ti-334.941 nm and Zn-213.856 nm.* Dilution factor was applied to the concentration data. The metal of interest included: *Al, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Ti and Zn* (Dimpe, Ngila, Mabuba & Nomngongo, 2014; Scientific, 2009; Scientific., 2009; Wiel, 2003). Calculation of the concentration of the elements in the aqueous sample and in the digested solid sample is shown in (Eq. *3.1* and (Eq. *3.2* respectively (Wiel, 2003).

$$C = (C_1 - C_o) f_d f_a \qquad \text{Eq. 3.1}$$

$$w = (C_1 - C) f_a V/M \qquad \text{Eq. 3.2}$$

Where:

C = concentration of the elements in the aqueous sample in *mg/L*

C_1 = concentration of the elements in the test sample in *mg/L*

C_0 = concentration of the elements in the blank sample in *mg/L*

f_d = dilution factor due to digestion of an aqueous sample; in all other cases $f_d = 1$

f_a = dilution factor of the test portion

w = mass fraction of the elements in the solid sample in *mg/kg*

V = volume of the test sample *(digest)* in litres

M = mass of the digested sample in *g*

3.5.4.3 Instrumentation for the organic compound analysis

3.5.4.3.1 Liquid chromatography-mass spectrometry analysis of organics

The liquid chromatographic separation of the organic compounds was performed on a *Nexera UHPLC (Shimadzu corporation, Kyoto, Japan)* interfaced to an electrospray-triple quadruple

(ESI-QqQ) mass spectrometer and fitted with an ultra-reverse phase biphenyl *column (Restek USA)*. The separation was achieved on an ultra-reverse phase biphenyl column and *C-18 column (Restek, USA)*. A binary solvent mixture composed of *MilliQ water (Mobile phase A)* containing *0.1%* formic acid and methanol as mobile phase *B* was employed for the gradient elution optimisation and analysis to achieve the analyte separation (Madikizela, Muthwa & Chimuka, 2014). Stock and working standards solutions of triclosan, haloacetic acids and parabens was prepared in *HPLC* grade methanol. A six-point calibration curve for each group of standards ranging from *5* to *100 µg/L* was prepared in the mobile phase. A *1 µg/mL* mixed standard solution was used in optimisation of instrument parameters such as linearity assessment, column temperature and mass spectrometric operating conditions for maximum sensitivity. This was done through direct infusion into the mass spectrometer (Paíga *et al.,* 2015).

3.5.4.3.2 Gas chromatography-mass spectrometry analysis of organics

A *two-dimensional* gas chromatography time of flight mass spectrometer *(GC×GC-TOFMS)* system consisting of an Agilent *7890N GC* system *(Agilent Technologies, Paloalto, CA, USA)* equipped with an Agilent *7683* autosampler and a single-jet liquid nitrogen cryogenic modulator and coupled to a Pegasus *4* dimension time-of-flight mass spectrometer *(4D TOF) (LECO Corporation, St. Joseph, MI),* operating in the electron ionization *(EI)* mode, was used for analysis. This involved screening and quantification of the analytes in the samples after *SPE* procedure for analysis of organochlorines and organophosphorus pesticides, and chlorinated disinfection-by-products *(DBPS).* The separation was performed using a fused silica capillary Stabiwax-*DA* column *(29.650 m × 0.32 mm × 0.5 µm, Restek, Bellefonte, PA, USA).* Confirmation of analytes was done by matching the retention times, structures, mass to charge ratios *(m/z)* with those on the mass spectrometer *(MS)* libraries with an accuracy of not less than *70%.* The oven temperature programming for the *GC* and *TOF-MS* conditions was optimised to obtain the most suitable conditions for the analysis. After screening, wastewater samples identified as having the *PAHs,* pesticide, and *DBPS* was re-analysed in triplicate for quantification purposes using reference calibration standards ranging from *1-100 µg/L* prepared in *DCM* solution (Skoczyńska, Korytár & Boer, 2008).

3.5.4.3.3 Solid phase extraction of organics in wastewater

The solid phase extraction *(SPE)* system was optimised to obtain the best extraction conditions for organics in with good sensitivity and precision. The *SPE* procedure involved cartridge conditioning, sample loading, analytes isolation and finally elution of the analytes. This was carried out off-line on a *12*-position vacuum manifold (Dimpe & Nomngongo, 2016). The *500 mg C18 SPE* cartridges was conditioned by passing *5 mL* methanol, *5 mL* ethyl acetate: *DCM (50:50), 5 mL* methanol and *5 mL* water to avoid dryness (Moja & Mtunzi, 2013). The wastewater samples were filtered before *SPE* analysis to avoid clogging in the cartridge. A volume of *500 mL* of wastewater sample was loaded automatically through the *500 mg C18* cartridge by use of a vacuum pump. After loading the samples through, the cartridge was washed with *5 mL* deionized water. The cartridge was air-dried, using vacuum for at least *30 min,* and then eluted with *5 mL* methanol. Where sensitivity was low, the eluate was concentrated by nitrogen drying and thereafter the pre-concentrated extract was reconstituted in an appropriate solvent and transferred to sample vials via microfiltration and made ready for injection on *GCXGC-TOFMS* or *LC-MS/MS* (Kanchanamayoon & Tatrahun, 2008; Ma, 2009). This process was applied to both spiked samples and wastewater samples.

3.5.4.3.4 Liquid-liquid extraction of organics in sludge

The sludge samples were extracted using liquid-liquid extraction followed by pre-concentration and final analysis. The sludge samples was analysed on a dry weight basis. Acetone was used in the initial step of extraction with *10 g* of dried sample with moderate shaking for *15 minutes*. Thereafter, the acetone extract was subjected to liquid-liquid extraction by addition of *100 mL* deionized water, *20 mL* of saturated *NaCl* solution and *50 mL* of dichloromethane. The organic phase was collected by filtering through a funnel containing Na_2SO_4 salt. The sample extract was then pre-concentrated using a rotary evaporator to near dryness and thereafter reconstituted with *1:9*, acetone: hexane or for *GCXGC-TOFMS* analysis. For *LC-MS/MS* analysis the sample was pre-concentrated to dryness and reconstituted in methanol. Sample extracts were then filtered through *0.22 µm* syringe filters prior to chromatographic analysis (Verlicchi & Zambello, 2015; Zuloaga *et al.,* 2012).

3.5.4.3.5 General standard methods for the wastewater analysis

The measures influent variable: total *COD*, filtered *COD,* soluble *COD, (after flocculation and filtration),* total nitrogen *(N),* total kjeldahl nitrogen *(TKN),* ammonia nitrogen *(NH_4-N),* nitrate/nitrite nitrogen, free and saline ammonia *(FSA),* total phosphorus (*TP),* phosphates *(PO_4^{3-}),* volatile fatty acids *(VFA),* total suspended solids *(TSS),* chlorine *(Cl)* and the performance measured data: effluent organics, effluent nutrients, mixed liquor *(MLSS and MLVSS),* dissolved solids *(DO),* temperature, *pH,* alkalinity, ortho phosphate were measured according to the standard methods for the examination of water and wastewater by American Public Health Association *(APHA),* Water Environmental Federation *(WEF),* American Water Works Association *(AWWA),* and Water Pollution Control Federation *(WPCF)* (Association & Federation, 1915).

3.6 Wastewater Treatment Process Model Set-up

This involved setting up wastewater treatment process models by translating real experimental data into a simplified mathematical description of reality. The models were used in a steady state, *i.e.* seasonal averages *(winter and summer),* monthly simulations and yearly average performance. ***Figure 3.5*** shows models' steps for the wastewater treatment.

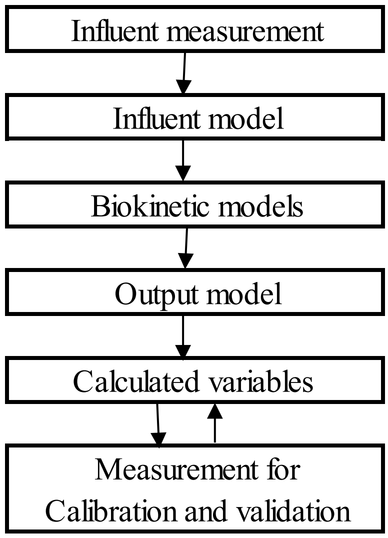


Figure 3.5: *Overview of the modelling process*

This included a decision on the model layout, sum-models structure, setting up models output graphs and tables. The analysis of the historical plant raw influent data and performance data were carried out for the period of *2015-2017* to establish the *WWTP* performance and efficiency. An *MS excel* spreadsheet was developed for data recording. Model layout involved translating of existing process flow scheme and mixed behavior into model concept. Modelled process units were each selected and connected to the sub-models. Mass balance was used to detect the inconsistence within the *WWTP* datasets through identification and confirmation of the mass flow into and out of the systems. The model approach was based on different levels of simplification of the real system but are both justified by accepted scientific and engineering principles.

CHAPTER 4:
MATHEMATICAL MODELLING AND MASS BALANCE FOR THE ORGANIC AND INORGANIC COMPOUNDS IN THE WASTEWATER TREATMENT PROCESSES

4.1 Summary

Wastewater treatment is inherently dynamic because of the large variation in the influent wastewater concentration, flowrates and composition *(i.e. organics, inorganics, and micro-pollutants).* The variations are to a large extent impossible to control in terms of time-varying process parameters. Mathematical modelling and simulation have become essential to describe, predict and control the complicated interaction of the wastewater treatment processes. The study aims to apply mass balance equations and International Association of Water Quality *(IAWQ);* Activated Sludge Model *(ASM) No.1*, abbreviated as ASM1, in the prediction of the flow rates, organics *(substrate and biomass growth),* inorganics concentration and their composition. This combined knowledge of the process dynamics with mathematical methods for estimation and identification. Emphasis was put on the numerical solution's ability to approximate the analytical solution of the conservation law of mass balance. Review on the existing models were taken into consideration that reached on a consensus concerning the simplest models having the capability of realistic predictions of the performance of the activated sludge and biofilm wastewater treatment plant on the nitrification-denitrification, oxygen demand *(DO), pH,* alkalinity, phosphorus, temperature, mixed liquor of the suspended solids, nitrogen, primary settling, sludge retention time, emerging micro pollutants-parabens, chlorination, and lastly the *COD* model using the *ASM1* and the conventional mass balance in the course of diurnal variations. The database was analyzed to determine bio-kinetic model's parameters range by considering the specific parameters correlation. *ASM1* and mass balance were used as simulation models to simulate the wastewater treatment process. Mass balance was used to detect the inconsistency within the wastewater treatment plant *(WWTP)* data sets through identification and confirmation of the mass flow into and out of the systems. *ASM1* facilitated better communication to stakeholders on the complex models that were essential to the bio-kinetic modelling. Mass balance was a powerful tool that allowed detection of inconsistencies within the *WWTP* datasets and assisted in identifying the systematic errors. Most alternative biological models were influenced by large extent the *IAWQ*. Calibration of the models was adjusted with the set of influent data in the process of modification of the input data until the simulation models result match the dataset. Validation was identified to meet the

modelling objectives with the level of confidence. The overall results on the mathematical modelling of the *WWTP* formed a framework that could be used in whole plant modelling such as activated sludge and biofilm models, metabolic approaches, the fate of micro-pollutants and trace metals reduction processes.

4.2 Introduction

Wastewater treatment processes can be considered as the largest industry in terms of treated mass of raw materials (Jeppsson, 1996). Wastewater treatment is inherently dynamic because of the large variation in the influent wastewater concentration, flowrates and composition *(i.e. organics, micro-pollutants and trace metals).* The variations are to a large extent impossible to control in terms of time-varying process parameters. Mathematical modelling and simulation become essential to describe, predict and control the complicated interaction of the wastewater treatment processes (Jeppsson, 1996). The models provide an idealized representation of an actual physical system of the wastewater treatment system (WEF, 2011). Wastewater originates from domestic wastewater, industrial wastewater, infiltration/inflow, groundwater, stormwater and surface water. Untreated water results in odour, depletion of dissolved oxygen and the release of the toxic, nutrients, pathogens and contaminants to the environment. Wastewater is currently considered as a renewable recoverable source of energy, water and resources. Wastewater treatment can be achieved by combining a variety of physical *(screening, grits, mixing, flocculation, sedimentation, settling, filtration and adsorption),* chemical *(oxidation, coagulation, precipitation, membrane processes, oxidation, gas transfer, adsorption and disinfection),* biological *(suspended or attached biomass conversion, nitrification and denitrification)* and thermal *(drying, incineration)* processes. Micro-organisms are used to oxidize/convert the particulate and dissolved carbonaceous organic matter into simple end products. They are also used to remove the nitrogen and phosphorus in wastewater treatment processes. The major purpose of the secondary treatment is to oxidize the readily biodegradable *COD* that escapes primary treatment and provides further removal of the suspended solids and this includes nitrogen and phosphorus removal (Mackenzie, 2011). Oxygen, phosphate and ammonia are nutrients needed to the conversion of the organic matter respective simple products. Biological processes are configured to encourage the growth of bacteria with the ability to take up and store a large amount of inorganic phosphorus in phosphorus removal. Ammonia through nitrification is oxidized into nitrite and nitrate. Other bacteria reduce the oxidized nitrogen into nitrogen gases (Metcalf *et al.,* 2010). The two typical biological processes for the wastewater treatment are attached growth *(biofilm)* and the suspended growth.

In the attached growth process, the microorganisms are attached to the packing materials *(sand, rocks, gravel, slag, synthetic materials and a wide range of plastic materials)* where the organic matter and nutrients are removed from the wastewater flowing past the attached growth processes. Attached growth processes can be operated aerobic or anaerobic and mostly referred to as trickling filters. In the suspended growth processes, the microorganisms responsible for the treatment are maintained in liquid suspension by appropriate mixing methods. Mostly, suspended growth in the treatment of industrial and municipality wastewater for biodegradation of organic matter are operated with dissolved oxygen *(aerobic)* or nitrate/nitrite *(anoxic)* utilization with the support of growth anaerobic *(with the absence of oxygen)* reactors (Metcalf *et al.,* 2010). The automation of the wastewater treatment processes instrumentation, control and automation *(ICA)* is the best approach to enhancing the efficiency of wastewater treatment process. Developing countries still use elementary controls which still pose major drawback up to date. These elementary controls are often fed with off-line data where the on-line sensors that are both robust and accurate, are either in-line *(operating in a side stream*) or in-situ *(operating within the process)*. This is due to; (i) lack of understanding in the treatment processes and proper understanding of mathematical models; (ii) plant constraints in flexibility to manipulate the process; (iii) lack of fundamental knowledge concerning benefits versus costs of the automated treatment processes; (iv) Inadequate instrumentation and reliable technology; (v) Unsatisfactory communication in designing of the plants among the designers, operators, researcher, government regulatory agents, equipment manufacturers and supplier; and lastly (vi) lack of proper training to the operators on how to operate the advanced sensor and control equipment (Jeppsson, 1996).

Mathematical modelling and simulation have become essential to describe, predict and control the complicated interaction of the wastewater treatment processes. The study therefore aims to apply mass balance equations and IAWQ and ASM1, in the prediction of the flow rates, composition and concentrations of organics which are substrates for biomass growth, and the composition and concentrations of inorganics.

4.3 Modelling

4.3.1 A State-of-the-Art Model

This section provides an overview of activated sludge modelling practice and mass balance of the suspended and substrate growth of the treatment process of the wastewater. This is with regards to the theoretical view, reality prediction, history of the models and validation of the activated sludge modelling. The models' objectives, structures and construction involve identification, estimation, reduction and validation. The model can be defined as a purposely representation or description that is often simplified of a system of interest. The model can present a system that can predict some system behaviours. Mathematical models are used as a simplification of reality that is relevant to understand and to deal with (Henze, Van Loosdrecht, Ekama & Brdjanovic, 2008). The mathematical model of activated sludge systems usually consists of many linked algebraic and differential equation that need to be solved efficiently under different conditions. These calculations are performed by various algorithms 'solver' that form part of the simulator's numerical *'engine'*. Mathematical models are used for research, plant optimization, plant designs, training, modelling based development and testing of the process control (Rieger *et al.,* 2012). A numerical model represents a real-life situation using mathematical equations. Simulation describes the use of the numerical model within a software package known as simulator (Rieger *et al.,* 2012). Modelling can be described into three groups; dynamic state, steady state and frozen state where variation occurs as a function of time (Henze *et al.,* 2008; Wentzel & Ekama, 1997). Mathematical modelling of the activated sludge systems has become a widely accepted tool for plants designs, training of the process operators and engineers, and research tools. According to Rieger *et al. (2012)*, models are only useful in practice if the model predictions are reliable. For the *WWTPs* modelling, generally steady-state and dynamic models are used.

The dynamic models are useful in predicting time-dependent systems response to an existing or proposed system. Dynamic modelling demand much more stoichiometric and kinetic constants for the systems design parameters that must be specified. The steady state models have constant flows and loads and are relatively very simple that their simplicity makes models very useful for designs.

Steady-state models are useful for calculating the dynamic models such as recycle and waste flow, reactor volume, concentrations and cross-checking on the simulation models output (Henze *et al.,* 2008). Modelling of activated sludge processes has become a common part of the control, operation, research and design. The objective of this study was to mathematically model wastewater treatment using International Water Association *(IWA);* Activated Sludge Models *(ASMs)* and their practice on application matrix notation of bio-kinetics models and unified protocols of project definition, data collection and reconciliation, plant model set-up, calibration/validation and lastly, simulation and results interpretation (Rieger *et al.,* 2012). Numerical models can be calibrated to one or more data set before applied and then followed by validation that ensures that the model can be used to predict the behavior of the system under operation. Numerical models can be educational purposes, diagnostic *(understanding mechanisms or processes)* or prognostic *(predict the future)* (Rieger *et al.,* 2012).

Frozen state means that the process changes with time, but not in the time interval that one is interested in. Usually, the hydraulic retention time is *30 days*, resulting in a characteristic time of change in the digester being in the order of two to three weeks. The process taking place in a digester can be taken as frozen state. There are processes that are so fast that they are steady state or are in equilibrium condition. The process occurs so rapidly that the speed of change exceeds by the dynamics that one is interested in. In the dynamic state, the process is time varying. Frozen and steady-state processes can be considered continues processes with stable concentrations under certain conditions like in the digester. The gradient of concentrations inside the activated sludge floc that can theoretically be described by a model. In a standard activated sludge modelling it is neglected as being not relevant enough to be considered.

4.3.2 Conventional mathematical modelling

The basis for the development of reliable conventional mathematical models is a thorough understanding of the involved process. Activated sludge systems are usually described by mathematical models based on the mass balance equations that relate to change of the state variables of the system *(flow rates, concentration and composition)* due to transport and the transformation mechanisms (Jeppsson, 1996).

Activated sludge models *(ASMs)* are usually not designed to describe the system at the length scale of an activated sludge floc but at the length scale of a reactor. Modelling of microbial activity is important although black-box approach focuses on the wastewater treatment plant influent and effluent characterization with nothing or very litter of microbial activity in the system. Black-box model can work out well in practice as *F/M ratio > ASM1,2,2D > ASM3 >* Metabolic models (Gujer, Henze, Mino & Van Loosdrecht, 1999; Smolders, Van der Meij, Van Loosdrecht & Heijnen, 1995). The application of black-box models depends very much on the purpose of the model. One can refine the approach of the plant design towards grey-box models as activated sludge model 1 *(ASM1),* Activated sludge model *2, 2d (ASM2, 2d)* and Activated sludge *3 (ASM3)* (Henze *et al.,* 2002). The metabolism of the organisms and metabolic routes inside the organism is described by glass-box modelling such as *ASM3, TU Delft EBPR* model (*TUDP* model) (Henze *et al.,* 2008; Van Veldhuizen, Van Loosdrecht & Heijnen, 2015). A brief history of the wastewater models was based on *BOD* and mixed liquor suspended solids *(MLSS) UCT* in *60s* and carbon and nitrogen removal in *1983 ASM1* (Henze, Grady, Gujer, Marais & Matsuo, 1987; Henze *et al.,* 2002). The bio-phosphorus *(bio-P)* removal included

ASM2 (Rieger *et al.,* 2012), Barker and Dold (Barker & Dold, 1997) and *ASM2d* (Henze *et al.,* 1999). The new concept of the *C* and *N* removal *(ASM3)* (Gujer *et al.,* 1999), *ASM3+Bio-P (EAWAG)* (Rieger, Koch, Kühni, Gujer & Siegrist, 2001), *UCTPHO+* (Hauduc *et al.,* 2010; Hu, Wentzel & Ekama, 2007), metabolic model *(Delft University)* and elemental balances (Takács & Vanrolleghem, 2006). Academic wastewater treatment models are characterized as *ASM1/2/2d/3, ASM3+Bio-P,* Barker and Bold, *UCTPHO+, TUDelft, etc.* The engineering models are integrated into commercial simulators, *i.e.* AQUASIM, BIOWIN, GPSX, STROAT, SIMBA, WEST, MATLAB SIMULINK, SUMO, CHEMCAD, ASPEN PLUS, BALAS, DTS PRO, DYNOCHEM, *etc.* (Committee, 2013). The *ASM1* database contains *31* parameters set, where *22* are optimized parameters sets, and *9* are proposed new default parameters (Rieger *et al.,* 2012).

Steady-state and dynamic models are the mathematic models that describe wastewater treatment systems. Steady state model simplicity makes them relatively simple to use in design and process efficiency determination due to constant flows and loading rate. Dynamic models are useful in prediction time-dependent systems response of an existing or proposed system. Dynamic model guide in the development of the steady-state design models by identifying the design parameters that have a major influence on the system response (Henze *et al.,* 2008). Wastewater treatment plant models are used to indicate the ensemble of the activated sludge models, oxygen transfer model, hydraulic model and sedimentation tank model (Gernaey, Van Loosdrecht, Henze, Lind & Jørgensen, 2004).

4.4 Experimental Procedures

The mathematical modelling-mass balance project was undertaken at Plant A Wastewater treatment plant, South Africa. Models show the capability of realistic predictions of the performance of the activated sludge and biofilm wastewater treatment plant on the nitrification-denitrification, oxygen demand *(DO), pH,* alkalinity, phosphorus, temperature, mixed liquor of the suspended solids, nitrogen, primary settling, sludge retention time, emerging micro pollutants-parabens, chlorination, and lastly the *COD* model using the *ASM1* and the conventional mass balance in the course of diurnal variations.

4.4.1 Mass balance of wastewater treatment plant

Mass balance is an engineering tool that allowed the identification and confirmation of the mass flow into and out of a processing system based on a mass conservation principle. Open and closed mass balance was applied. The measured influent organic and suspended input data *(influent wastewater characteristics)* for the *WWTP* mass balance included: chemical oxygen demand *(COD),* nitrogen compounds (*i.e.* N_2, N_2O, NO_X-N, NH_X-N, *TKN),* phosphorus $P_{tot,}$ phosphates (PO_4^{3-}), volatile fatty acids *(VFA),* total suspended solids *(TSS),* chlorine *(Cl)* and trace metals. The physically measured data *(operation variables)* were tank volume, depth and layouts, flow connections and hydraulic behaviours and flow rates. The performance measured data were effluent organics, effluent nutrients, mixed liquor *(MLSS* and *MLVSS),* dissolved oxygen *(DO),* temperature, *pH*, alkalinity, ortho-phosphate. The total suspended solids *(TSS)* denoted as X_{TSS} consisted of volatile suspended solids *(VSS).* The inorganic suspended solids *ISS* was described by *(ISS = TSS-VSS).* Alkalinity was introduced to the models to predict possible *pH* changes and guarantee the continuity in the ionic charge of the biological processes.

4.4.2 Primary settlement sizing and velocity

The particle settling velocity *(V)* at the primary settling tank was calculated with measured influent flowrate *(Q),* the surface of the sedimentation basis *(A),* depth of the sedimentation tank *(H)* and time required for the degree of removal *(t).*

$$V = \frac{H}{t} \qquad \text{Eq. 4.1}$$

and

$$V = \frac{Q}{A} \qquad \text{Eq. 4.2}$$

4.4.3 Organic volumetric loading rate

The organic volumetric loading rate *(OVLR)* applied to the aeration tank volume per day was quantified in terms of *COD* as in (Eq. 4.3:

$$L_{org} = \frac{QS_o}{(V)(10^3 g/kg)} \qquad \text{Eq. 4.3}$$

Where: L_{org} = volumetric organic loading rate, *kg COD/m*^{3}*. d, Q* = influent wastewater flowrate, m^3/d, S_o = influent *COD* concentration, g/m^3 and *V* = aeration tank volume, m^3.

4.4.4 Sludge retention time or sludge age

The sludge retention time *(SRT)* or sludge age in the completely mixed activated sludge *(CMAS)* was selected to impact the solids production on the operation and design parameters for activated sludge processes and was calculated by (Eq. 4.4:

$$SRT = \frac{VX}{(Q - Q_W)X_e + Q_W X_R} \quad \text{Eq. 4.4}$$

Where: *SRT* = sludge retention time, *d, V* = reactor volume *(i.e. aeration tank), m^3, Q* = influent flowrate, *m^3/d, X* = concentration of biomass in the aeration tank, *g VSS/m^3, Q_W* = waste sludge flowrate, *m^3/d, X_e* = concentration of biomass in the effluent, *g VSS/m^3* and *X_r* = concentration of biomass in the return activated sludge line from the clarifier, *g VSS/m^3*.

4.4.5 Specific organic loading rate

The specific organic loading rate *(L)* to a maximum organic removal rate used as an indicator of stability was defined as:

$$L = \frac{QC_i}{VX} \quad \text{Eq. 4.5}$$

Where: *L* = specific organic input rate, *h^{-1}, Q* = volumetric flow rate, *m^3/h, Ci* = influent organic concentration, *g/m^3,* and *V* = volume of reactor, *m^3*.

4.4.6 Effect of temperature on metabolic activity

The effect of temperature on the metabolic activities of the microbial population on a wastewater biological and chemical reaction-rate constant was calculated as:

$$k_T = k_{20}\ \Theta^{(T-20)} \quad \text{Eq. 4.6}$$

Where: k_T = reaction rate coefficient at temp *(T,°C),* k_{20} = reaction rate coefficient at temp *(20, °C),* *Θ* = temperature activity coefficient and varies from *(1.02 to 1.25),* and *T* = temperature *(°C).*

4.4.7 Effect of *pH* on metabolism

The *pH* of the wastewater treatment system was modelled on a range of *7.2* to *9.5* as described by (Eq. 4.7:

$$\mu_{AmpH} = \mu_{Am7.2}\Theta_{ns}{}^{pH-7.2} \quad \text{Eq. 4.7}$$

The modified model for the *pH* was used on declined out of range of *7.2* to *9.2* using the inhibition kinetics as described by (Eq. 4.8*:*

$$\mu_{AmpH} = \mu_{Am7.2}K_1 \frac{K_{max} - pH}{K_{max} + K_{\text{п}} - pH} \quad \text{Eq. 4.8}$$

The overall pH was modelled based on the formula shown by (Eq. 4.9:

$$\mu_{AmpH} = \mu_{Am7.2} 2.35^{pH-7.2} K_1 \frac{K_{max} - pH}{K_{max} + K_{\text{п}} - pH} \quad \text{Eq. 4.9}$$

Where: μ_{AmpH} = specific growth rate at *0* for $pH > 9.5$, $\Theta_{ns} = pH$ sensitivity coefficient *2.35*, $K_1 = 1.13$, $K_{max} = 9.5$, $K_n \approx 0.3$, $2.35^{(pH-7.2)}$ is set = 1 to pH >7.2 and $\mu_{AmpH}/\mu_{Am7.2} > 0.9$.

4.4.8 Biomass concentration mass balance

The biomass concentration mass balance was determined as a function of *SRT* in the aeration tank hydraulic retention time, the amount of the $(S_O\text{-}S)$, the synthesis yield coefficient and the specific endogenous decay coefficient was derived as:

$$X = \left(\frac{SRT}{\tau}\right)\left[\frac{Y(S_O - S)}{1 + b(SRT)}\right] \quad \text{Eq. 4.10}$$

Where: V = reactor volume (*i.e.* aeration tank), m^3, Q = influent flowrate, m^3/d, X_o = concentration of biomass in influent, $g\ VSS/m^3$, Q_W = waste sludge flowrate, m^3/d, X_e = concentration of biomass in effluent, $g\ VSS/m^3$, X_R = concentration of biomass in return line from clarifier, $g\ VSS/m^3$, r_x = net rate of biomass production, $g\ VSS/m^3$. D, X = concentration of the biomass in the reactor, g/m^3, r_{su} = substrate utilization rate per unit of reactor volume (g/m^3d), L = mass load of the balancing variable in influent *(IN)* or effluent *(OUT) (kg/d)*, i = indices for the system influent streams, j = indices for the system effluent streams, ΔM = change of stored mass of variables in the system for the balancing period *(kg)*, τ = balancing period *(d)* and r_v = volumetric reaction rate $(kg/m^3/d)$.

4.4.9 Substrate mass balance

The substrate mass balance for the complete mix activated sludge process as a function of time and the kinetic coefficient for the growth and decay was determined as:

$$S = \left[\frac{(K_s[1 + b(SRT)]}{SRT(Yk - b) - 1}\right] \quad \text{Eq. 4.11}$$

4.4.10 Mixed liquor solids concentration and solids production *(MLVSS)* mass balance

Mixed liquor solids concentration and solids production *(MLVSS*) was quantified in terms of the total suspended solids *(TSS),* volatile suspended solids *(VSS),* biomass and *SRT* provided a convenient expression to calculate the total sludge produced daily from the activated sludge process as follows:

$$Mass\ to\ be\ wasted = increase\ in\ MLSS - TSS\ lost\ in\ effluent \qquad \text{Eq. 4.12}$$

$$P_{X_T,VSS} = \frac{X_T V}{SRT} \qquad \text{Eq. 4.13}$$

or

$$P_x = Y_{obs} Q (S_o - S)(10^{-3} kg/g) \qquad \text{Eq. 4.14}$$

Y_{obs}, observed yield, *g VSS/g* substrate removed was equal to:

$$Y_{obs} = \frac{Y}{1 + b(SRT)} + \frac{(f_d)(b)(Y)(SRT)}{1 + b(SRT)} \qquad \text{Eq. 4.15}$$

Where: $P_{XT,\ VSS}$ = total/net solids wasted daily, *g VSS/d,* X_T = total *MLVSS* concentration in aeration tank, *g VSS/m*^{3}*,* *V* = volume of reactor, *m*^{3} and *SRT* = solid retention time, *d.*

4.4.11 Nitrogen biological removal mass balance

The nitrogen biological removal *(NBR);* nitrification modelled on activated sludge system in a single completely mixed reactor system with a hydraulic control of sludge age was calculated as:

$$N_a = N_{ac} = \frac{K_{nT}(b_{AT} + \frac{1}{SRT})}{\mu_{MT} - (b_{AT} + \frac{1}{SRT})} \qquad \text{Eq. 4.16}$$

Where: *Na* = reactor ammonia concentration, N_{ae} = effluent ammonia concentration, K_{nT} = half saturation coefficient, b_{AT} = endogenous respiration rate, *SRT* = sludge retention time and μ_{MT} = maximum specific growth rate. ***Table 4.1*** presented the kinetic constants on *20°C* sensitivity for the Autotrophic Nitrifier Organisms *(ANO)* for the Activated Sludge Models.

Table 4.1: *Kinetic constant and their temperature sensitivity for Autotrophic Nitrifier Organisms (ANO) for the ASM models*

Coefficient	Unit	At 20°C	ϴ
μ_{Am}	*g VSS/g VSS.d*	0.33	1.0
K_n	*mg/L*	1	1.23
Y_A	*g VSS/g substrate oxidized*	0.1	1
b_A	*g VSS/g VSS.d*	0.04	1.029

In order to be able to compare the data collected at different temperature in nitrification, all the kinetic constants were corrected to a standard value of *20°C (temperature dependencies)*.

$$\mu_{mT} = \mu_{m20}.\,1.0123^{(T-20)} \quad \text{Eq. 4.17}$$

$$b_{AT} = b_{A20}.\,1.0123^{(T-20)} \quad \text{Eq. 4.18}$$

$$K_{nT} = K_{n20}.\,1.0123^{(T-20)} \quad \text{Eq. 4.19}$$

$$Nitrogen\ oxidised = Nitrogen\ in\ influent - Nitrogen\ in\ effluent - Nitrogen\ in\ cell\ tissue \quad \text{Eq. 4.20}$$

$$NO_X = TKN_O - N_e - 0.12(\frac{P_X}{Q}) \quad \text{Eq. 4.21}$$

Where: NO_X = nitrogen oxidized, *mg/L,* TKN_O = influent total Kjeldahl nitrogen, *mg/L,* and N_e = effluent NH_4-N, *mg/L*.

4.4.12 Biological phosphorus removal

In the biological phosphorus removal *(BPR),* the total discharge or organic phosphorus with the effluent was determined by the following equation:

$$P_{ope} = f_p.X_{ve} = f_p.f_v.X_{te} \quad \text{Eq. 4.22}$$

Where: P_{pe} = inorganic phosphate, P_{oe} = organic phosphorus, P_{ose} = soluble organic phosphorus, typically between *0.1* and *0.2* mg $P.1^{-1}$, f_p = phosphate residual *(0.025 g P.* g^{-1} *VSS),* X_{ve} = concentration of *VSS,* f_v = *VSS* residual, typically between *(0.70 to 0.85 VSS .*mg^{-1} *TSS), and* X_{te} = concentration of *VSS.*

The phosphate release in the anaerobic zone in the presence of an adequate *(VFA, such as acetate),* the *bio-P* organisms transform internally stored polyphosphate into phosphate, a process that releases the energy required for the absorption of *VFA* was determined by the following equation:

$$P_r = f_{pr}.S_{VFA} \quad \text{Eq. 4.23}$$

Where: P_r = phosphate concentration released to the liquid phase *(mg P.1^{-1})*, S_{VFA} = concentration of the volatile fatty acids *(mg COD.1^{-1})* and f_{pr} = phosphorus release constant = *0.5 mg P. mg^{-1} COD* absorbed.

4.4.13 Oxygen demand mass balance

The oxygen required for the biodegradation of carbonaceous material was determined from a mass balance using *bCOD* concentration of the wastewater treated and the amount of biomass wasted from the system per day:

$$R_O = Q(S_O - S) - 1.42P_{X,bio} \quad \text{Eq. 4.24}$$

Where: R_o = oxygen required, *kg/d, Q* = wastewater flow rate into the aeration tank, *m^3/d*, S_o = influent bCOD, *g/m^3, S* = effluent bCOD, *g/m^3*, and $P_{x,\, bio}$ = biomass as VSS wasted per day, *(waste activated sludge produced) kg/d.*

Dissolved oxygen concentration was formulated as follows:

$$\mu_{AO} = \mu_{AmO} \frac{O_2}{K_o - O_2} \quad \text{Eq. 4.25}$$

Where: μ_{Ao} = maximum specific growth rate *(/d)*, μ_{AmO} = specific growth rate at *DO* of *O (mg/L)*, O_2 = oxygen concentration in liquid *(mgO$_2$/L)*, and K_o = half saturation constant *(mgO$_2$/L)*, range *0.3-2.*

4.4.14 Biological removal of recalcitrant and trace organic compounds

The mass balance for the biological removal of emerging organic compounds *(emerging micro-pollutants)* resists conventional biodegradation in biological treatment processes referred to as refractory *(methylparabens, ethylparabens, propylparabens)* was represented by:

$$S = [\frac{(K_s[1 + b(SRT)]}{SRT(\mu_m - b) - 1}] \quad \text{Eq. 4.26}$$

Where: QS_o = mass of the compounds in wastewater influent, *g/d*, r_{su} = biodegradation rate, *g/d*, r_{ad} = solid adsorption rate, *g/d*, r_{rv} = volatilization rate, *g/d, QS* = mass of compounds in wastewater effluent, *g/d, Q* = hydraulic flow rate *(m^3/d), V* = Aeration tank volume, *m^3*, S_O =

influent concentration *(mg/L), S* = effluent concentration *(mg/L), SRT* = solid retention time, X_T = total *MLVSS* concentration that includes all the biomass grown on various substrates plus the nonbiodegradable *VSS*, X_S = biomass concentration capable of degrading the specific organic compounds, *Y* = synthesis yield coefficient, *g biomass/g substrate* used, $K_L\ a_s$ = gas-liquid mass transfer coefficient, of organic compound, *d* , K_P = partition coefficient, *(L/g)*, τ = aeration tank retention time *(hydraulic retention time)* and μ_m = maximum specific growth rate *(g/g.d)*.

4.4.15 Disinfectants used in the wastewater treatment

Pathogens *(fungi, viruses, helminth, protozoan oocysts, bacteria)* were removed in the effluent by the application of disinfectants; chlorine. The chemical disinfectant kinetics of the chlorine was based on the pseudo-first order decay rate constants are shown below (Mackenzie, 2011; U.S EPA, 1986):

$$C = C_O exp(-k_d t) \qquad \text{Eq. 4.27}$$

Where: *C* = disinfectant concentration, *mg/L*, k_d = first order decay rate constant, $time^{-1}$ *(0.0011 to 0.0101* min^{-1} surface water with the *TOC* of *2.3 to 3.8 mg/L, 0.71 to 11.09* d^{-1} distribution system pipe, and *0.36* to *1.0* d^{-1} for distribution system storage tank, *t* = time, and complementary units to k_d.

4.4.16 Food to microorganism ratio

Food to microorganism *(F/M)* ratio was defined as the rate of *COD* and applied per unit mixed liquor as:

$$\frac{F}{M} = \frac{Total\ applied\ substrate\ rate}{Total\ microbial\ biomass} = \frac{QS_O}{VX} = \frac{S_O}{\tau X} \qquad \text{Eq. 4.28}$$

Where: *F/M* = food to biomass ratio, *bsCOD/g VSS.d*, *Q* = influent wastewater flowrate into the aeration tank, m^3/d, *So* = influent biodegradable soluble *bsCOD* concentration, *mg/L*, *X* = mixed liquor biomass concentration in the aeration tank, *mg/L* and τ = hydraulic retention time of aeration tank, *V/Q, d*.

4.4.17 Removal efficiency of the organic compounds' removal

The process removal efficiency (*E)* as percent *COD* across the activated sludge system was defined by:

$$E = \frac{S_o - S}{S_o}(100) \quad \text{Eq. 4.29}$$

4.4.18 Calibration and validation

Mathematical models were introduced at elucidating the mechanisms of the activated sludge processes. Calibration of the models were adjusted with the set of influent experimental data in the process of modification of the input data until the simulation model results match the data set. The effluent results were counter checked for compliance with Department of Water; wastewater treatment License, *Appendix D*. Validation was identified to meet the modelling objectives with the level of confidence.

4.5 Results and Discussions

4.5.1 Modelling analysis using microbial growth kinetics, mass balance, and activated sludge model *No. 1* of the *WWTP*

The key objective for developing a model of the wastewater system included obtaining reliable measurements *(observation),* the selection of the key behaviour and characteristic, approximations and assumptions, the accuracy of the simulation model output *(calibration/validation)* and realistic of the predictions. Mass balance was a powerful tool that allowed detection of inconsistencies within the *WWTP* data sets and assists to identify the systematic errors. Mass balance was carried under steady state to identify potential data sampling and analytical errors monitoring. Steady-state modelling was again essential for plant performance under various loading conditions and for future *WWTP* design and redesign. The steady state satisfied the long-term behaviour of the flow rate and where there was no significant inherent dynamics. The setting up of the influent characteristic was calibrated prior to the kinetic parameters and the influent characteristics. According to Rieger *et al. (2012)*, mass balance does not provide information on the precision of a specific measurement. It was possible to identify mass balance based on many variables that were set up of parallel mass balance utilizing process variables. This was useful in identifying systematic measuring errors in the overlapping mass balance. The rule of thumb expected for the mass balance on the data was average *7%,* close to residual in a range of ±5 to *10%* (Rieger *et al.,* 2012). All the models were benchmarked according to the *IWA* task group on the control strategies of the *WWTP* (IWA, [(Accessed February 2018]).

4.5.2 Impact of primary settlement sizing and velocity

The particle settling velocity at the primary settling tank was calculated with measured influent flow rate, the surface of the sedimentation basis, depth of the sedimentation tank and time required for the degree of removal. The settling velocity was observed to be *1317.6* m^3/day or *0.9125* m^3/min of biomass in the primary settling. High settling velocity gave the high efficiency of the wastewater treatment. The quantity and quality of carbon, nitrogen and phosphorus were much affected by primary settling tank due to sludge discharge before the activated sludge reactor. It was important that the primary sedimentation on the wastewater *C, N,* and *P* could be determined to enable the settled sewage characterization to be estimated. According to Mackenzie, 2011, sedimentation was characterized by particles that settle discretely at a constant settling velocity and individual particles *(sand and grits)* do not flocculate during settling.

4.5.3 Change of design flowrate (loading) with the hydraulic retention time

Hydraulic retention time *(HRT)* was fundamental to the wastewater treatment and sludge age. The maximum organic removal rate used served as an indicator of stability in the *WWTP*. ***Figure 4.1*** and ***Figure 4.2*** present the dynamic of flowrates and hydraulic retention time in the wastewater treatment processes. *HRT* was a function of the volume and the volumetric flow rate.

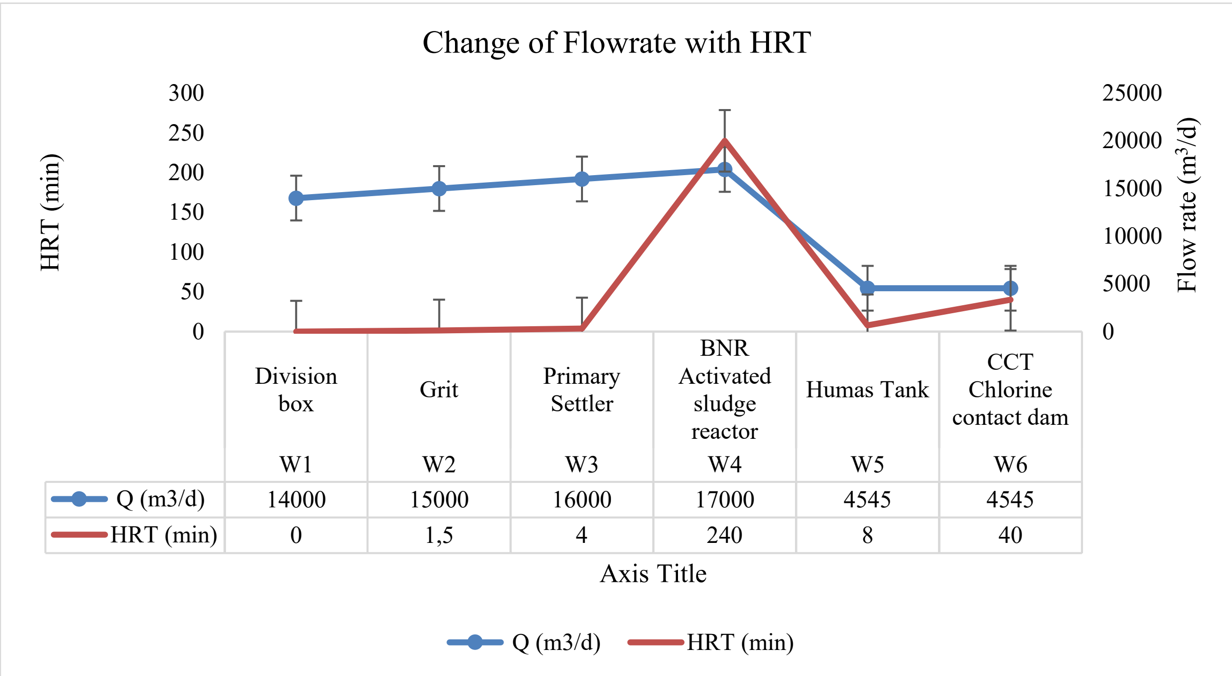


Figure 4.1: *Change of flow rates with HRT in the activated sludge wastewater treatment plant*

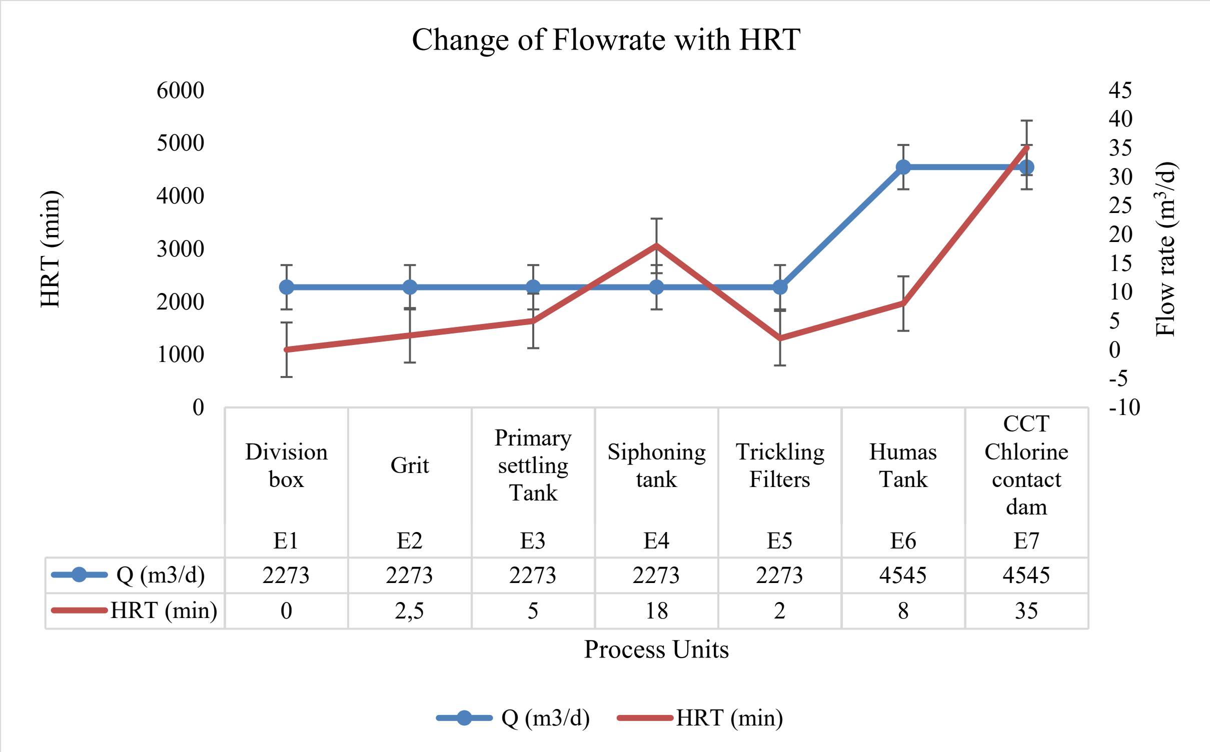


Figure 4.2: *Change of flow rates and HRT in the biofilm wastewater treatment plant*

From ***Figure 4.2***, there were high flow rates due to the sludge recycle and high hydraulic retention time because of the aeration in the biological nutrient removal *(BNR)* unit. Sludge controlled the food to microorganisms' ratios in the *WWTPs*. The hydraulic control of sludge age revolves a greater responsibility to plant operators and in the redesign of the biological processes to improve effluent quality. Activated sludge plant recorded a maximum flow rate of *17000* m^3/d and *HRT* of *0.16 d* at the biological nutrients removal *(BNR)* unit with a minimum flow rate of *4545* m^3/day and *0.005 d* at the chlorination zone. High retention time at the biofilm plant was observed at the chlorination unit. Chlorination unit provided prolong contact between chlorine and wastewater during the disinfection process. This created the pathogen-free effluent. The biofilm plant recorded a maximum flow rate of *4545* m^3/d and *HRT* of *0.006 d* with a minimum flow rate of *2273* m^3/day and *0.001 d*. According to Mackenzie *(2011)*, the design flow rates range from *1.2* to *4.3* times the annual average daily flow rate where the typical value is *2.0* times the average daily flow rate. The dynamics created by the daily flow rate of the inflow could be tapped with the installation of the whirlpool turbines to provide power to run the operations of the *WWTP* and at the same time supply electricity to the local communities.

4.5.4 Effect of the solid retention time in the WWTP

Solid retention time *(SRT),* cell residence time *(Θ)* or sludge age, net specific bacteria growth rate *(μ_{net})* and effluent concentration *(S)* of the biomass was calculated using measured values of the reactor volume *(V),* influent flowrate *(Q),* waste sludge flowrate *(Q_W),* concentration of biomass in the aeration tank *(X),* concentration of biomass in the effluent *(Xe),* Concentration of biomass in the return activated sludge line from the clarifier *(X_R)* and return activated sludge *(Q_R)*. The algorithm assumed that the loss of solids with the effluents and secondary settling tank was negligible relative to that in the biological reactor. According to Henze *et al. (2008)* this assumption holds where the system was operated at relatively high recycle ratios *(1:1)* and the sludge age was longer than *3 days*. ***Figure 4.3*** shows the seasonal variation of the sludge retention time.

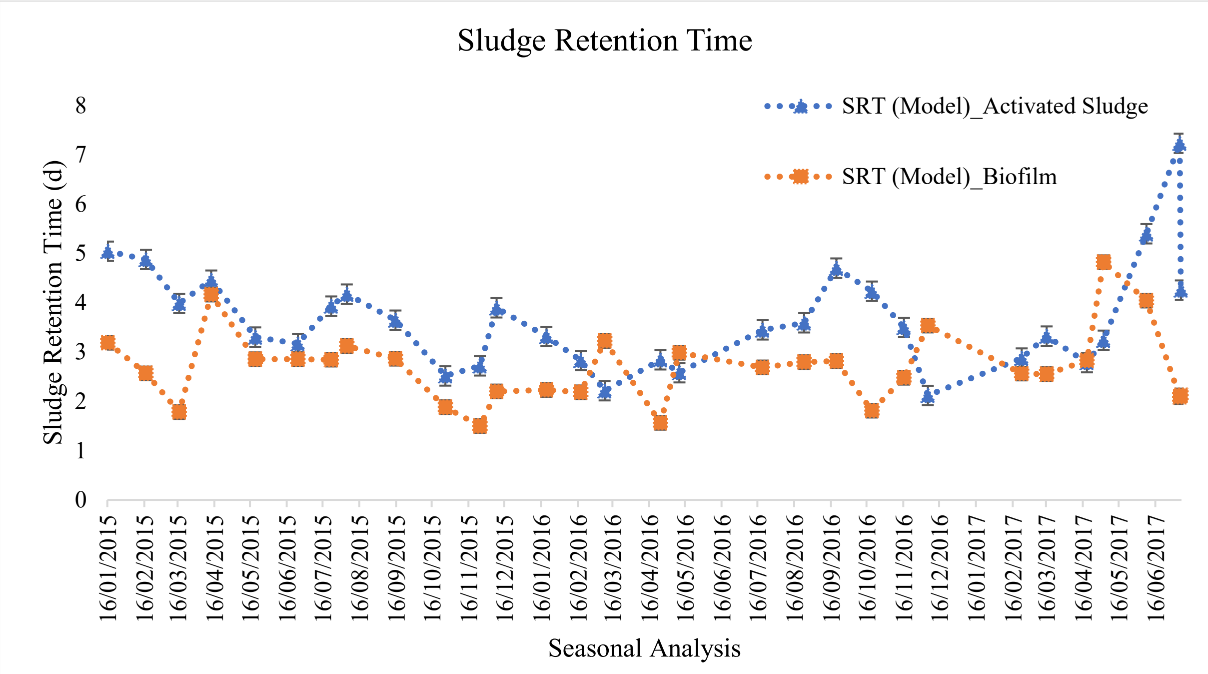


Figure 4.3: *Seasonal sludge retention time for the wastewater treatment plant*

The effluent concentration of the biomass obtained after simulation was *38.06 mg/L* that was almost equal with the measured and analysis concentration from the plant activated sludge at Daspoort *WWTP* of *33 mg/L*. From biofilm at *Plant A WWTP*, the concentration of *33 mg/L* was obtained. This was with converge to the measured value of *30 mg/L*. The *SRT* showed the average time the activated sludge solids were in the systems with the assumption that the solids inventory in the clarifier was negligible compared to that of the aeration tank. The *SRT* could be controlled by the wasting rate a given percentage of the aeration tank volume on each day.

Controlling the *SRT* by sludge wasting affects the net specific biomass growth rate and the reactor substrate concentration. The *SRT* helped control the sludge age and the underflow and overflow. Mass balance could not be used to detect time-dependent errors like draft because of averaging over typically longer periods. Solid retention time *(SRT)* was typically on the order of *1* to *4 days* to reduce the sludge wastage and achieve endogenous decay. The wasting of solids was required to prevent an accumulation of solids in the oxidation ditch. It was essential that the designer consider the sludge mass more exactly to provide sufficient reactor volume under design organic load that allowed proper concentration at the specified process unit. The increased in *COD* mass load increased the sludge concentration automatically and maintained the sludge age. Maintaining the *COD* mass load constant automatically maintained the sludge concentration constant.

4.5.5 Effect of temperature on microbial growth

The analysis of the historical plant's raw influent data and performance data were carried out for the period of *2015-2017* to establish the *WWTP* performance and efficiency as shown in ***Figure 4.4***. Temperature has a significant effect on the growth rate of the microorganisms in the biological wastewater treatment.

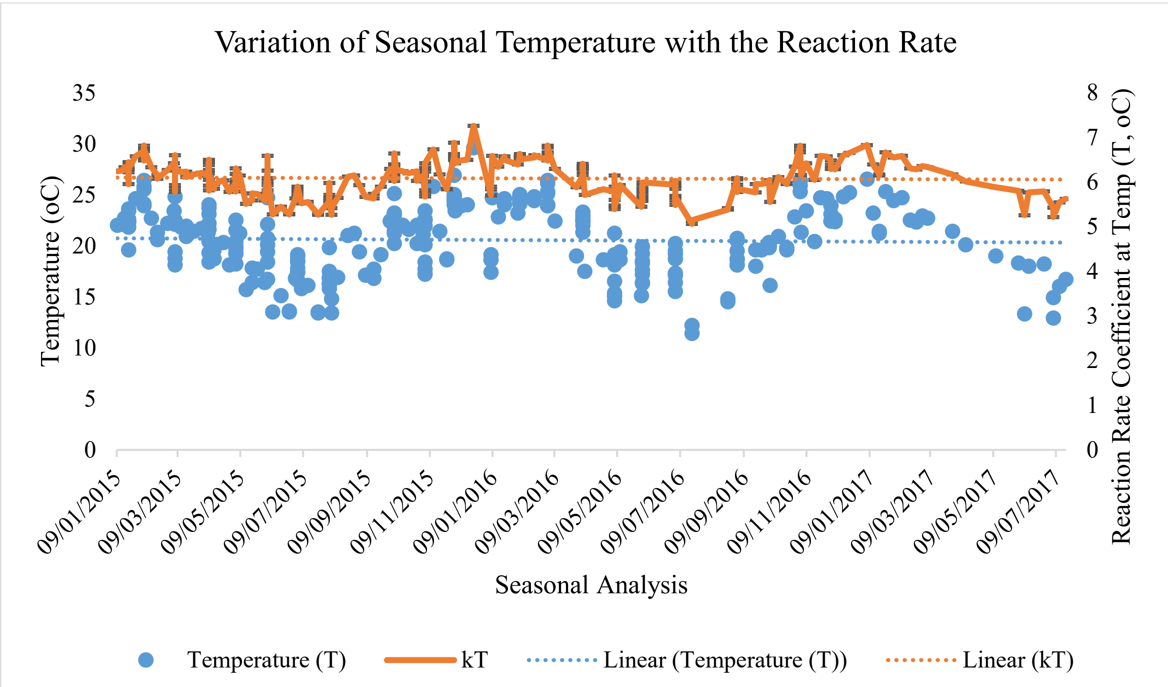


Figure 4.4: *Variation of seasonal temperature and reaction rate coefficient at the reaction temperature*

The average reaction temperature according to the analysis was *22°C* and the reaction coefficient of the reaction temperature respectively resulted to an average of *6*. The higher mesophilic temperature in the wastewater treatment process created an enabling environment for the microbial growth and thus influencing the metabolic activities of the microbial population. This had a profound effect on factors such as gas transfer and the settling characteristics of the biological solids. The biological reaction rate was directly dependent on the temperature on the assessment of the overall efficiency. According to Henze *et al.,* 2008 the increase in temperature shows a gradual increase in growth rate and much higher temperature denature the proteins. This reciprocated the same at the Daspoort wastewater treatment plant. Thus, those operating at optimum temperature have a higher maximum growth rate than those operating at longer and over optimum temperature ranges. The different temperatures that works well under different temperature are; psychrophilic below *15°C*, mesophilic *15-40°C* and thermophile at *40-70°C*. Temperature effects on the secondary sludge production were small but high in biological nutrient removal unit. According to Hellinga *et al. (1998)*, Arrhenius type temperature functions are used in a limited range and when the operation temperature exceeds the valid range, of the *WWTP* industrial application, the extrapolation of the Arrhenius equation is explored. Nevertheless, the nitrifiers have an upper-temperature limit of approximately *40°C* that was not observed in our analysis. According to Metcalf *et al.,* 2010, the optimum temperature for the bacteria activity are in range of *25-35°C (mesophilic temperature)*. When the temperature drops to about *15°C*, methanogen becomes quite inactive and about *5°C*, the autotrophic nitrifying bacteria ease to function. When the temperature rises to *50°C (thermophilic temperature),* aerobic digestion and nitrification stop. The optimum temperature *22°C* of the wastewater treatment process proves to be effective with the other process parameters.

4.5.6 Impact of pH and pH dependency at the WWTP

The *pH* is a vital parameter to be considered in the wastewater treatment processes. *pH* is related to the alkalinity in the biological activity. In the microorganism activity, microbes are more dependent on *pH,* unlike the alkalinity. ***Figure 4.5*** and ***Figure 4.6*** show the effect of the *pH* in the activated sludge and biofilm wastewater treatment plants respectively.

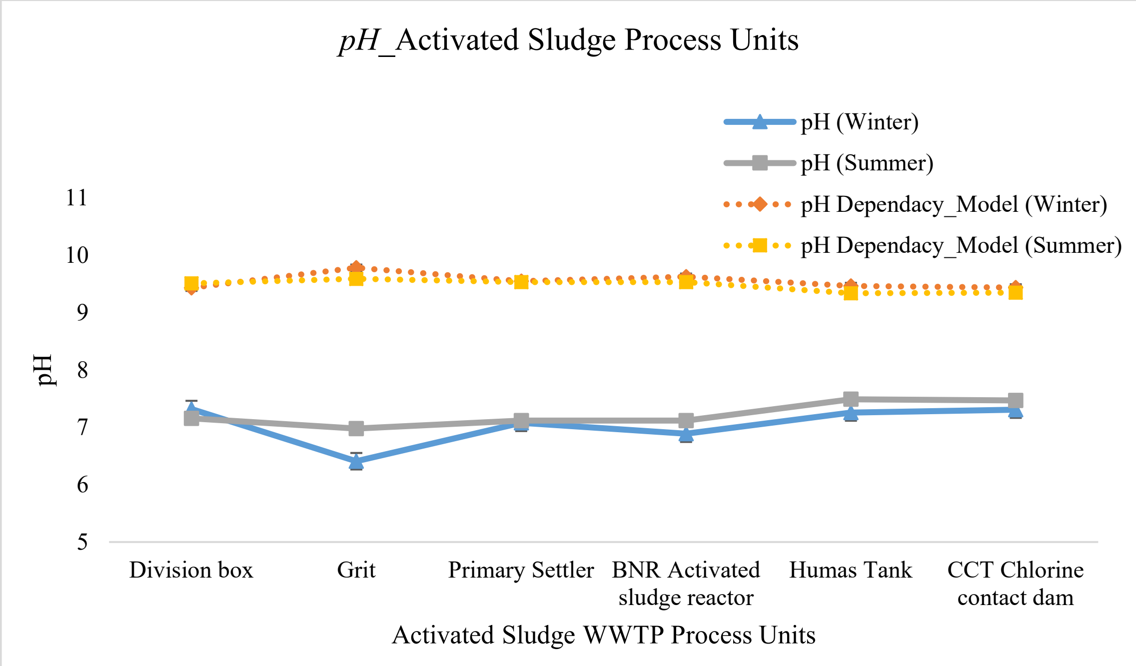


***Figure 4.5:** Change of pH in the activated sludge WWTP*

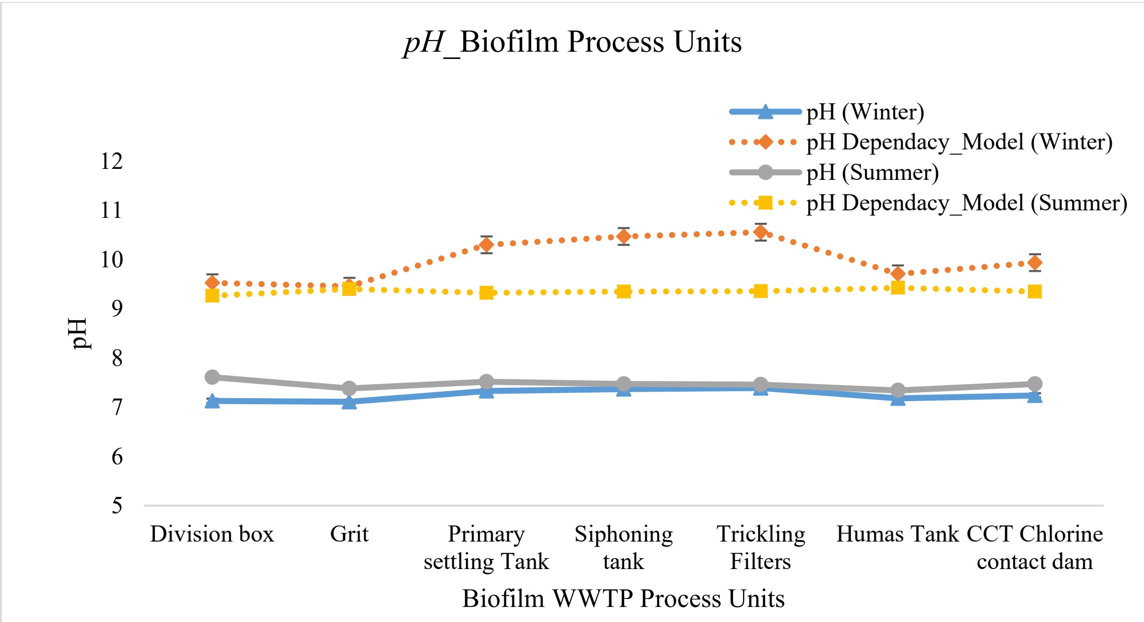


***Figure 4.6:** Change of pH in the biofilm WWTP*

The *pH* range of *7-8* in the wastewater treatment plant suppressed the maximum specific growth rate by increasing the nitrification processes in the conversion of free and saline ammonia to nitrite *(ANOs),* nitrite to nitrate *(NNOs)* and maintaining the balance of food to microorganism conditions that enhance the efficiency of biomass removal. The model showed a smooth curve with the activated sludge plant, unlike biofilm plant that had slight variation. This assisted in the prediction of the pH dependency on the process parameters. The behaviour of the pH was considered in the models of the wastewater. Seasonal pH variation and pH dependency was shown in ***Figure 4.7***.

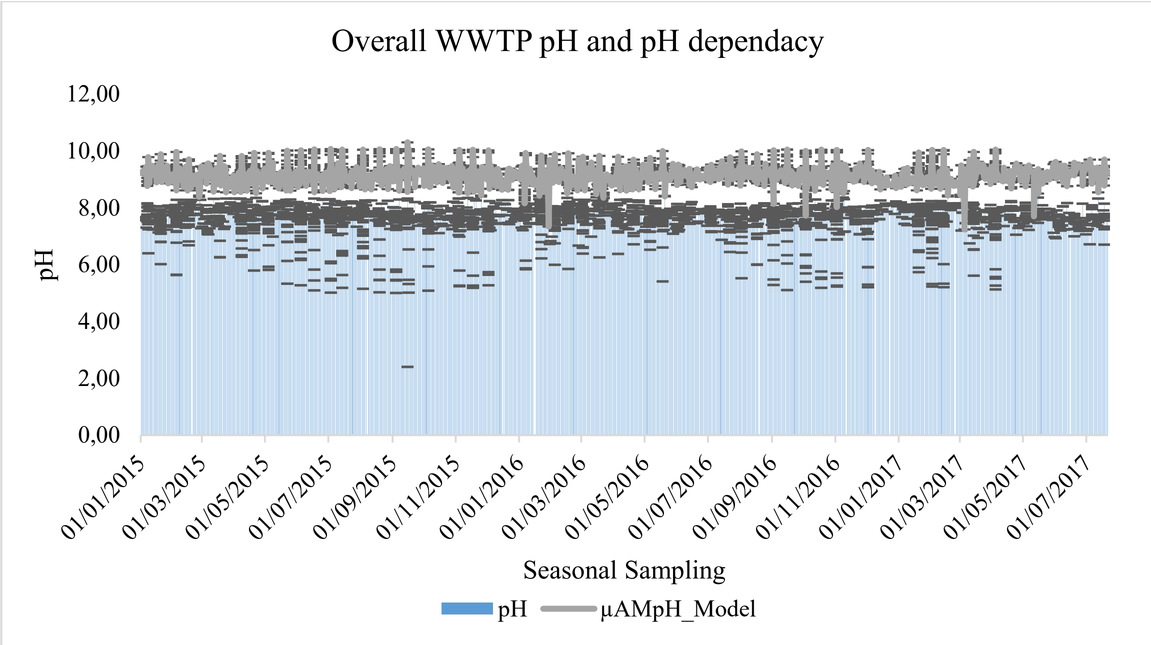


Figure 4.7: *The seasonal variation of the pH and pH dependency in the wastewater treatment process*

The optimum pH of the wastewater treatment is defined within the range of *7-8.5* with shape declines outside the range. μ_{Am} rate was extremely sensitive to pH of the mixed liquor outside the range of *7-8*. This happens when the range of pH increases above *8,* they increase the hydroxyl (OH^-) or decreases hydrogen (H^+) when below *7* as described by Hu *et al.,* 2007. The activated sludge systems treating reasonably well-buffered wastewater, quantifying the effect of pH on nitrification where pH reduction could be limited or completely obviated by including anoxic zones thereby ensuring alkalinity recovery via denitrification as elaborated by Jenkins, Richard & Daigger, 1993. The specific growth rate of the *ANOs* (μ_{Am}) was a function of both K_o and μ_{AmT}. The value of K_{nT} governs the effluent ammonia concentration once nitrification took place at *SRT*. μ_{AmT} remained at pH range of *7* to *8* as identical results shown by Sotemann *et al. (2005)*. Declining μ_{Am} values at $pH > 8.0$ have been observed and that nitrification effectively ceases at the pH of about *9.5* (Antoniou *et al.,* 1990) and $pH > 7.2$ to *9.5* (Sötemann *et al.,* 2005) as a function of $\mu_{Am7.2}$ using inhibition kinetics. The pH dependency observed was on an average of *9.5* similar to observation done by Rieger *et al.,* 2012. According to Rieger *et al.,* 2012, the influence of pH could be very low but provided the reactor pH stays neural, treatment of the wastewater could be achieved. If such plants are overloaded but lack sufficient oxygen supply, the residuals organic acids could lower the reactor pH. Lower pH below the optimum range of *7-8* for biological growth leads to the formation of acetic acid concentration and this further lowers the *pH* level that reduces the *WWTP* performance.

4.5.7 Seasonal variation of the total alkalinity

Alkalinity was introduced to predict the possible *pH* change as it guarantees the continuity in ionic charge of the biological processes in the concentration of $CaCO_3$, where *(50 mg* $CaCO_3/L$*= 1 mg* HCO_3^-/L*)* (Rieger *et al.,* 2012). The concentration of alkalinity was important because of biological and chemical treatment process. Alkalinity in wastewater resists change in *pH* caused by the addition of acids because wastewater is normally alkalinity from the groundwater, water supply and chemical added to wastewater treatment process. Typically, alkalinity was required to buffer the nitrification reaction (Metcalf *et al.,* 2010). ***Figure 4.8*** shows the variation of the total alkalinity in the wastewater treatment plant.

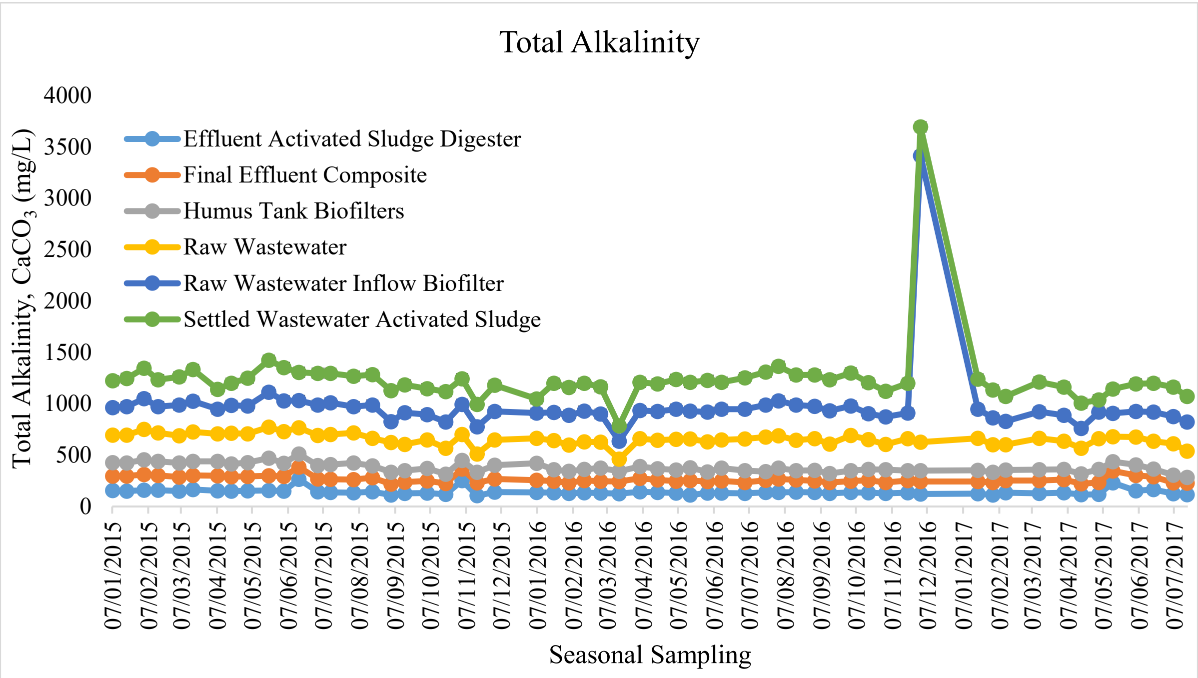


Figure 4.8: *Total alkalinity of the wastewater treatment plant*

For the overall stoichiometric equation for nitrification, nitrification releases hydrogen ions which in turn decreases alkalinity of the mixed liquor. All the process units of the *WWTP* recorded alkalinity above *40 mg/L* with a slight spark of alkalinity in summertime due to change in temperature. According to Jenkins *et al. (*1993), when alkalinity falls below *40 mg/L* as $CaCO_3$, irrespective of CO_2 concentration, the *pH* becomes unstable and decreases low values. The problems associated with fall of *pH* include poor nitrification efficiency, effluents aggressive to concrete and the possibility of development of bulking *(poor settling)* sludges. According to Rieger *et al.,* 2012, low alkalinity concentration may lead to unstable *pH,* that could reach inhibiting levels. Low alkalinity is always encountered where the source of wastewater is from underlain sandstone area. In such cases, it was advisable to dose with lime dose or anoxic zone is created to denitrify some, or entire nitrate generated. Nitrate is considered as hydrogen ions that are equivalent to generating alkalinity. Half of the alkalinity consumed in nitrification was suggested by Mackenzie, 2011 to be recovered through the process of the denitrification. Incorporating nitrification and denitrification in a system is said to cause a net loss of alkalinity above *40 mg/L* and consequently the *pH* above *7* as observed in our analysis. To maintain an effluent alkalinity above *50 mg/L,* influent alkalinity was sufficiently put high.

4.5.8 Impact of the electrical conductivity

The electrical current *(EC)* was one of the most important parameters used as a surrogate measure of the total dissolved solids *(TDS)* concentration. The *EC* of water was a measure of the ability to conduct an electrical current as they transport ions in the solution. The conductivity increased with increase in ions. The *EC* estimated the ionic strength of the wastewater.

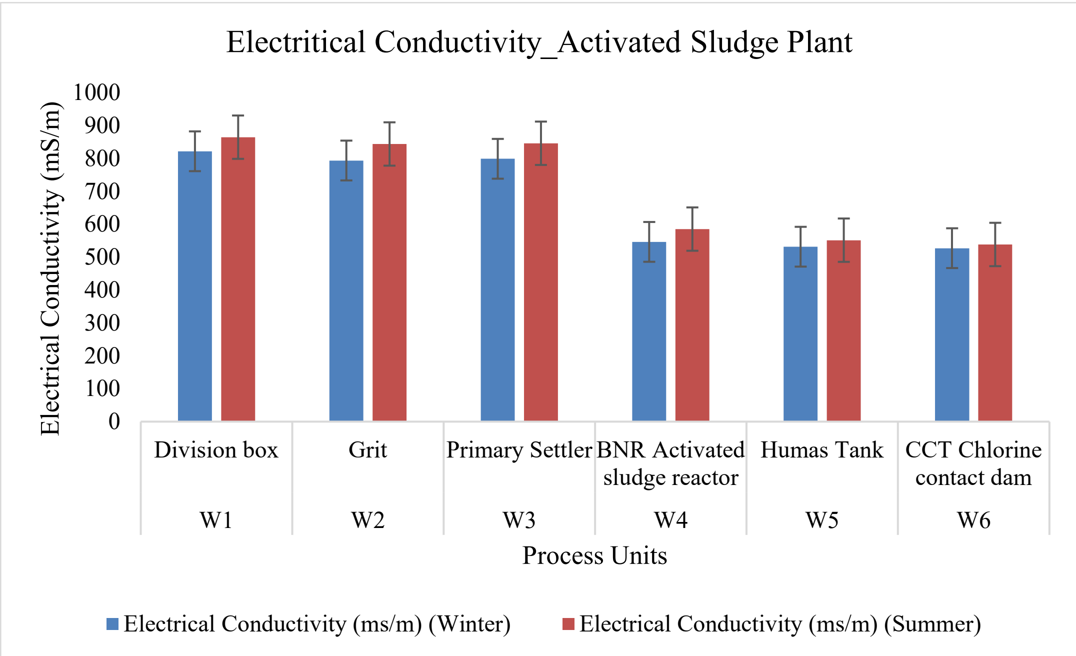


Figure 4.9: *Electrical conductivity of the activated sludge WWTP*

Figure 4.9 show the declining trend of the electrical current with reduction of total dissolved solids and metal ions in the activated sludge wastewater treatment plant.

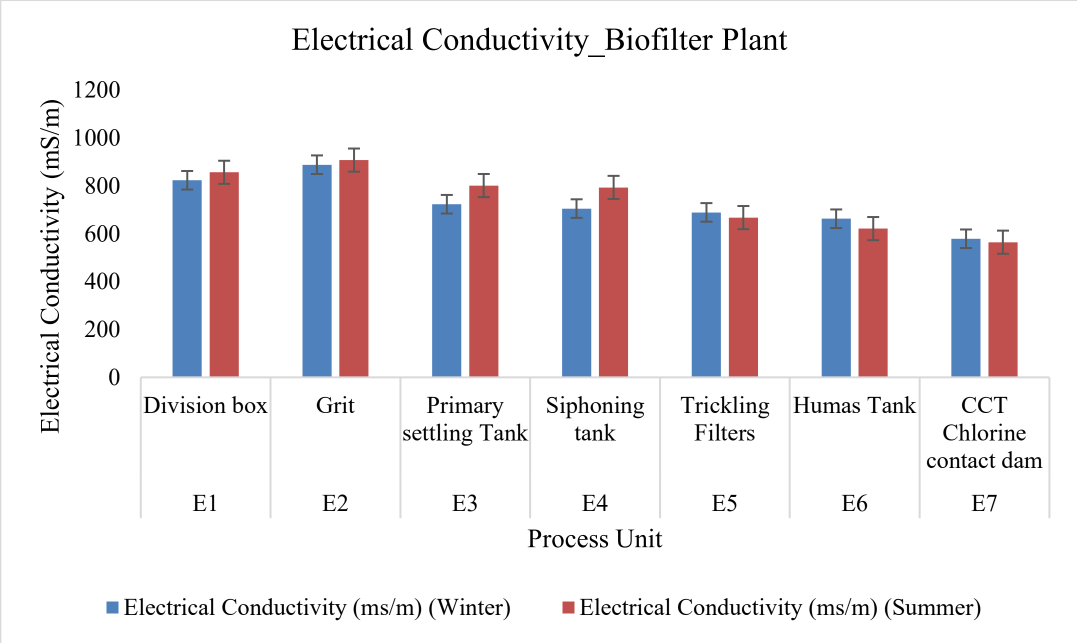


Figure 4.10: *Electrical conductivity of the biofilm WWTP*

Figure 4.10 show the declining trend of the electrical current with reduction of total dissolved solids and metal ions in the biofilm wastewater treatment plant.

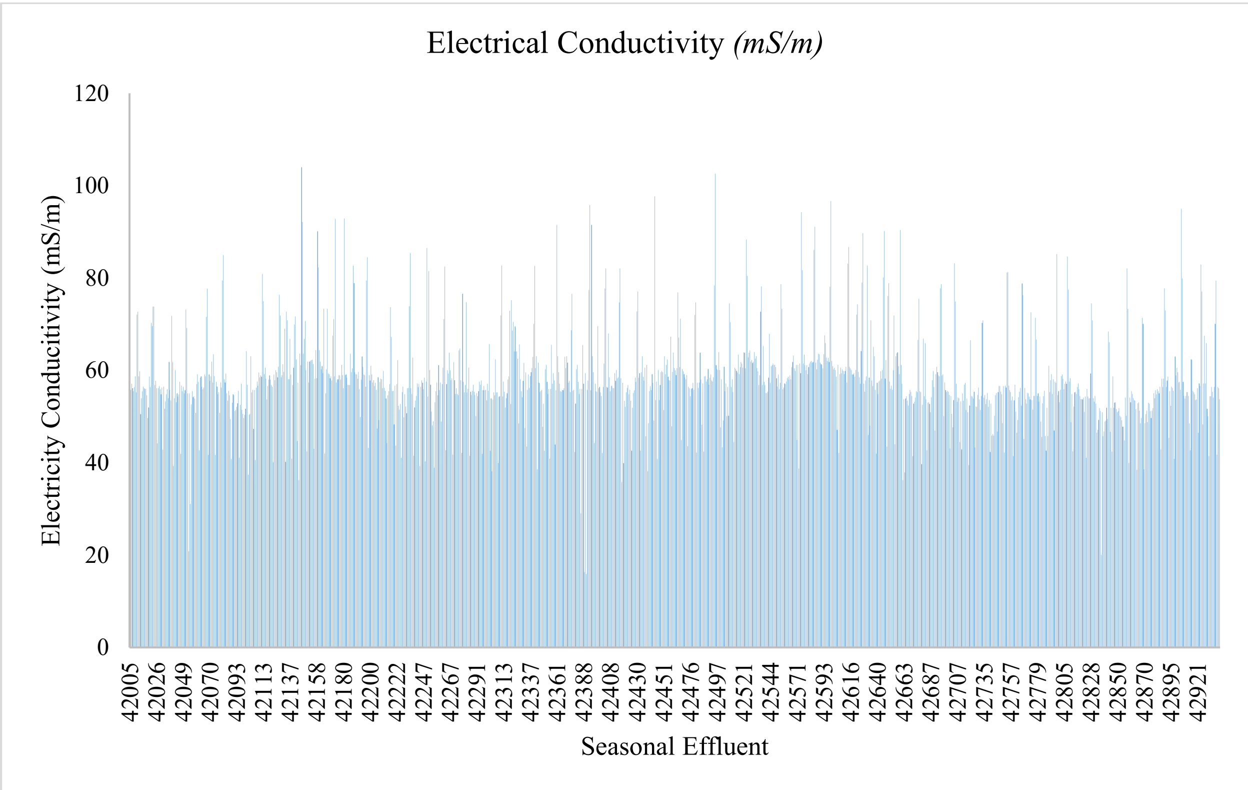


Figure 4.11: *Seasonal variation of electrical conductivity in the WWTP*

Seasonal variation of the entire plant was shown in ***Figure 4.11***. The final effluent indicated an average of *57.8 mS/m* with a maximum of *95.8* to a minimum of *15.9 mS/m*. The *EC* was within the required range as indicated in the *Appendix D*. This anticipated high efficiency in the plant performance in the removal of the total dissolved solids *(TDS)* and the ions.

4.5.9 Fate and transport of emerging organics compounds

Due to the environmental and health effects of toxic and recalcitrant compounds, it was important to understand fate and transport of the emerging organic compounds in the biological treatment processes. ***Figure 4.12*** and ***Figure 4.13*** show the parabens presence in the activated sludge and biofilm wastewater treatment plants respectively.

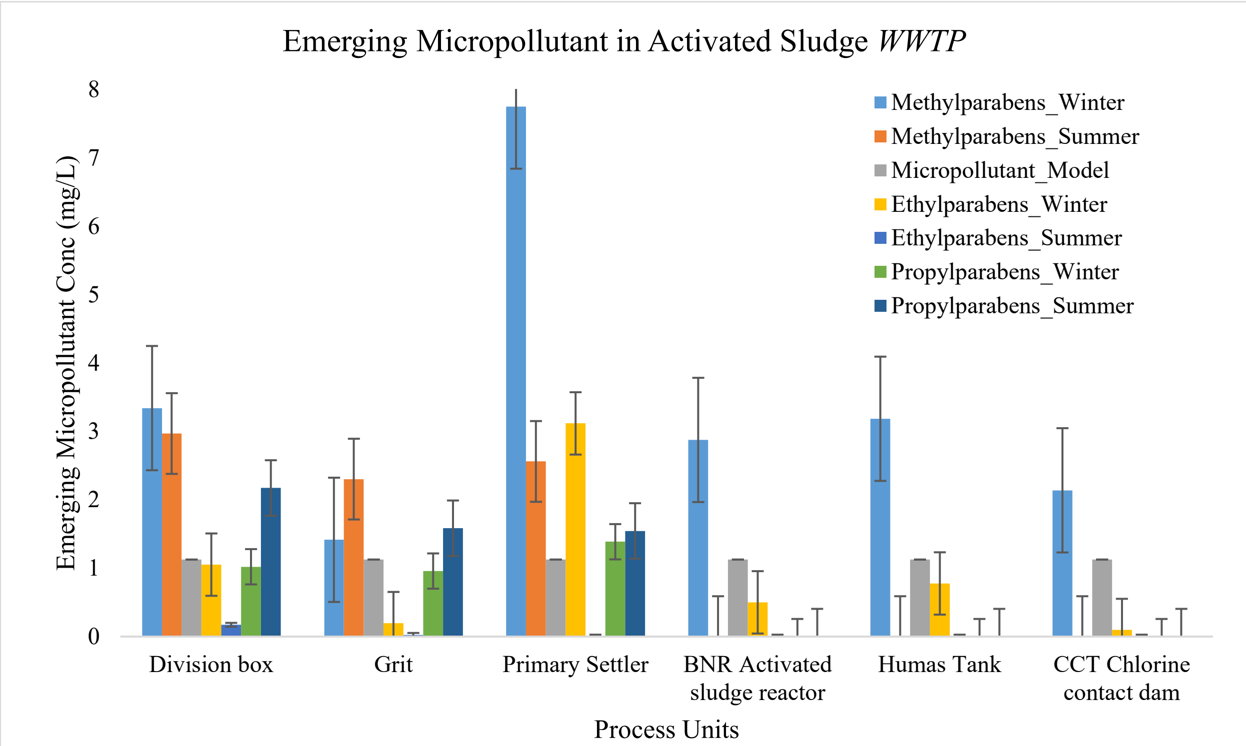


Figure 4.12: *Emerging micropollutants in the activated sludge WWTP*

Primary pretreatment treatment units are shown a high concentration of the methyl, ethyl and propyl parabens with a slight decrease in the *BNR* unit after treatment. The ability of degradation of the parabens depended on the specific microbes and acclimation time. Other means considered for the removal of the parabens were activated sludge aeration. Ethylparabens dominated in concentration in all the units at least been methylparabens overall in the activated sludge *WWTP*. The model indicated an average of *1.13 mg/L* of the overall parabens concentration that was below the threshold of the emerging micropollutants.

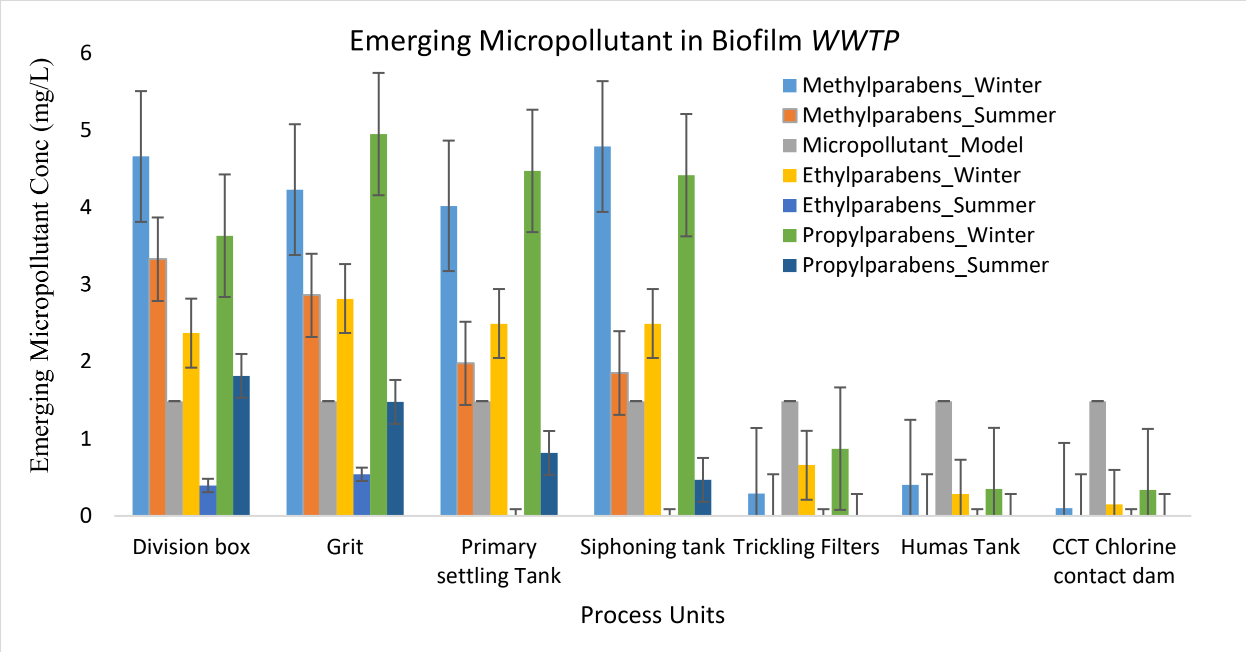


Figure 4.13: *Emerging micro-pollutants in the biofilm WWTP*

High concentration was recorded in the primary pretreatment treatment units at the biofilm *WWTP.* This shown a high concentration of the methyl, ethyl and propylparabens with a slight decrease in after the trickling biofilter unit. The model indicated an average of *1.49 mg/L* of the overall parabens concentration that was below the threshold of the emerging micro-pollutants. According to Metcalf *et al.,* 2010, the three principles of emerging micro-pollutant removal are; *i)* the compound serves as a growth substrate, with proper environmental conditions; seed source, acclimation time, a wide range of parabens have been found to serve as growth substrate for the heterotrophic bacteria. *ii)* the compounds are degraded by cometabolic degradation; the compound is degraded but not part of the microorganism metabolism as it has no benefits to the microbe's cell growth and lastly *iii)* the organic compound provides an electron acceptor.

4.5.10 Degradation of the organic matter inform of chemical oxygen demand

The fundamental aspect of most of the models in this study was based on the mass balances. This was trivial for phosphorus, nitrogen but impossible for organic material measured in *TSS,* and *VSS*. Organic materials were only possible measured in *COD* as oxygen units and widely linked to influent loading, sludge production and oxygen required on a mass balance basis. Chemical oxygen demand *(COD)* was much needed for the mass balance in wastewater treatment. The models were highly mechanistic where the major component of the relevance and the most important biological processes were identified. According to Henze *et al.,* 2008 the *COD* is a powerful tool for checking the results calculated for design from the steady-state model, data measured on experimental systems and the results calculated by dynamic simulation models. Suspended, soluble and total *COD* was considered in the mass balance of the organic matter. Microbial growth kinetics were used to calculate substrate utilization rate per unit of reactor volume (r_{su}), bacteria growth rate from substrate utilization (r_g), maximum specific bacteria growth rate (μ_m). The results assisted to calculate the effluent concentration before discharge *(S)*. In the conventionally activated sludge modelling *(ASMs),* these variables or coefficients were assumed to be constant for at *22°C* temperature, since they do not appreciably affect system performance as indicated by Water Environment Federation *(WEF 2011);* (Hocaoglu, Insel, Cokgor & Orhon, 2011). An elementary characterization of the organic matter was required in the model, *i.e.* biodegradable, unbiodegradable, soluble and particulate *COD* concentration. *COD* mass balance was a parameter considered in the nitrification and denitrification because it was a very powerful tool for checking the data sampled and analyzed on the *WWTP,* under steady-state models. The mass balance for the mass microorganisms in the complete-mix reactor is shown in ***Figure 4.14*** for the activated sludge plant and ***Figure 4.15*** for the biofilm *WWTP*.

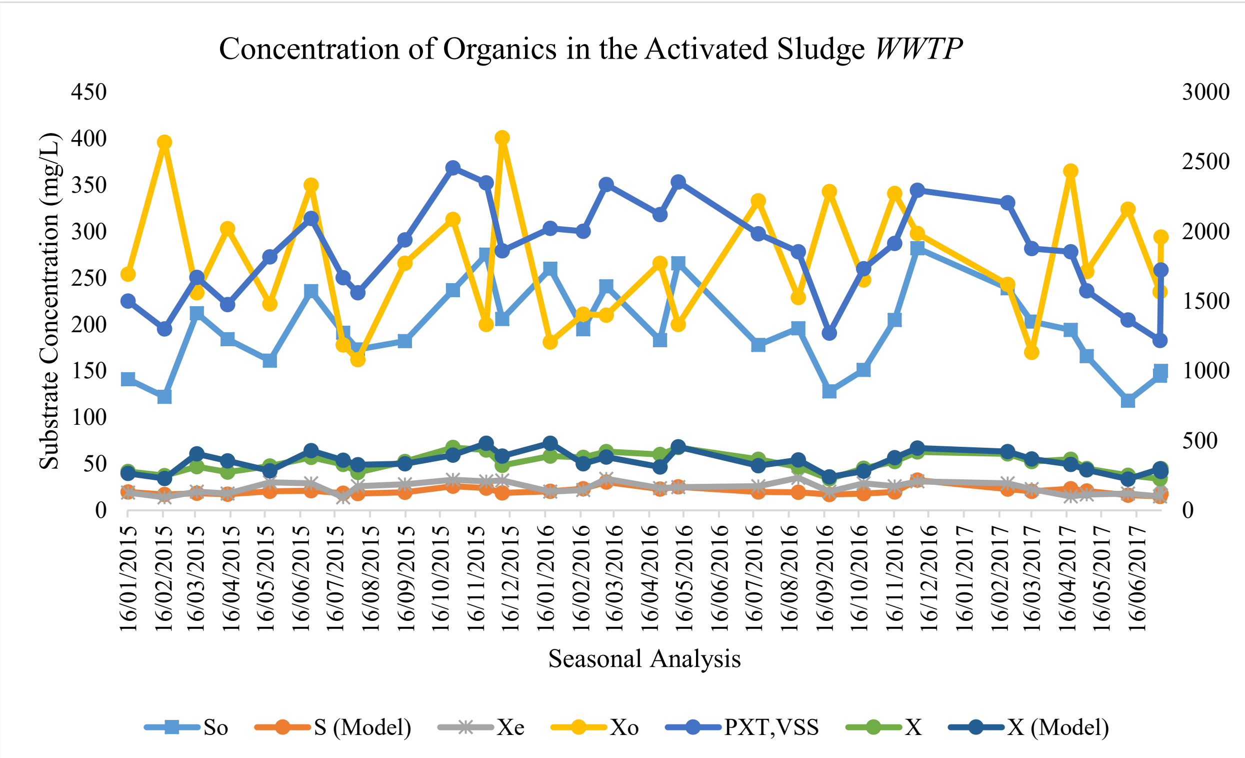


Figure 4.14: *Modelling of organic compounds in the activated sludge of the WWTP*

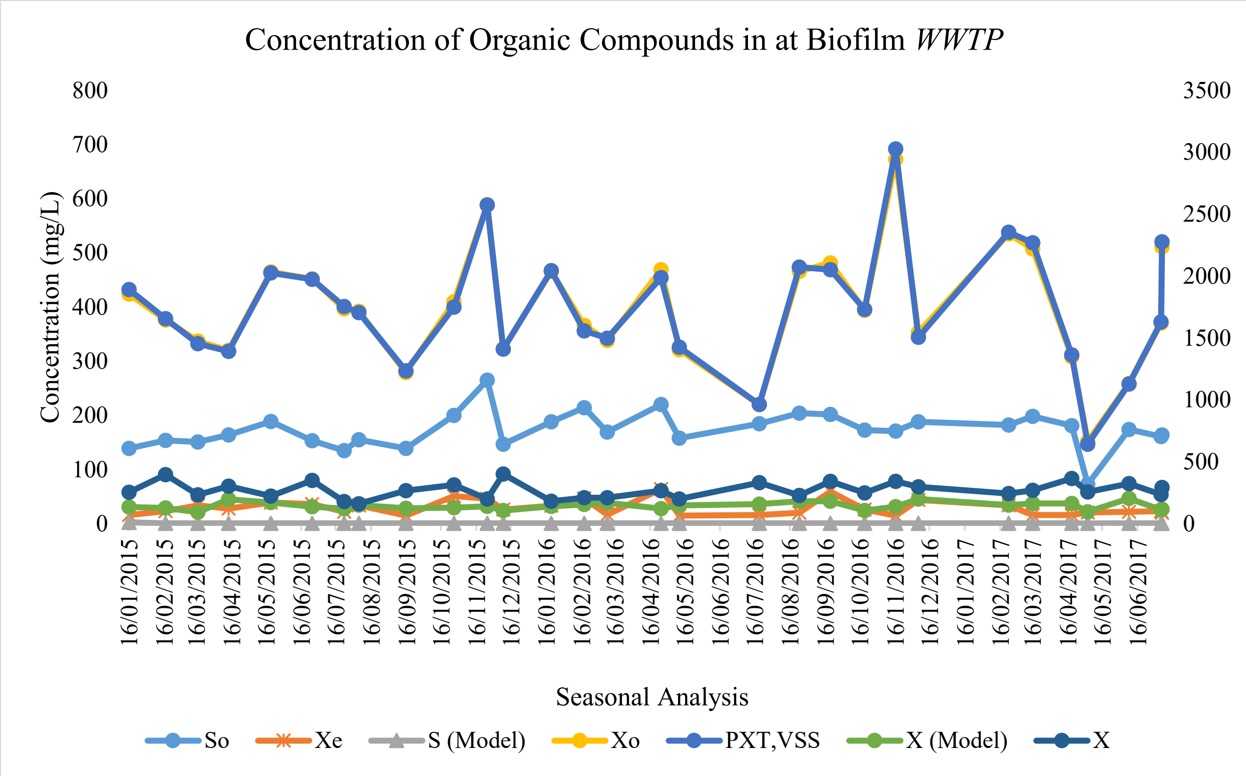


Figure 4.15: *Modelling of organic compounds in the biofilm of the WWTP*

From ***Figure 4.14*** and ***Figure 4.15*** for the activated sludge and biofilm wastewater treatment respectively, high influent of *COD* concentration was recorded with lower concentration recorded in the effluent of both plants. The concentration of biomass in the effluent, concentration of the substrate in the effluent and total/net solids wasted in a daily basis were all predicted and a smooth curve to show level with limited errors anticipated high efficiency and trust in the prediction. To show the fate of the substrate, *COD* mass balance was carried out because the substrate concentration in the wastewater could be defined in terms of oxygen equivalence that accounted for by being conserved in the biomass or oxidized. Biomass is mostly organic matter and an increase in biomass measured by particulate *COD (total COD minus soluble COD)* or volatile suspended solids *(VSS).* A study carried out by Metcalf and Eddy (2016) show that the same approach could be used to treat wastewater with particulate biodegradable *COD* by assuming that is equal to *bsCOD* and for complete mix suspended growth with more than *3 days SRT,* all the degradable particulate *COD* will be converted to *bsCOD*. The *COD* and *VSS* represent the organic matter and the new cells and its determination shows the biomass yield in the wastewater treatment. It was noted that the effluent soluble substrate concentration for a complete-mix activated sludge process was only a function of solid retention time *(SRT)* and the biokinetics coefficients for the growth and decay as described by Metcalf *et al.,* 2010. Another worth noting is that the effluent substrate concentration was not related to the influent soluble substrate concentration thus the influence substrate concentration affects the reactor biomass concentration. The effluent *COD* concentration comprised virtually the soluble unbiodegradable organics *(COD)* from the influent plus the *COD* of the sludge particles that escaped with the effluent due to the imperfection of operation of the secondary settling reactor. The average final effluent *COD* recorded and predicted was less than *20.72* and *0.74 mg/L* for the activated sludge and biofilm wastewater treatment plant. The *COD* was below the plant license limit. The model accuracy was indicated as *95-98%* range. That made a lot of sense on the prediction of the experimental data and reliability and accuracy of the mass balance. Calibration was done as there was no extra compound added in the model algorithm and thus straightforward shifting some model parameters.

The fate and transport of the *COD* based on the hydraulic retention time and seasonal variations *(summer and winter)* was significant to the study and was shown in ***Figure 4.16*** and ***Figure 4.17*** for the activated sludge and biofilm *WWTPs.* The *COD* of the sludge particles and effluent *COD* concentration comprises of the soluble unbiodegradable organics *(COD)* from the influent that escape with the effluent. Because the settled wastewater was produced from the raw wastewater, the soluble concentration was the same as in raw wastewater. Because the *COD* concentration changes with primary settling, the soluble constituent fraction increases with primary settling.

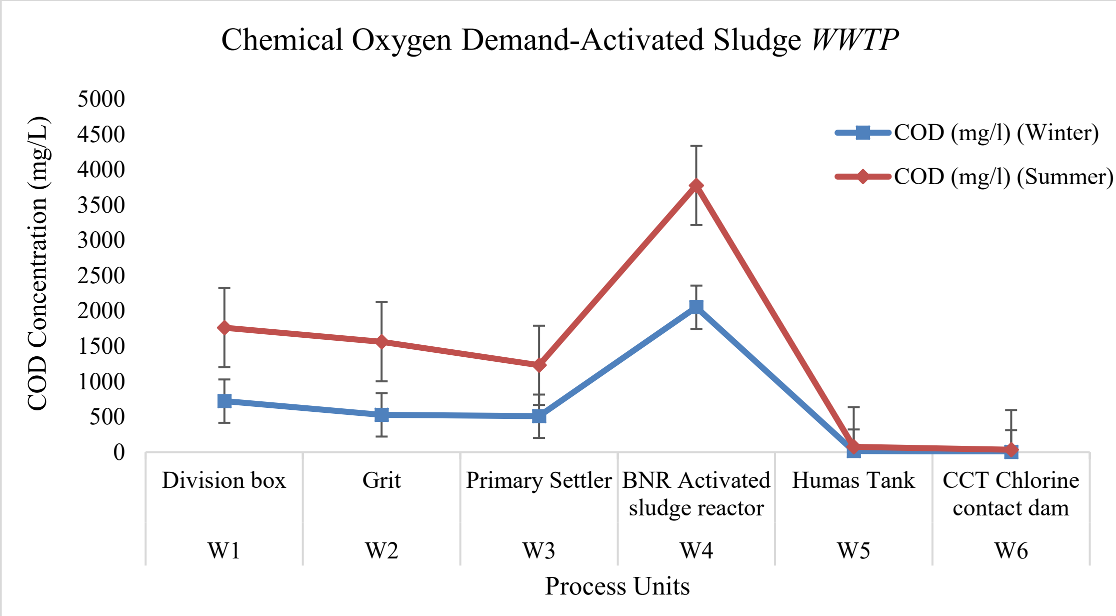


Figure 4.16: *Biological nutrient removal informs of COD from activated sludge WWTP*

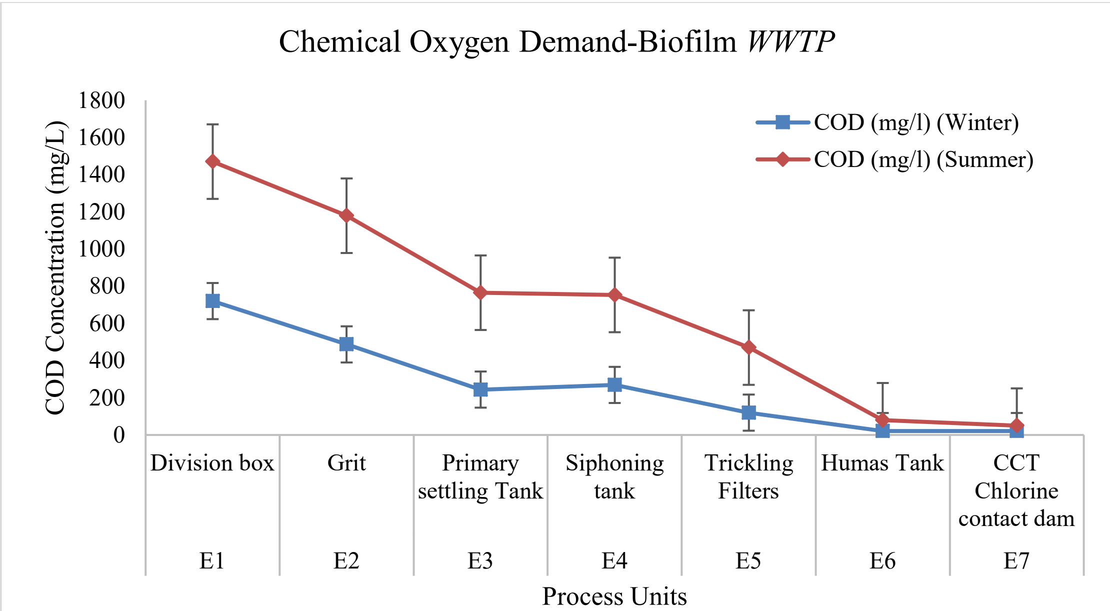


Figure 4.17: *Biological nutrient removal informs of COD from biofilm WWTP*

High inflow of the *COD* was observed in the two plants. There were *COD* recorded in summer than the winter season and most probably due to human activities with organic compounds that end up in the wastewater treatment plant. The high percentage of reduction of the *COD* was recorded at the biological nutrient removal *(BNR)* unit in the activated sludge plant and the trickling filters in the biofilm units respectively. High sludge with extended aeration in the activated sludge system allowed the endogenous process to approach completion. This provided not only wastewater treatment in the reactor but also a significant measure of aerobic stabilization of the activated sludge to achieve a low active fraction so that waste sludge could be discharged directly to the drying beds without much further treatment in the stabilizer. Treating settled wastewater resulted in lower secondary sludge production per unit *COD* load on the biological reactor than treating raw wastewater. To ensure nitrification and biological nutrient removal *(BNR)* under normal activated sludge systems operating conditions where sludge age was more than 3 days, the nature of the influent organics in *WWTP* was such that *COD* concentration in the effluent was inconsequential and soluble readily biodegradable organics were completely utilized in a short time of less than *2 hours* while the particulate organics are enmeshed with the sludge mass in the secondary settling tanks. The average final effluent *COD* recorded and predicted was less than *17.50* and *25 mg/L* for the activated sludge and biofilm wastewater treatment plant. The *COD* was below the plant license limit. This indicated the moderate efficiency of the plant performance.

4.5.11 Effect of the mixed liquor suspended solids

In the conventional aerobic oxidation process, mixed liquor suspended solids (*MLSS)* flows from the aeration tank to secondary clarifier where the activated sludge is settled down. The return sludge maintained the concentration of the microorganisms in the aeration tank by the high the population of the microbes that permits rapids breakdown of the organic compounds. The volume of sludge return to the aeration basin typically was 2*0* to *30* percent of the wastewater flow. A balance to achieve the growth of new microbes and their removal by wasting *(WAS-waste activated sludge)* was instituted by control of the waste portion of the microbes each day to maintain the proper number of microorganisms by efficiency oxidizing the biodegradable *COD (bCOD).* According to Mackenzie (2011), when too much sludge is wasted, the concentration of the microorganisms in the mixed liquor will become too low for effective treatment and little sludge wasted resulted into a large concentration of microorganism that accumulates and ultimately overflow the secondary tank and flow into the receiving stream. The increase in *MLSS* was estimated by assuming the *VSS* in some fraction of *MLSS* in range of *60-80%.* The increase of *MLSS* was estimated by dividing P_x by a factor of *0.6* to *0.8 (or multiplying by 1.25 to 1.67).* The *MLSS* concentration was expressed to be on the range of *2000* to *5000 mg/L* as expressed by Mackenzie, (2011) and Metcalf *et al. (*2010) on a reasonable reactor volume on fairly settling sludge.

4.5.12 Impact of total suspended solids in the concentration of suspended solid fraction

Total suspended solids *(TSS)* was an important variable in the concentration of the suspended solid fractions. It consisted of volatile suspended solids *(VSS)* and inorganic suspended solids *(ISS=TSS-VSS)* (Rieger *et al.,* 2012). *TSS* was calculated based on the *COD* state variable of the total concentration of particulate and a factor according to the measured *TSS/COD* ration as indicated at the *Appendices B2* in activated sludge model *No. 1* (*ASM1)* implementation.

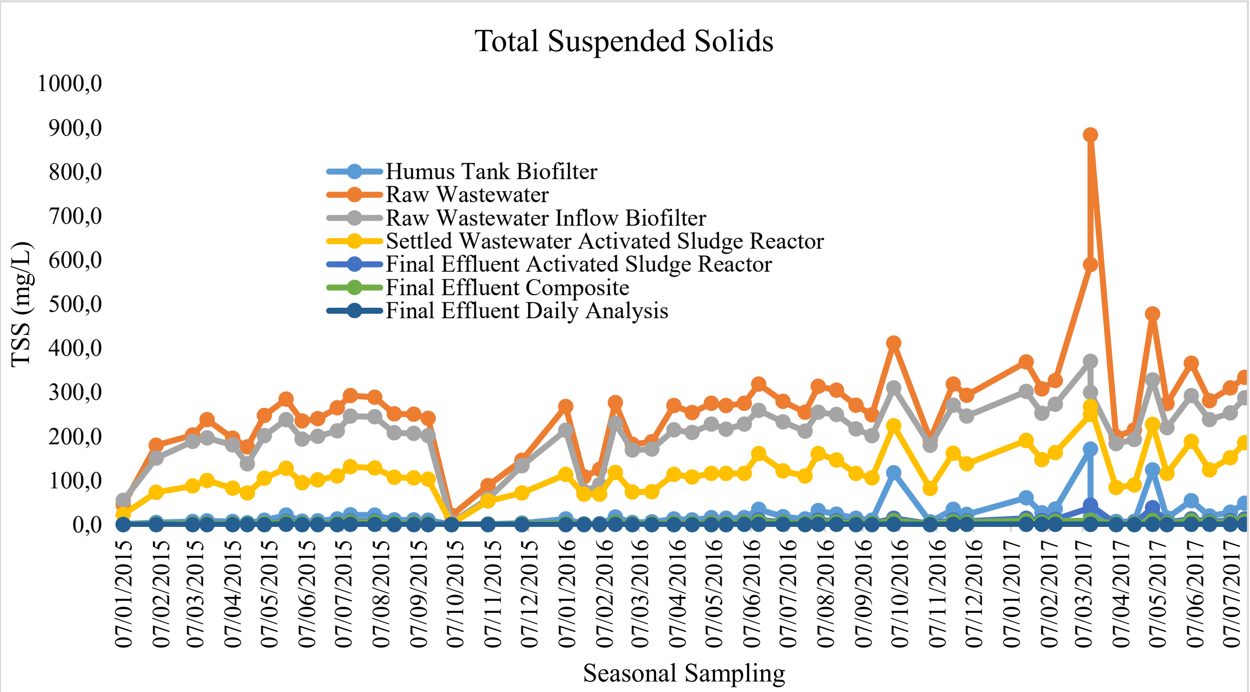


Figure 4.18: *Seasonal variation of the total suspended solids in the wastewater treatment plant*

From ***Figure 4.18***, it was observed that raw wastewater had high total suspended solids *(TSS)* with lower concentration recorded in the effluent of the wastewater treatment process. The highest concentration was recorded in raw wastewater was in summertime due to the source of the influent. The trend of the *TSS* reduction in all the process units was inevitable due to the *WWTP* efficiency. The mass of total suspended solids *(TSS)* in the reactor was a function mainly of the daily mass loads of chemical oxygen demand *(COD)* and inorganic suspended solids *(ISS)* on the reactor and the sludge age. The active fraction of the humus tank reactor, raw wastewater inflow biofilter and settled wastewater activated sludge reactor was too high for direct discharge to direct beds. This required higher oxygen to treat the sludge. According to Henze *et al.,* 2008, the choice of treating settled or raw wastewater requires weighing their merits and demerits; for settled sewage smaller reactor volume, reduced secondary sludge and lower oxygen demand, but deals with secondary and primary sludge and their stabilization but for raw sewage and larger reactor volume, higher oxygen demand and increased secondary sludge production, but having no primary sludge to deal with. The *TSS* concentration difference from the settled, raw wastewater arises because the sludge settle ability in conventional systems could be poorer than extended aeration system and the wastewater flow *per kg COD* loaded on the reactor for raw wastewater was significantly greater than that for settled wastewater. *TSS* was used to assess the performance of the conventional treatment process and the need for effluent filtration in reuse application. It was one of the universal used effluent standards by which the performance of treatment plants was judged for the regulatory control purposes.

4.5.13 Variation of the volatile suspended solids in *WWTP*

The mass of volatile suspended solids *(VSS)* in the reactor was a function of the daily *COD* mass load on it and the sludge age. ***Figure 4.19*** presents the seasonal variation of the *VSS* in the wastewater treatment plant.

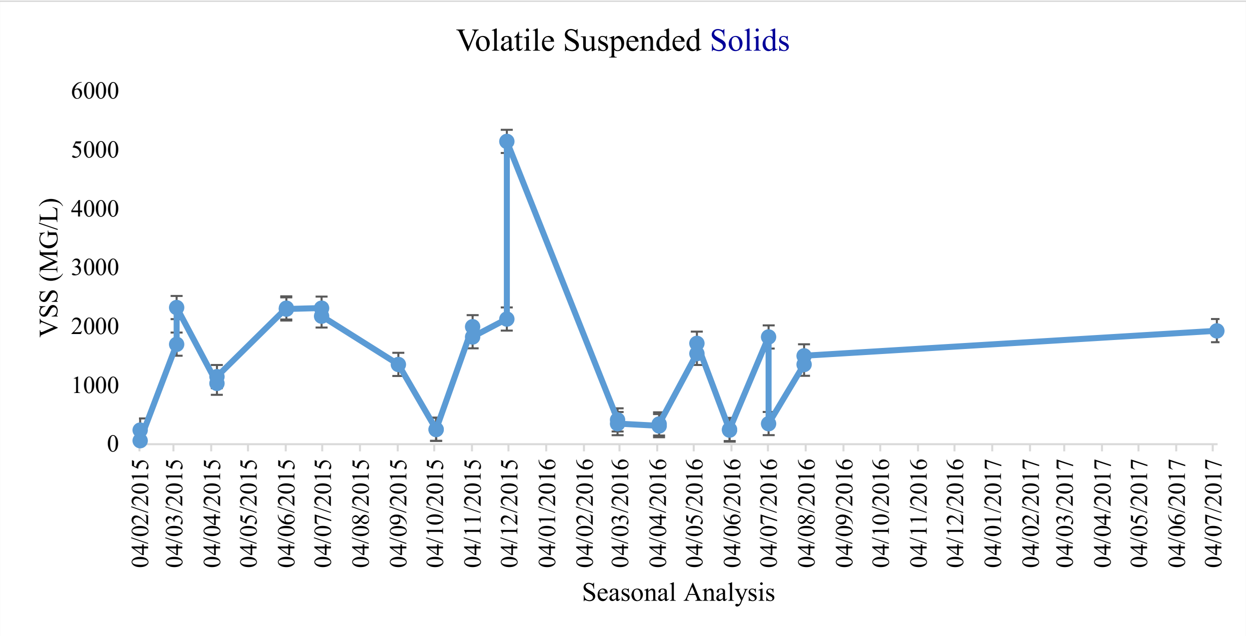


Figure 4.19: *Seasonal variation of the volatile suspended solids-mixed mixed liquor of the WWTP.*

A higher *VSS* of *5145 mg/L* was recorded on the summer time with lower *VSS* of *64 mg/L* recorded in summer period again. This showed inconsistency in the efficiency with volatile suspended solids in the plant's operation and most probably the source of the influent defined the source of the *TSS* in the plant. The average *VSS* was indicated as *1356.97 mg/L* that was in compliance with the wastewater treatment license *(Appendix D)*.

4.5.14 Effect of dissolved oxygen in the wastewater treatment processes

Dissolved oxygen *(DO)* in the biological treatment was a measure of oxygen dissolved in wastewater to sustain the microbial growth that enhances the breakdown of the organic compounds by the blended biomass and microbes in the aeration reactor. Oxygen is less soluble in the summer time than in winter time. The solubility is enhanced by the change in temperature that is paramount to the chemical reaction, aquatic life and suitability of the water for the beneficial use. Increase in temperature decrease the rate of the dissolved oxygen in the summer time. Temperature influence the oxygen transfer on the bases on saturation *DOs.* According to Van Haandel & Van Der Lubbe, 2012, local atmospheric pressure differs from the standard pressure at sea level of *1 atm* (*1.0123 bar* or *760 mm Hg*), the saturation concentration of dissolved oxygen *(DO)* in water could be related to the actual atmospheric pressure and water vapor pressure. Most of the oxygen transfer took place at the surface area of suspended droplets *(atmospheric pressure)*. ***Figure 4.20*** and ***Figure 4.21*** represent analyzed and modelled of the demand of dissolved oxygen in the activated sludge and biofilm wastewater treatment plants respectively.

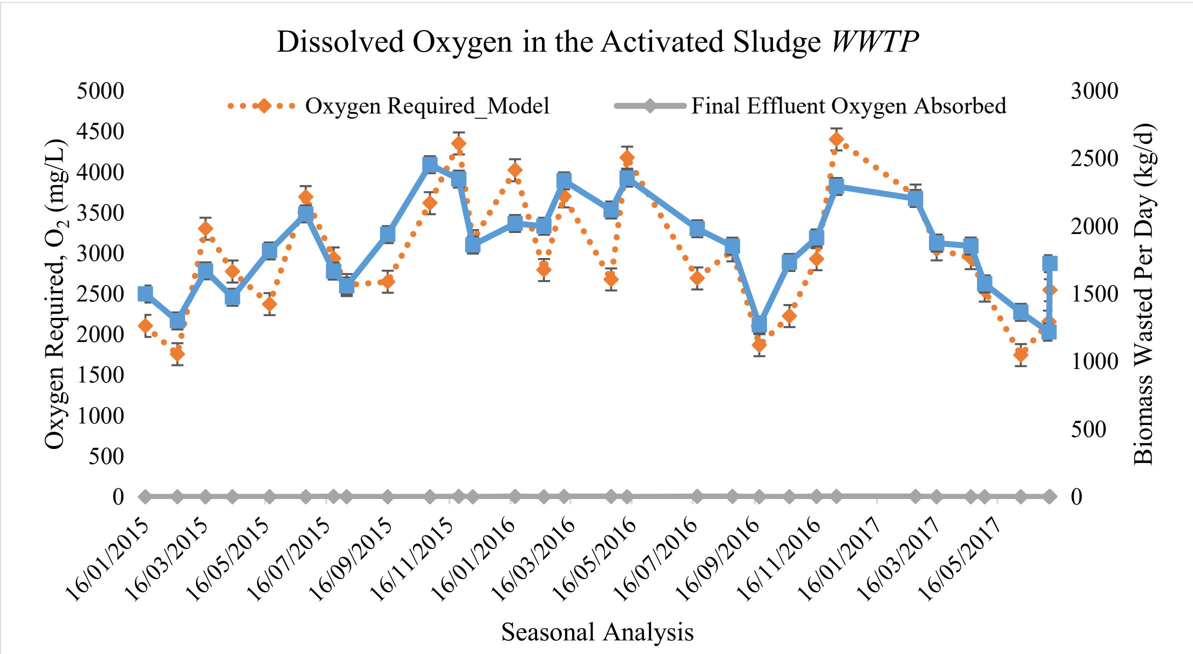


Figure 4.20: *Dissolved oxygen demand of the activated sludge WWTP*

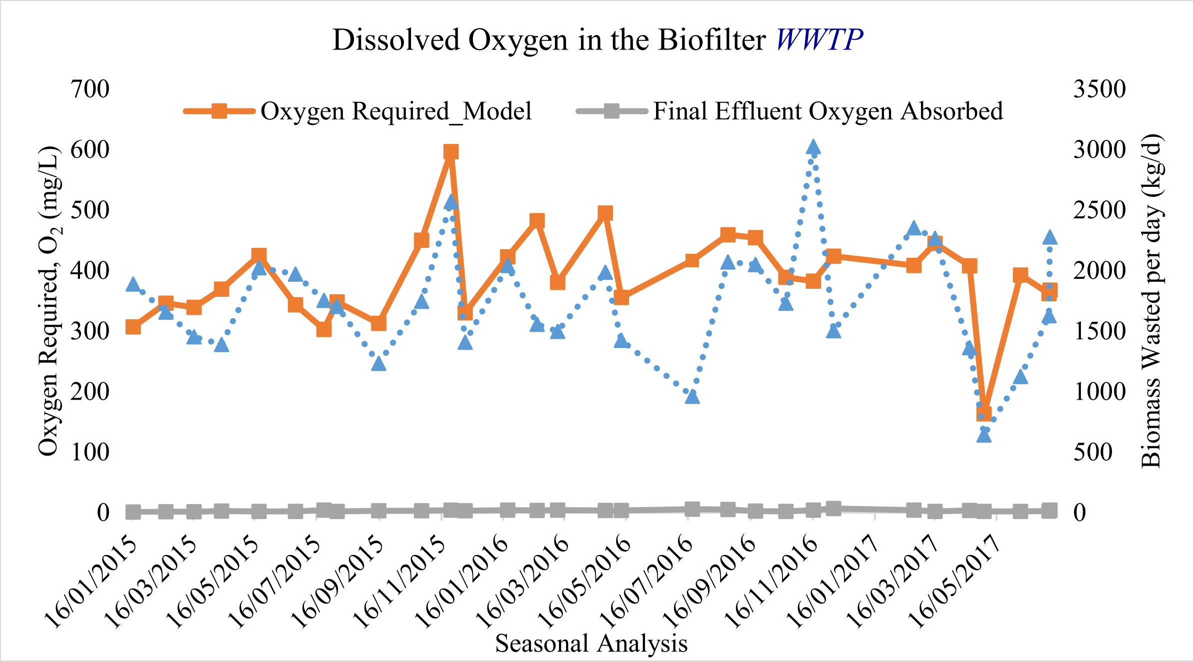


Figure 4.21: *Dissolved oxygen demand of the biofilm WWTP*

The activated sludge plant showed the smooth curve of the model and analyzed *DO,* unlike the biofilm where there were small errors in the variation due to lack of recycled stream to circulate the oxygen like the *MLSS* in the aeration reactor. For the *COD* balance, the more oxygen that is utilized in the system, the lower the sludge production and the lower the active fraction of the sludge observed. An adequate supply of dissolved oxygen enhanced nitrification. Our findings recorded high oxygen requirement from the model of a maximum of *596.70 mg/L* and minimum of *307.16 mg/L* in the biofilm *WWTP*. Higher *DO* required was recorded in the activated sludge due to plant capacity with the *4355.5 mg/L* and minimum of *1759.5mg/L.* At *DO* value below K_o, the growth rate declined to less than half the rate where oxygen was present in adequate concentration. High range of K_o risen when the concentration of *DO* was not same as biological floc where the oxygen consumption took place. The *DO* level acted as the main diffusion control parameter regulating the extent of simultaneous nitrification and denitrification with different *MLSS* levels. The variation of *DO* depend on mixing intensity, sludge settling properties floc size, microbial community, reactor volume due to discrete points of oxygen input *(mechanical aeration),* and oxygen diffusion rate into the floc. The factors that affect oxygen diffusion in flocs among others included the variation between measured results due to steady-state and dynamic measuring techniques. According to Guo *et al.,* 2009, lower *DO* produces sludge with power settling properties but attain lower turbidities of the effluent that high *DO. DO* deficiency was believed to be one of the most frequent causes responsible for the most filamentous bacteria proliferation in activated sludge processes. The final effluent oxygen absorbed recorded was *3.3 mg/L* for the both activated sludge and biofilm *WWTP*. According to Stenstrom & Poduska (1980), the maximum growth rate of both nitrification reaction to be affected by dissolved oxygen concentration was in excess of *0.4 mg/L* while others have found that the most reliable range of *DO* concentration in nitrification to be achieved as *0.5-2 mg/L*. Another study by Henze *et al.,* 2008 state that high dissolved oxygen concentration up to *33 mg* O_2*/L* do not appear to affect the nitrification rates. However, low oxygen concentration reduces the nitrification rates. Energy saving by low *DO* will be feasible if sludge settleability did not become weak to affect the separation of sludge and effluent. It was advisable for nitrification to proceed without inhibition by oxygen limitation though adequately designed aeration equipment to supply the total oxygen demand. The *DO* above *2 mg/L* allowed nitrification to proceed with efficiency because the surface aerators, adequate velocity and aerator spacing were well fixed.

4.5.15 Sequence in the biological nitrogen removal

4.5.15.1 Nitrite and nitrate in form of N

All the biological materials and some unbiodegradable organic compounds contain nitrogen *(N)*. Biological nitrogen removal *(BNR), (nitrification-denitrification-NDN or BNDN)* requires both anoxic and aerobic zone (Mackenzie, 2011; WEF, 2006). The volatile suspended solids *(VSS)* that accumulate in the biological reactor comprises unbiodegradable particulate organics (X_I), active organisms (X_{BH}), and endogenous residue (X_{EH}). Nitrogen removal was assesses based on monthly average data with the target effluent limit of *10 mg/L* total nitrogen using a steady state model.

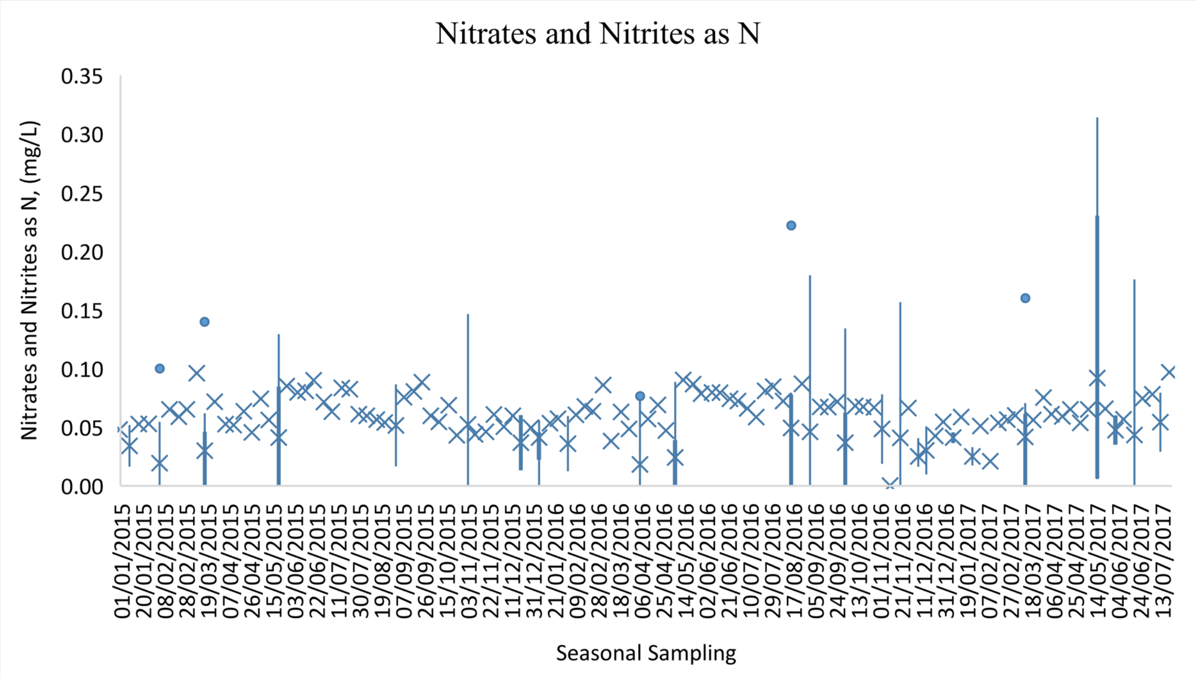


Figure 4.22: *Seasonal variation of the nitrates and nitrites as N in the WWTP*

From the observation of the seasonal variation of the nitrite and nitrates in the *WWTP* (***Figure 4.22***) an average of *4.36 mg/L* of nitrite and nitrate was recorded with the maximum of *26.38 mg/L* that was beyond the limit of *10 mg/L* and the minimum of *0.01 mg/L*. Once nitrification took place, the temperature has relatively little effects on the different effluent *N* concentration. Relative change in temperature causes a significant change in the minimum sludge age for nitrification. Increasing the sludge age in the *BNR* systems increases the nitrification capacity so more nitrate denitrified to achieve the same *N* removal. The increase in the nitrate concentration with increase with sludge age was due to the reduction in *N* required for sludge production. Denitrification is the prerequisite for the nitrification where without it, biological *N* removal was impossible. Once the nitrification took place, *N* removal by denitrification becomes possible and should be included even when *N* removal was not required by incorporating zones in the reactor that are intentionally unaerated. The sludge was long due because of the need for unaerated in the specific growth rates, the uncertainty of specific growth rate of the biomass and low temperature during the winter season. According to Henze *et al. (2008)*, the benefits for the denitrification is for the recovery of the alkalinity, reduction in nitrate concentration that ameliorates the problem of arising sludge from denitrification in the secondary settling tanks, reduction in oxygen demand and lastly under anoxic conditions, nitrate serves as electron acceptor instead of dissolved oxygen in the degradation of organics *(COD)* by facultative heterotrophic organisms. Van Haandel & Van der Lubbe, 2012 stated that the only reasons that were difficult to obtain the desired level of nitrogen removal efficiency were because *i)* when nitrogen systems were overloaded; the anoxic sludge mass fraction is often reduced to a level that insufficient denitrification capacity remains for proper denitrification; *ii)* At anaerobic digestion, much quantity of nitrogen are released together with solid digested to the liquid phase that returns to the activated sludge systems, this increase the *TKN/COD* ratios of the influent; *iii) TKN* and *COD* ratios are high and that makes nitrogen removal more difficult as nitrate produced is directly related to the *TKN* concentration in the influent, whereas the denitrification capacity is directly linked to the presence of *(biodegradable) COD; iv)* low sludge age enhance the bio-P removal at the expense of nitrogen removal, whereas the opposite is true for a high sludge age; *v)* Primary clarifier or anaerobic pre-treatment units increases the ratio between *COD* and *TKN* in the pre-treated wastewater.

4.5.15.2 Total Kjeldahl nitrogen

The dominant forms of *N* coming into a conventional facultative wastewater treatment system are referred to as total Kjeldahl nitrogen *(TKN),* it's the sum of organic nitrogen *(N),* ammonia (NH_3) and ammonium ions (NH_4^+) (Environmental Protection Agency, 2011). In the component-based models, the organic nitrogen was typically split into a soluble and particulate fraction where particulate fraction underwent a hydrolysis step to the soluble matter before it was transformed into ammonia in an ammonification process. Nitrogen is produced in microbial aggregates in which local physiochemical conditions differ from those in bulk liquid. It was necessary to analyses in-situ N_2O production and microbial community relation to local physiochemical conditions to gain insight into N_2O emission mechanisms as referenced by Rathnayake *et al.,* 2015. ***Figure 4.23*** shows the seasonal variation of the *TKN* in the *WWTP.*

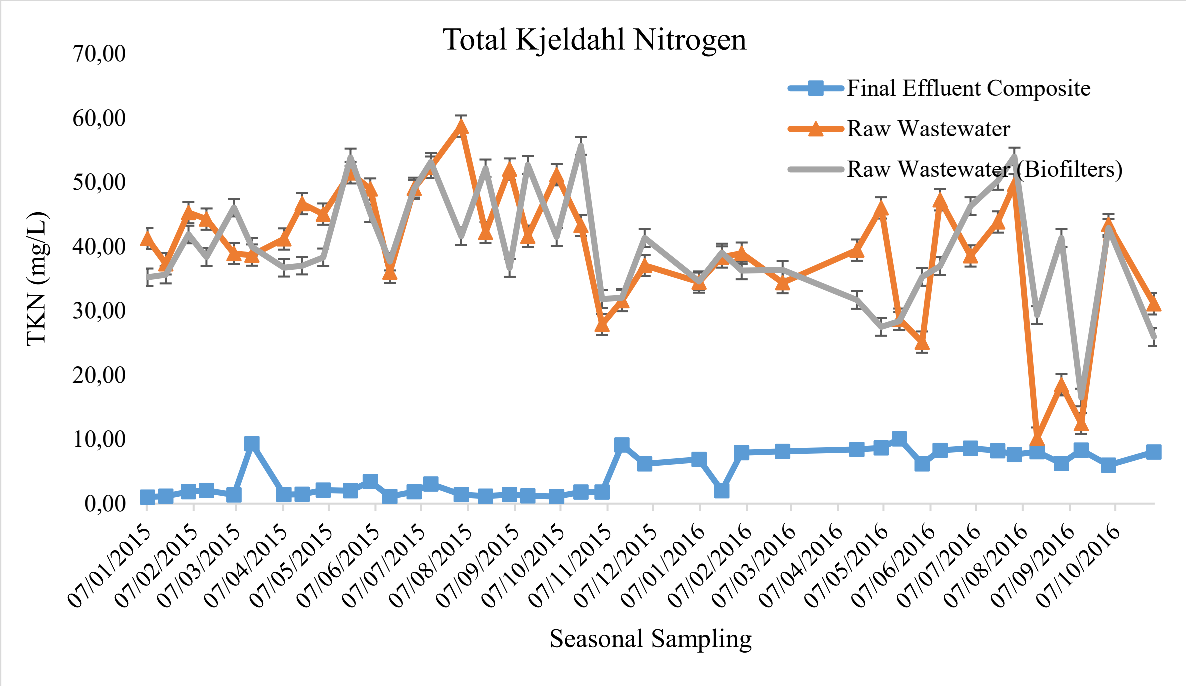


Figure 4.23: *Seasonal variation of the total Kjeldahl nitrogen in the WWTP*

From the analysis conducted, it was found that the *TKN* at the effluent ranged from *1.03* to *10.40 mg/L*, raw wastewater at *BNR* range from *10.20* to *58.78 mg/L* and raw wastewater at biofilter range *16.52* to *55.70 mg/L*. The total Kjeldahl nitrogen *(TKN)* load on the reactor varies with day in an approximately similar fashion to organic load. The raw *COD* and *TKN* increased due to increase in both flow, *COD* and *TKN* concentration reaching a peak. Lower peak in *TKN* is observed due to lower treatment, lower temperature, and lower microbial population. It was evident that the high concentration of *TKN* was required for the sludge production of the raw than that of the settled wastewater ***(Figure 4.24)***.

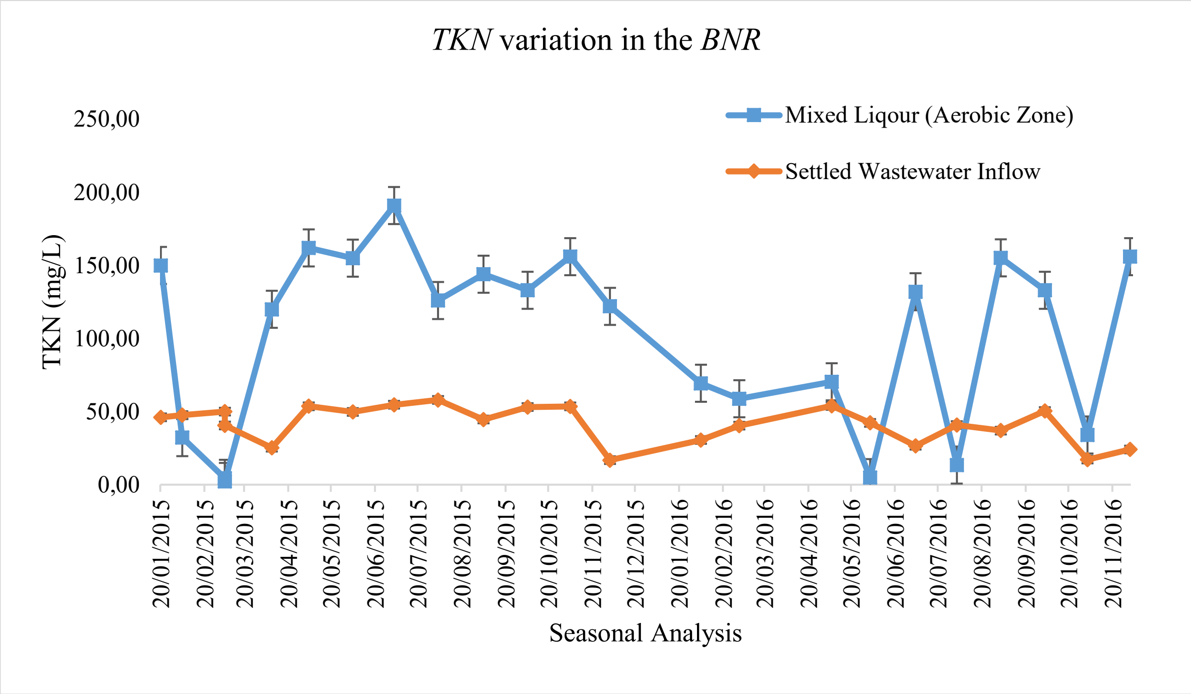


Figure 4.24: *Variation of the TKN in the biological nutrient removal*

Higher *TKN* was observed in the mixed liquor due to recycling of the sludge in the *BNR* with a steady settling *TNK* in the wastewater inflow throughout the season. According to Guo *et al.,* 2009 by selecting properly *DO* level and adopting process control method is not only of the benefit to the achievement of novel biological nitrogen removal technology but also favourable to sludge population optimization. Mass transfer limitation for nitrogen and oxygen compounds was interpreted in terms of the corresponding half saturation coefficients in the adopted models, yielding specific values that justified simultaneous nitrification and denitrification sustained at high sludge age. Poorly buffered wastewater with high influent *N (anaerobic digester liquors),* the interaction between the biological processes, nitrification and *pH* was the single most important for the *N* removal activated sludge system (Henze *et al.,* 2008). The effluent concentration of *TKN* was dependent on the efficiency of the nitrification. It depended on the system configuration and the subdivision of the sludge mass into aerated and unaerated mass fractions. Nitrification increased at summer seasons unlike on the colder season of winter as high temperature increases the nitrification efficiency. According to Henze *et al.,* 2008, high *TKN/COD* ratio with low alkalinity in the influent are reliable indicator warning of potential problems in fully aerobic nitrifying systems. Because the *COD* concentration changes with primary settling, the soluble constituent fraction increases with primary settling. The difference in the *TKN* and oxygen demand was brought about by the primary settling tank removal on a small fraction of the influent and settled wastewater results in lower sludge production.

4.5.15.3 Free and saline ammonium

Nitrogen has an influence on the treatment options for the wastewater. Since most of the nutrients are normally soluble, they cannot be removed by settling, flotation, filtration or other means of solids-liquid separation. Nitrification takes place into sequential oxidation steps; nitrite oxidizing organisms *(NNOs)* that convert nitrite to nitrate and ammonia-oxidizing organisms *(ANOs)* that convert free and saline ammonia to nitrite. ***Figure 4.25*** shows the free and saline ammonium in form of *N* in the wastewater treatment and the model that predicted the effluent of ammonium.

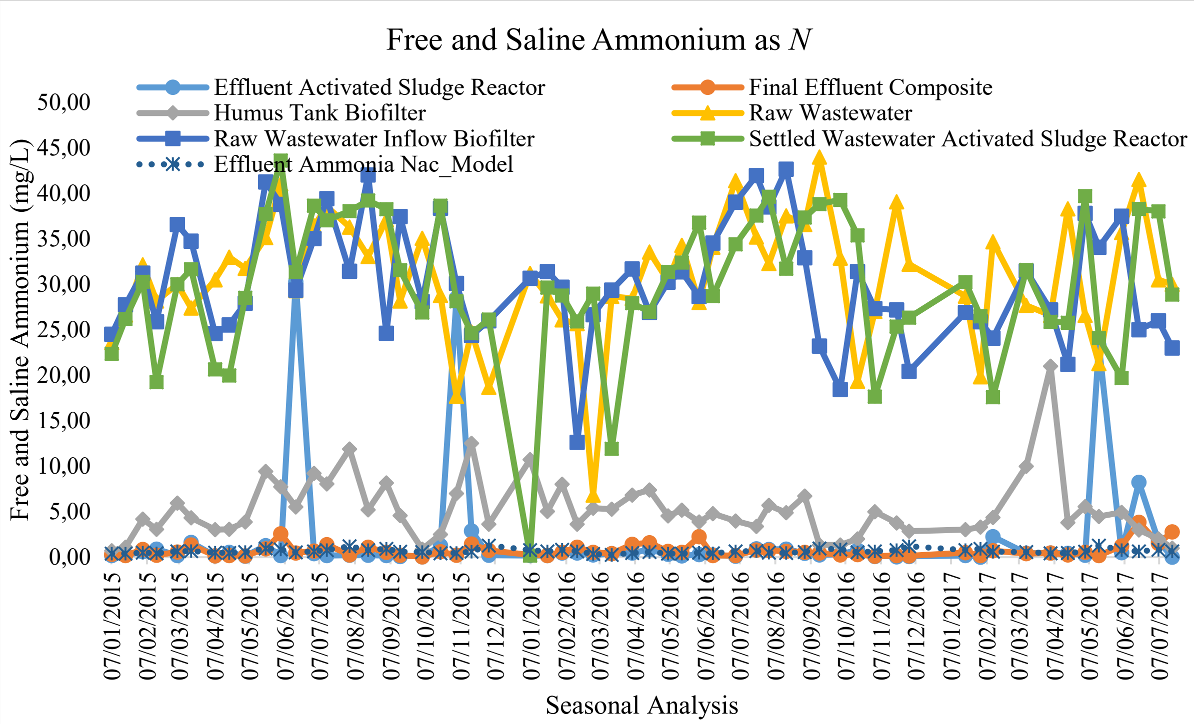


Figure 4.25: *Seasonal variation of the free and saline ammonium as N in the WWTP*

The free and saline ammonium as *N* content contains almost the same concentration from raw wastewater inflow biofilter, raw wastewater *BNR* to settled wastewater activated sludge reactor with a slight reduction in humus tank biofilter due to sludge production per mg *COD/L* organic load and lowest at the effluent activated sludge reactor. The lowest reduction in the effluent *N* of less than *1* was due to *WWTP's* efficiency. The effluent model was in correspondence with the analyzed effluent that was in compliance with the plant license *Appendix D*.

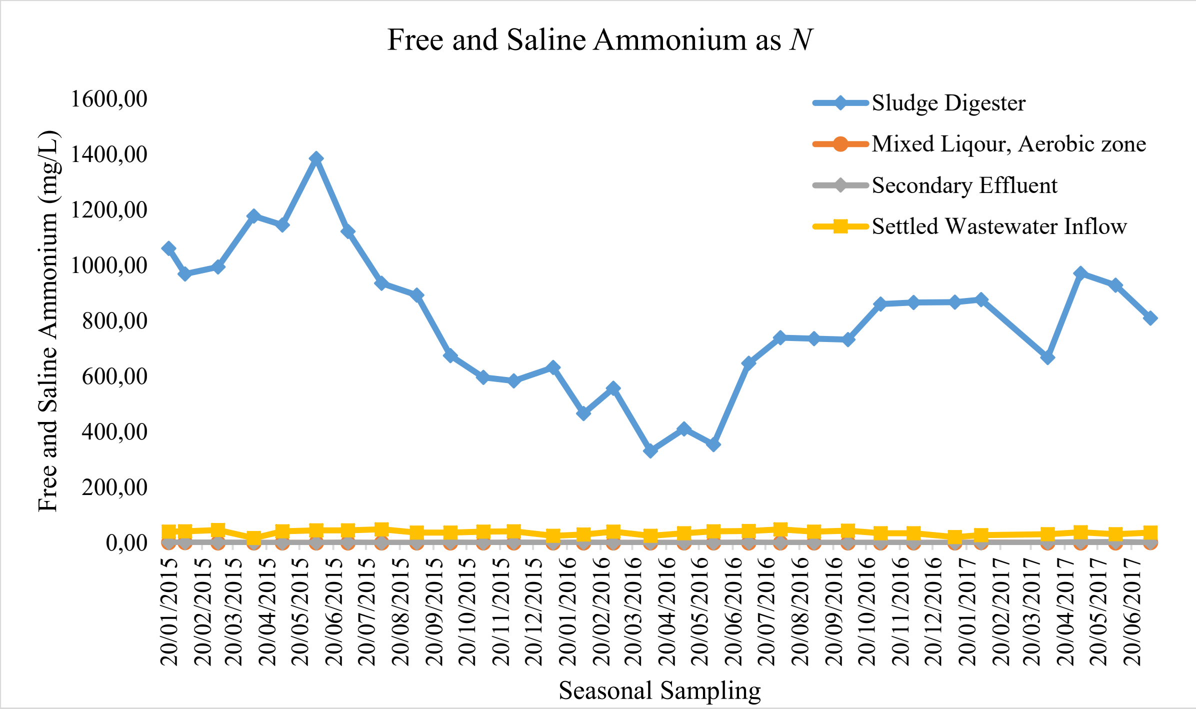


Figure 4.26: *Seasonal variation of the free and saline ammonium as N for the mixed liquor in the WWTP*

The free and saline ammonium was recorded highest in the sludge as the large portion of solids end up in the digester for stabilization or biogas digestion. Low free and saline ammonium was recorded in the mixed liquor aerobic zone, secondary effluent and settled wastewater inflow (***Figure 4.26***). Henze *et al.,* 2008 made an observation that the ammonia requirement for synthesis was, however, a negligible fraction of the total ammonia nitrified to nitrate by the nitrifiers at *1%*. The nitrifiers were said to utilize ammonia and nitrite principally for synthesis energy requirements *(catabolism)* but some ammonia used anabolically for the synthesis of cell mass nitrogen requirement. The temperature increased the maximum specific growth rate of the biomass and increase in half saturation coefficient that enhances the efficiency of the biological processes in *WWTP*. The adequate supply of dissolved oxygen enhanced nitrification. The kinetic b_{n20} rate was taken as a constant of *0.04/d* as it had not much effect. According to Henze *et al.,* 2008, the effect of temperature affects the b_{AT}, K_{nT} and μ_{AmT} constants, where they were calibrated as *0.04, 1.23* and *1.0* respectively. Sensitivity in temperature drop by *6°C* is said to reduce the values by μ_{AmT} half and that the minimum sludge age for nitrification doubles, this was not the case with our observation.

4.5.16 Effect of biological phosphorus removal

Phosphorus in *WWTPs* was presented predominantly in form of ortho-phosphate. Phosphorus is essential to the growth of algae, biological organisms and agricultural crops. Since of its nature not to have a gaseous form to be discharged into the atmosphere like nitrogen, phosphorus needed to be regulated due to the noxious algal blooms from the effluent discharge. Phosphorus has an influence on the treatment options for the wastewater. Since most of the nutrients are normally soluble, they cannot be removed by settling, flotation, filtration or other means of solids-liquid separation. Due to higher nitrates concentration or low concentration of volatile fatty acids *(VFAs),* the biological phosphorus removal *(BPR)* was enhanced. *BPR* was enhanced by anaerobic/aerobic zone, *i.e.* A/O^{TM} (Filipe, Meinhold, Jørgensen, Daigger & Grady, 2001; Mackenzie, 2011; Mamais & Jenkins, 1992). All the biological materials and some unbiodegradable organic compounds contains phosphorus *(P).* The volatile suspended solids *(VSS)* that accumulate in the biological reactor comprised of unbiodegradable particulate organics (X_I), active organisms (X_{BH}), and endogenous residue (X_{EH}). Phosphorous removal was assessed based on monthly average values with a target effluent of *1 mg/L* total phosphorus using a steady state model as in ***Figure 4.27*** and ***Figure 4.28***.

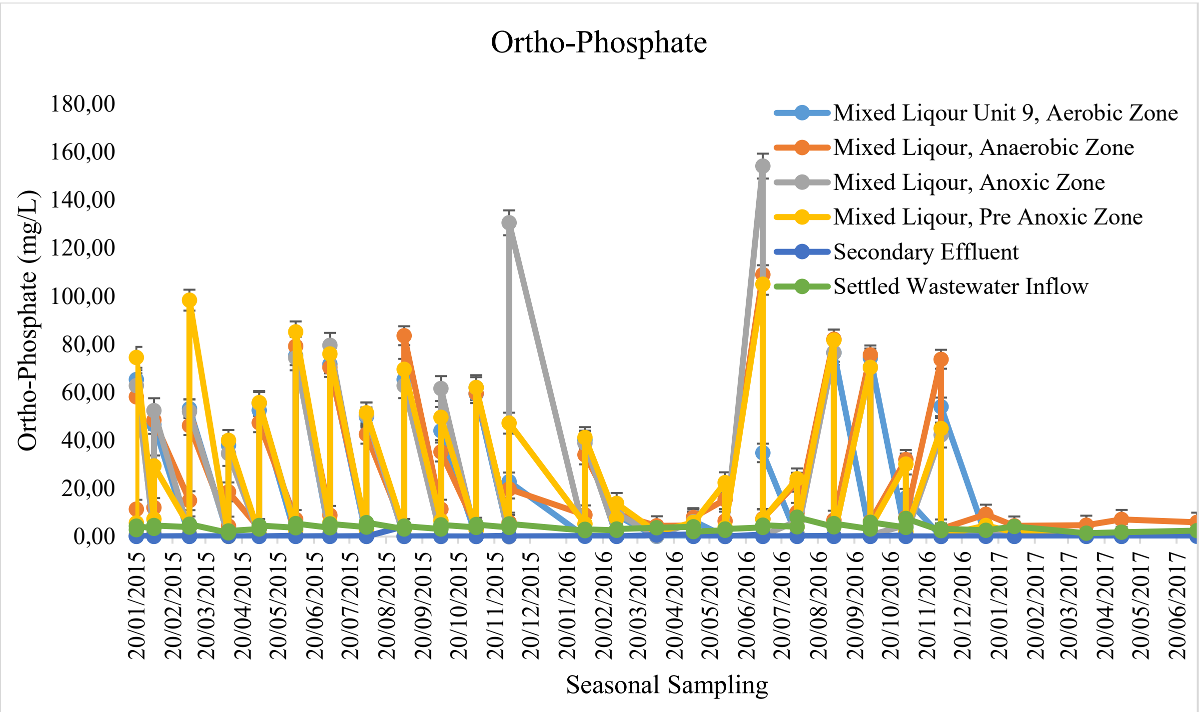


Figure 4.27: *Effect of phosphate in the biological in-between process units of the wastewater treatment plant*

There were high concentration levels of phosphorus reported in the mixed liquor; aerobic, anaerobic, pre-anoxic and anoxic zone in the activated sludge plant with average of *19.14, 25.35, 25.51, 19.14 mg/L* respectively with lower levels at the secondary effluent and settled wastewater inflows of average concentration of *0.26* and *3.38 mg/L* respectively. High phosphorus in the mixed liquor served as macro-nutrients to the microbes in the wastewater treatment process.

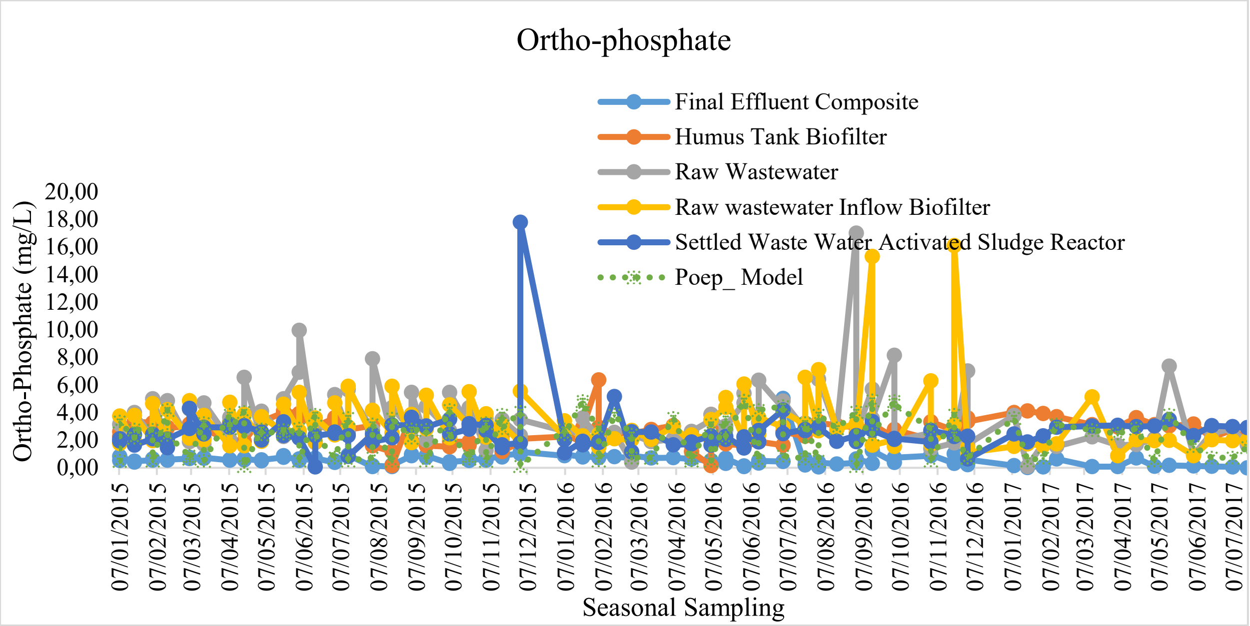


Figure 4.28: *Effect of phosphate inflow and outflow in the wastewater treatment plant*

The phosphate in the raw wastewater was observed to have a higher concentration of *3.46* and *3.26 mg/L* in the activated sludge plant and biofilm plant respectively. Lower concentrations were detected in the settled wastewater of activated sludge plant and in humus tank in the biofilm plant with an average of *2.58* and *2.66 mg/L* respectively. The high reduction in the final effluent of an average of *0.59 mg/L* was due to high efficiency of the *WWTP* in the phosphorus removal. The phosphorus requirements decrease as the sludge age increases because net sludge production decreases as sludge age increases. Sludge age of more than *10 days* enhanced removal of the *N* removal from the reactor to balance the *C/N ratio*. This attributed to net sludge production. For the phosphorus requirement in the sludge production, *P* was wholly aerobic system without biological excess *P* removed. Organic phosphorous models hydrolyze and particulate organic fraction directly to phosphates. According to Henze *et al.,* 2008 it was not possible to transform dissolved *ortho-P* to gaseous form so as to increase the *P* removal from the liquid phase because additional *ortho-P* needs to be incorporated into the sludge mass into two forms; biological and chemically. The demerits of the removal of *P* was noted as; increase in the sludge production due to the inorganic solids formed, increases in salinity of the treated wastewater and increase in the complexity and cost of the wastewater treatment plant (Henze *et al.,* 2008). Modelling of the chemical phosphorus precipitate anticipated a smooth curve that was directly proportional with the measured data of the final effluent. This could assist to estimate the performance of the *BPR* process and serve as an advisability of the chemical addition to augment the *BPR*. Due to large inorganic fraction in *bio-P* organism *(mainly internally stored polyphosphates), (f_v)* was low as *nil mg VSS.mg^{-1} TSS,* significantly smaller than f_v value of normal activated sludge ranging between *0.70* to *0.85 mg VSS.mg^{-1} TSS*. Excess *bio-P* was reported high at the excess sludge production.

4.5.17 Behavior of sulphates in wastewater treatment plant

The presence of sulphates in the wastewater treatment process did not have any major impact in the process as indicated in ***Figure 4.29***.

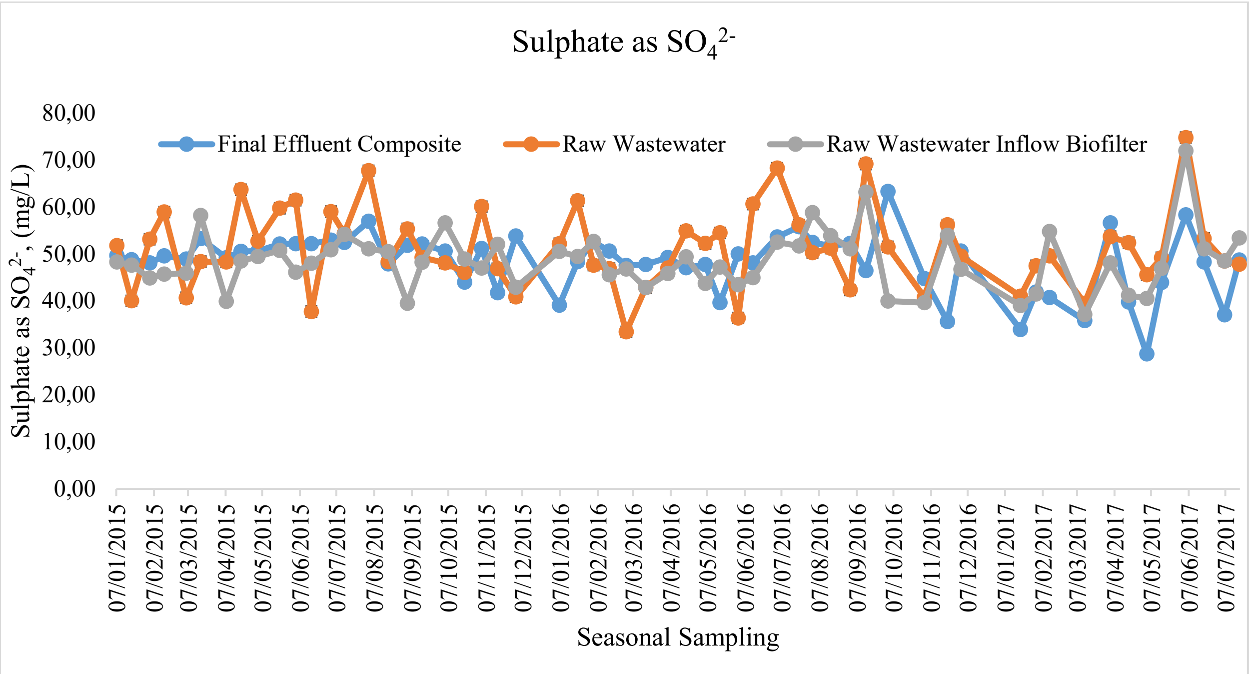


Figure 4.29: *Presence of sulphates in the wastewater treatment plant*

The low change in the deviation of seasonal analyzed sulphates in raw wastewater-*BNR* plant, raw wastewater inflow biofilters and final effluent composite with the concentration of *51.24, 48.47* and *48.22 mg/L* respectively was an indication of static change or nonbiological reaction of the sulphates in the biological wastewater treatment process.

4.5.18 Impact of chlorides in the disinfection of the wastewater

Chlorides are of concern in wastewater as they affect the final reuse of the effluent wastewater. Chlorides in wastewater originate from the source of influent in the region with high leaching of chloride containing coastal areas, geometers, saltwater intrusion and human excreta and nevertheless disinfection of the wastewater at tertiary process unit. Chlorine was used in disinfection of wastewater effluent because its performance of disinfectant was paramount and the factors that may have influenced the effectiveness of the chlorination process was of consideration to the potential impact of the discharge of disinfection by-products *(DBPs)* to the environment. ***Figure 4.30*** shows the concentration of chlorides in different process units in wastewater treatment plant.

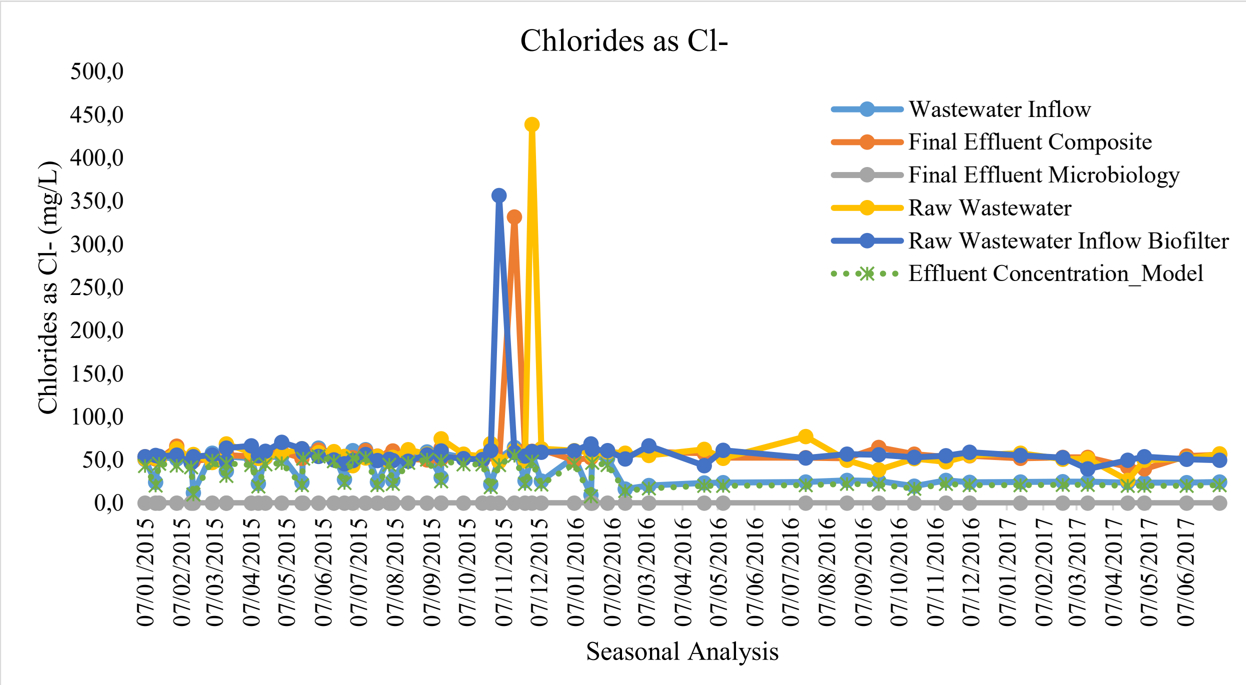


Figure 4.30: *Presence of chlorine in the wastewater treatment plant*

High chlorides were recorded in the raw wastewater inflows in the biofilm and activated sludge plant and final effluent composite. Lower chlorides were recorded in the final effluent. The spike in the summer time might have been due to the variation of the change in temperature and high flow rate with the higher concentration of chlorine during the season. The *DBPs* are of major concern to the environment because free chlorine has competing reactions such as the formation of chloramines *(free chlorine was moderately soluble in water, the solubility of about 1% at 10°C).* It reacts with organics constituents in *WWTP* to produce odour compound like carcinogenic and mutagenic. The unconfined rapidly reduction of liquid chlorine in the effluent after dosing was due to vaporization of gas at standard temperature and pressure with one litre of liquid yielding *450 L* of gas as described by Metcalf *et al.,* 2010. The chlorine added to the water was present as free chlorine, after satisfying any immediate and nitrogenous chlorine where some of the chlorine was used to satisfy the demand of the residual nitrite or/and ammonia. The wastewater and water bodies have been taken as disposal points for the chlorides, but chlorides are always removed using conventional methods. According to Mackenzie, 2011, chlorine reacts with natural organic matter *(NOM)* to form a number of carcinogenic byproducts that include but not limit to haloacetic acids *(HAAs),* trihalomethanes

(THMs), haloketones, haloacetonitriles, chloropicrin, chlorophenols, and cyanogen chloride (U.S. EPA, 1991; US, 1994). The model shown a smooth curve that was in correspondence with the measured data. The analyzed effluent data were in compliance with the license as shown in *Appendix D*.

4.5.19 Impact of food and microbial (f/m) ratio and the efficiency of nutrients removal

The ratio between food and microorganisms in wastewater had a significant influence on the selection and functioning of wastewater treatment processes. According to the analysis, activated sludge *WWTP (**Figure 4.31**)* recorded average of *3* that indicated higher oxidation while biofilm *WWTP (**Figure 4.32**)* indicated an average of *0.3* that indicated lower oxidation in the treatment. This was an indication of the rate of the *COD* applied per unit volume of mixed liquor. Lower *COD* requested for more return liquor in order that the biological denitrification functions fast and efficiently.

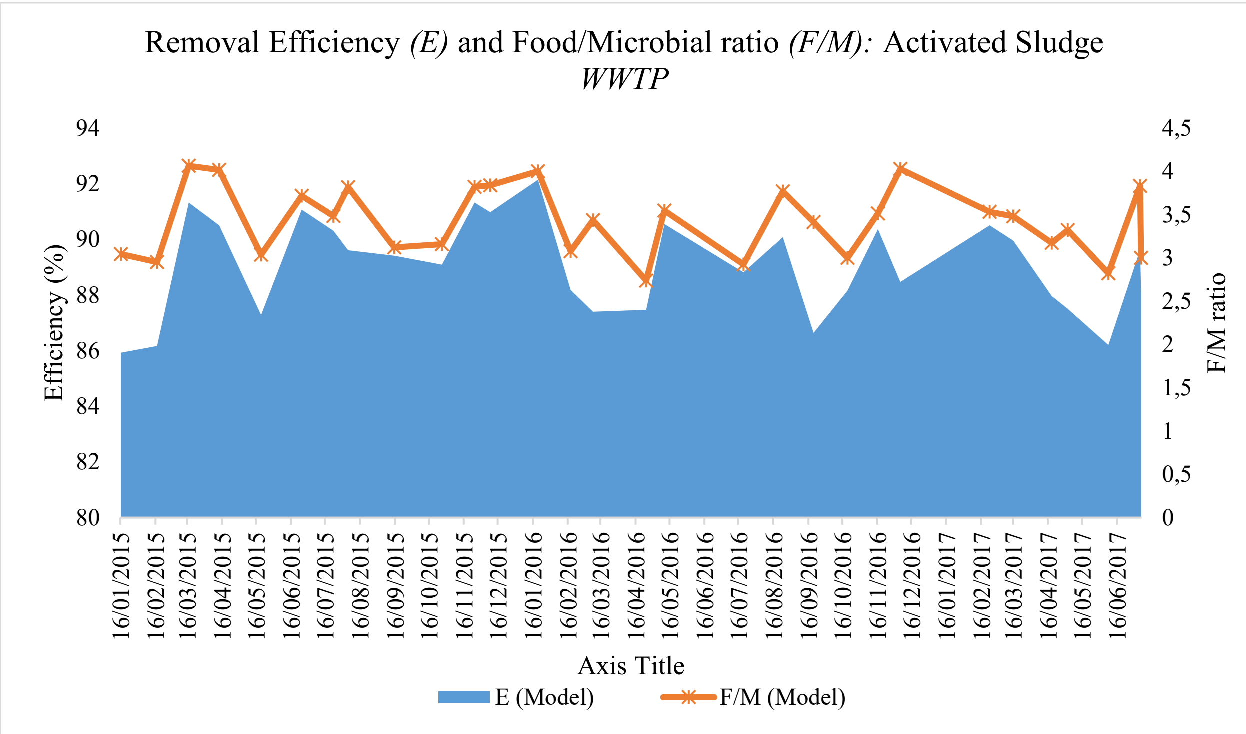


Figure 4.31: *Seasonal nutrient removal efficiency and the ratio of food to the microorganism of the activated sludge WWTP*

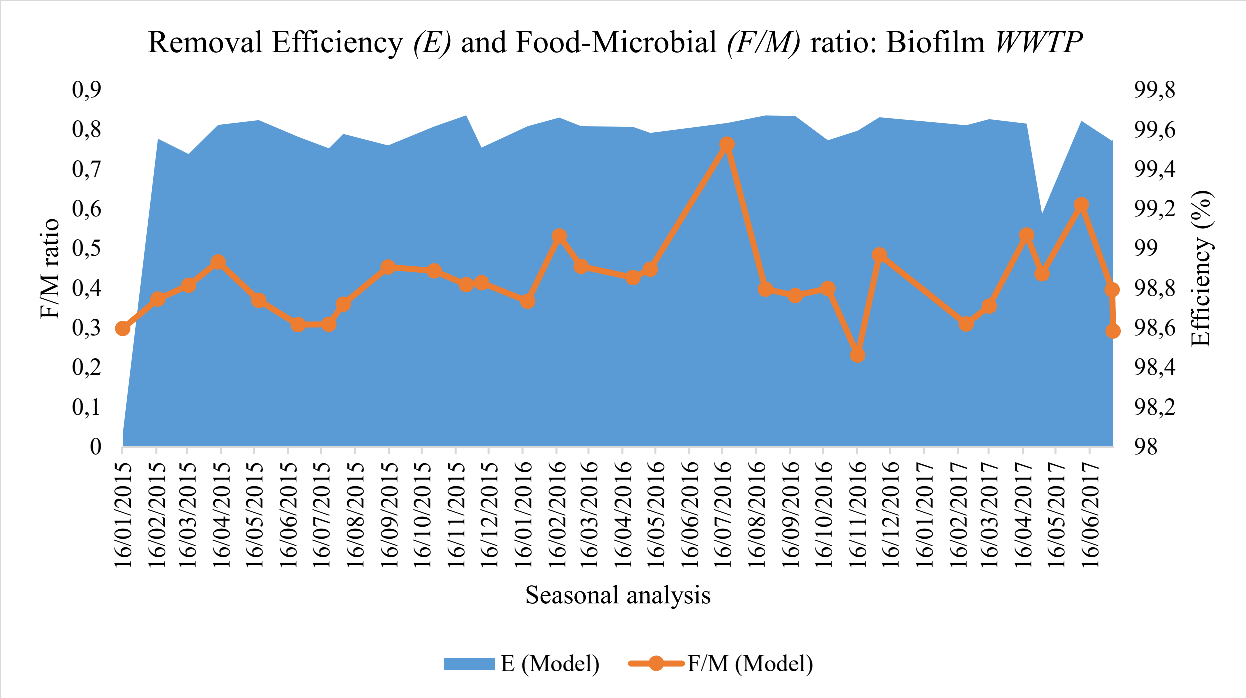


Figure 4.32: *Seasonal nutrient removal efficiency and the ratio of food to the microorganism of the biofilm WWTP*

The microorganism population shift was mainly cause by the wastewater characteristics and a shift in the influent. The *F/M* ratio was related to the system *SRT* by noting that the higher given substrate removal efficiency of *88.11-90.12* and *98.07-99.67* in the activated sludge and biofilm WWTP respectively. *F/M* ratio was useful to the understanding of the effect of transient loads on the system, i.e. the higher the *COD* loading rate, the faster is the substrate utilization rate and thus higher substrate concentration in the reactor for the wastewater treatment. The *F/M* assisted in fixing the sludge age by a means of simple control systems of the mass of sludge in the system by controlling the reactor mixed liquor volatile suspended solids *(MLVSS)* concentration at a specific value. The greater *COD* removal efficiency, the greater the difference between the parameter of settled and raw sewage. According to Henze *et al.,* 2008, the sludge age should replace *F/M* ratio as a control parameter, in particular, nitrification as it governs the mass of sludge to be wasted daily from the system. This keeps the *MLSS* concentration in the reactor at some specified value of the operation. To keep *F/M* within the desired limit, the reactor *COD* concentration and flow pattern needed to be measured regularly to determine the daily *COD* mass load. During the winter season, the sludge age and *F/M* ratio were lower due to decrease in temperature that lowers endogenous respiration rate. This kept the ammonia concentration low. From the observation, the data error was all below *7*. According to Rieger *et al.,* 2012, *ASM*-type models calibration and validation was within *2-7%*

of high-quality data, except at very low effluent concentrations where the acceptable margin was higher.

4.6 Conclusion

Wastewater treatment process can be considered as the largest industry in terms of waste management industries. The biological behaviour of biotechnological processes occurring in a bioreactor has a complexity unparalleled in the chemistry application principles. The complex systems, therefore, resulted in the involvement of the models based on the mathematical description of the process after the off-line sampling and analysis due to lack of the on-line sensor. The study applied practical knowledge of *IAWQ* Activated Sludge Model *No.1* and mass balance through a database that combines experience from expert knowledge and modelling experience. The basis for the development of reliable mathematical models was the thorough understanding of the involved process. Activated sludge systems were described by mathematical models based on mass balance equations that relate to change of the state variables of the system *(flow rates, concentration and composition)* due to transport and the transformation mechanisms. The authors combine the *ASM1* principles, substrate and microorganisms' kinetics in mass balance and thus resulting in a standardized methodology for expressing nomenclature that is useful for the *WWTP* modellers and other experts. This will enhance coding in the programming of the simulation software by eliminating error-prone part of the model implementation. The spreadsheet provided corrected matrices with all stoichiometric coefficient for the bio-kinetic models. The presence of emerging micro-pollutants *(methylparabens, ethylparabens, propylparabens)* and the inclusion of water chemistry indicated that the plant has the capability and is effective in removing the fate of micro-pollutants. *COD* mass balance made a lot of sense on the prediction of the experimental data that was reliable and accurate. Monitoring the reactor concentration and its changes at a fixed parameter created a long-term change in the loading rate on the *WWTP* and thus increase its efficiency. The structured framework of the models was useful among modellers, operators and management at the *WWTPs,* and other wastewater stakeholders. The models provided guidance in identifying the key design parameters and quantify system parameters that ensured optimal performance. The information provided an insight into the wastewater characteristic that included; biodegradability, flow distribution, contaminants and potential for the source control. These models provided the quantitative predictions of quality of effluent to be expected from a design of the existing *WWTP* and guidance to the direct attention needed in the system and control response. Use of the *ASM1* facilitated communication of the complex models and allowed the concentration of discussion on the bio-kinetics models. Mass balance was a powerful tool that allowed detection of inconsistencies within the *WWTP* data sets and assists to identify the systematic errors. The models were verified by conforming to internal mass balance and adequate validation against the experimental tests. The results contributed to the knowledge transfer on activated sludge and biofilm modelling.

CHAPTER 5:
TRACE METALS SPECIATION MODELLING IN THE WASTEWATER TREATMENT PROCESSES: GEOCHEMICAL MODELLING

5.1 Summary

The speciation of trace metals in the wastewater treatment plants *(WWTPs)* determines its ultimate fate in natural surface waters due to biological and chemical processes. The quantification of the trace metals speciation studies was undertaken in the influent and effluent of the *WWTP* and was of special concern due to their persistence and recalcitrance in the biosphere. The metals of interest included: *Al, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Ti* and *Zn.* Trace metals accumulated dependent and independent on metabolism; the biomass as well as in cellular products such as polysaccharides for metals removal were determined using geochemical modelling-mass balance. The mass balance model had a numerical cost optimization procedure that uses steady state together with a set of predefined constraints to evaluate operation points, plant dimensions and controller parameters. Mass balance model allowed detection of inconsistencies within the trace metals datasets and assisted in identifying the systematic errors in the metal reduction to quantify the overall removal and fate of these compounds in biological treatment plants. Mass balance comprising of seasonal programmable sampling showed a significant reduction in the number of trace metals. Removal of metals from biological treatment processes was mainly by complexation of the metals with microorganisms, precipitation and adsorption. The comparison of the available measured data indicated an increasing trend of high concentration in the sludge *(biomass)* that could be of danger to the human population, flora and fauna of the receiving water bodies. Geochemical modelling and computation of the speciation of the trace metals offer an extremely powerful tool for the process design, troubleshooting and optimization representing a multivariable system that cannot be effectively handled without appropriate modelling and computer-based techniques.

5.2 Introduction

The accelerating industrialization and urban activities in developing countries *(mining and commercial region)* introduces a significant amount of pollutants *(organics, inorganics, emerging contaminants, trace metals, etc.)* into the water systems, consequently ecological degradation, environmental and causing a high anthropogenic emission of the pollutants into the biosphere (Cheng, Grosse, Karrenbrock & Thoennessen, 2002; Kamika, Coetzee, Mamba, Msagati & Momba, 2014). In the recent years, trace metals production emission has decreased in many countries due to legislation, improved cleaning technology and altered industrial activities (Karvelas *et al.,* 2003). With the fourth industrial revolution *(FIR),* the exponentially increasing population push a need for controlling trace metals speciation into the environment in a more pronounced due to the high level of toxicity, bioaccumulation and wide range of source and persistence (Wang *et al.,* 2015). The xenobiotic of the trace metals allows them to accumulate in the environment (Burgess, Quarmby & Stephenson, 1999). To follow the fate of metallic species after that have intensified environmental pollution and deteriorate the ecosystems, with the accumulation of pollutants that has become persistence and recalcitrance in the biosphere (Veglio & Beolchini, 1997; Volesky, 2001). This results in health problems that demonstrate themselves on the acute as well as chronic levels that reflected in the society's spiraling health care cost (Volesky, 2001). The hazardous of trace metals pollution of wastewater to the environment is well explained by Fu and Wang *(2011)* (Fu & Wang, 2011). Growing attention has been given to the potential health hazard presented by the trace metals to the environment. Another emerging technological advancement *(nanotechnology)* with a sparkling bright future has nanoparticles entering water streams and wastewater treatment process (Shamuyarira & Gumbo, 2014). Mining industries and industrial activities have been considered as major sources of trace metals contaminants. The trace metals can be precipitated, dissolved, co-precipitated with metal oxides, adsorbed or involve in microbial metabolism. Trace metals can be found in form of hydroxides, oxides, sulphide, silicates, sulphates, organic binding forming complexes with humic compounds and complex sugar (Gawdzik & Gawdzik, 2012). To eliminate the environmental hazards associated with the trace metals wastewater steams should be treated using a robust technique (Singanan & Peters, 2013). The current economic, technical, effective conventional treatment technologies processes for the removal of the trace metals include: membrane technology, flotation, oxidation, electrodialysis, photocatalysis, coagulation-flocculation, ion-exchange, electrochemical, adsorption, chemical precipitation and biological process-microbial biomass *(biosorption)* based on trace metals binding capacities of various biological matters *(where bacteria, algae, yeast and fungi has proved to be potential metal sorbents)* (Barakat, 2011; Davis, Volesky & Mucci, 2003; Fu & Wang, 2011; Mohan & Pittman Jr, 2007; Sheoran & Sheoran, 2006; Veglio & Beolchini, 1997). The life cycle assessment *(LCA)* is put in place to analyze the environmental impact of different technologies for the wastewater treatment in the populations. Gallego, Hospido, Moreira &

Feijoo, 2008 describe *LCA* as an environmental tool that allows the calculation of all the environmental loads related to a service/process/product. It is thus important to treat trace metals contaminated wastewater prior to its discharge to the environment.

Besides the hazard posed by the high-level concentration of trace metals, WWTPs contain also necessary nutrients for the cell growth in microbiology within the concentration threshold (Karlsson *et al.,* 2012; Matheri, Mbohwa, Belaid, Seodigeng & Ngila, 2016; Schattauer, Abdoun, Weiland, Plöchl & Heiermann, 2011; L. Zhang, Ouyang & Lia, 2012). Many of the trace metals are important micro-nutrients and acts as microbial agents *(enzyme and co-enzyme)* however, an excessive amount may result in toxicity or inhibition (Bożym, Florczak, Zdanowska, Wojdalski & Klimkiewicz, 2015; Edokpayi, Odiyo, Popoola & Msagati, 2016; Schattauer *et al.,* 2011). Trace metals are adsorbed to the surface of negatively charged bacteria fibrils that extend into bulk solution from cells membrane through cell walls. The fibrils are negatively charged by the ionization from key functional groups such as hydroxyl-*OH* and *COOH*. Once adsorbed, trace metals are absorbed by bacterial cells. The inside cells trace metals attack enzyme systems. Trace metals toxicity is believed to occur through the structure disruption of the enzymes and proteins molecules with the cells. Zhang *et al.,* 2012 reported that selected trace metals are limiting factor when included in co-enzymes, where the cells' synthesis is seriously affected by the deficiency, or cell become more sensitive to inhibitory substances. Meanwhile, the trace metals are valuable resources that should be recovered as much as possible from the waste (Wang, Lu & Li, 2016). The maximum acceptance concentrations are regulated by the wastewater treatment plant license compliance, World Health Organization *(WHO),* US. Environmental Protection Agency *(EPA),* Agency for Toxic Substances and Diseases Registry *(ATSDR)* among others (Abdel-Shafy & Mansour, 2014; Department of Water and Sanitation, [Accessed June 2016]; Raval, Shah & Shah, 2016).

5.3 Geochemical Modelling

Modelling the fate of transport and occurrence of the micro-pollutants *(i.e. trace metal)* through the wastewater treatment plants is of the present concern (Pomiès, Choubert, Wisniewski & Coquery, 2013). Geochemical modelling and computation of the speciation of the trace metals offer an extremely powerful tool for the process design, troubleshooting and optimization representing a multivariable system cannot be effectively handled without appropriate modelling and computer-based techniques (Volesky, 2001). The modelling assumes basic mass balance principles *(model-based predictive)* and simple reaction kinetics (Srivastava & Majumder, 2008). The mass balance has a numerical cost optimization procedure that uses steady state or dynamic state together with a set of predefined constraints to evaluate operation points, plant dimensions and controller parameters. The constraints are selected to ensure that process variable and some controllability measures lie within specified bounds (Vega, Alawneh, Gonzalez, Francisco & Perez). The mass balance is valuable tools for investigating the general performance of the wastewater treatment plants and an effective method to assess the reliability of the available data (Gans, Mobini & Zhang). According to Sötemann, Wentzel & Ekama, 2006, the primary purpose of the steady-state model is to determine the fate of transport of trace metals, organic, organic and emerging contaminants, reactor volume, sludge age, oxygen demand or gas production of the main biological process units in *WWTP.* Once the parameters are determined, the individual process units can be modelled with the simulation models to check their load response, cyclic flow and performance. The step for modelling consists of the definition of the objectives, collection of the plant routine data and model selection, data quality control, evaluation of the model structure and experimental design, data collection for simulation study, and lastly calibration and validation (Langergraber *et al.,* 2004b).

The objective of the study was to predict the occurrence, fate and transport of the speciation trace metals in the wastewater treatment plant by carrying out a geochemical modelling using a mass balance.

5.4 Material and Methods

Sampling was undertaken from the inflow and outflow of the Daspoort wastewater treatment plant, Gauteng Province, South Africa. The sampling points were division box, primary clarifier *(settler),* biological nutrients removal *(BNR)* for activated sludge *WWTP* or trickling filter for the biofilm *WWTP,* humus tank, and chlorine contact dam *(CCT).* The samples were collected in *500 mL* plastic containers with no headspace volume to minimise aerobic biodegradation of organics substrates. They were marked with the indication of time, date and location of collection. Aliquots for trace metals analysis were acidified to a *pH* of about *2* with nitric acid *(16 M)* and stored in the dark at *4°C*. This was to protect trace metals from precipitation and sorption losses to the container walls (Mackenzie, 2011; Metcalf *et al.,* 2010).

5.4.1 Analytical methods for trace metals

Sample preparation methods for trace metals analysis involved using nitric acid *(12 mL)* and hydrogen peroxide *(4 mL)* for digestion of the sample *(10 mL)* by hot plate digestion at *120°C* for *2 hours*. Deionized water was added to dilute the sample and make *100 mL* after digestion. The sample was then filtered using cellulose acetate membrane filter *(0.22 µm)*. The classes of metals were: suspended metals, metals present in unacidified samples that are retained on the *0.45 µm* membrane filter; dissolved metals, present in unacidified samples that pass through a *0.45 µm* membrane filter; total metals, the total of the dissolved and suspended metals or the concentration of metals determined on an unfiltered sample after digestion, and lastly acid extractable metals, metals in solution after an unfiltered sample is treated with a hot dilute mineral acids according to the standard method (Beamish, 2012; Biller & Bruland, 2012). Calibration standards were prepared using multi-element calibration solutions prepared using-*100 mg/L* nitric acid and deionized water. The sample was then analysed using inductively coupled plasma optical emission *spectrometry (ICP-OES-model ICAP 6500 Duo) – (165 Spectro Arcos equipped with autosampler (Cetac ASX-520)* technique. The parameters for operating the *ICP-OES* was set as follows: instrument power *1400 W,* the flow rate of the auxiliary argon *2 L/min,* argon gas flow rate *13 L/min,* the flow rate of the argon nebuliser *0.95 L/min* and *iTEVA* software was used. Based on the optical metals wavelength *(lower determination 166.250 nm and extending to 847.000 nm),* the most prominent analytical lines were chosen as follows*: Al-396.152 nm, Cd-228.616.502 nm, Co-228.616 nm, Cr-283.565 nm, Cu-324.754 nm, Fe-259.933 nm, Mn-257.610 nm, Ni-221.647 nm, Pb-220.353 nm, Ti-334.941 nm and Zn-213.856 nm.* Dilution factor was applied to the concentration data. The trace metal of interest included: *Al, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Ti and Zn* (Dimpe *et al.,* 2014; Scientific, 2009; Scientific., 2009; Wiel, 2003). Calculation of the concentration of the elements in the aqueous sample and in the digested solid sample is shown in Equation 5.1 and Equation 5.2 respectively (Wiel, 2003).

$$C = (C_1 - C_o) f_d f_a \quad \text{Eq. 5.1}$$

$$w = (C_1 - C) f_a V / M \quad \text{Eq. 5.2}$$

Where: C = concentration of the elements in the aqueous sample in *mg/L*, C_1 = concentration of the elements in the test sample in *mg/L*, C_0 = concentration of the elements in the blank sample in *mg/L*, f_d = dilution factor due to digestion of an aqueous sample; in all other cases $f_d = 1$, f_a = dilution factor of the test portion, w = mass fraction of the elements in the solid sample in *mg/kg*, V = volume of the test sample *(digest)* in litres and M = mass of the digested sample in *grams (g)*.

5.5 Results and Discussion

5.5.1 Trace metals mass balance

The mass balance modelling of the trace metals was based on wastewater monitoring data *(measured data)* and theoretical data. Geochemical modelling of mass transport in fluid systems was mostly based on the chemical kinetics controlled only by basic/acid properties of the exposed cell wall surface as described by Mullen *et al. (*1989) and Fein, Daughney, Yee & Davis, 1997. Trace metals accumulated dependent and independent on metabolism; both living and dead biomass as well in cellular products such as polysaccharides for metal removal was determined using a mass balance of the completely mixed reactor as:

$$\frac{dC}{dt}V = QC_O - QC + r_C V \qquad \text{Eq. 5.3}$$

Assuming first order removal kinetics ($r_C = -kC$), where:

$$\frac{dC}{dt} = C' \qquad \text{Eq. 5.4}$$

$$ß = k + \frac{Q}{V} \qquad \text{Eq. 5.5}$$

Substituting and integrating gave:

$$C = \frac{Q}{V}\frac{C_O}{ß} + Ke^{-ßt} \qquad \text{Eq. 5.6}$$

But when $t = 0$, $C = C_o$ and K was equal to:

$$K = C_o - \frac{Q}{V}\frac{C_O}{ß} \qquad \text{Eq. 5.7}$$

Substituting the K to the expression at non-steady state solution gave Eq. 5.8.

$$C = \frac{Q}{V}\frac{C_O}{ß}\left(1 - e^{-ßt}\right) + C_o e^{-ßt} \qquad \text{Eq. 5.8}$$

At the steady state conditions when the rate of the accumulation was equal to zero *(dC/dt=0)* was given by:

$$C = \frac{C_O}{1 + k(\frac{V}{Q})} = \frac{C_O}{1 + k\tau} \quad \text{Eq. 5.9}$$

The complete mixed reactor in series at a steady state was presented as:

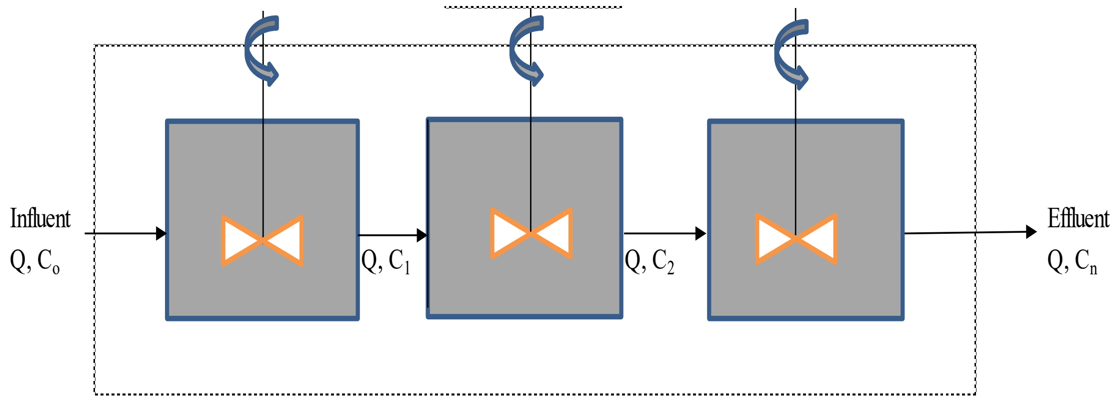


Figure 5.1: *Completely mixed reactor in series in the WWTP*

General mass balance:

$$\frac{dC_2}{dt}\frac{V}{2} = 0 = QC_1 - QC_2 + r_v\frac{V}{2} \quad \text{Eq. 5.10}$$

Assuming first order removal kinetics $r_C = -kC_2$, C_2 yielded:

$$C_2 = \frac{C_1}{1 + k(\frac{V}{2Q})} = \frac{C_1}{1 + k\frac{\tau}{2}} \quad \text{Eq. 5.11}$$

But from *Co,* the value of the C_1 was equal to:

$$C_2 = \frac{C_0}{1 + k(\frac{V}{2Q})} = \frac{C_0}{1 + k\frac{\tau}{2}} \quad \text{Eq. 5.12}$$

Combining the above expression yielded:

$$C_2 = \frac{C_0}{[1 + k(\frac{V}{2Q})]^2} = \frac{C_0}{[1 + k\frac{\tau}{2}]^2} \quad \text{Eq. 5.13}$$

The n^{th} reactor in series was represented by the corresponding expression:

$$C_n = \frac{C_0}{[1 + k(\frac{V}{nQ})]^n} = \frac{C_0}{[1 + k\frac{\tau}{2}]^n} \quad \text{Eq. 5.14}$$

Where: C = final Concentration *(mg/L), Co* = Initial Concentration *(mg/L), Q* = hydraulic flow rate *(m^3/d), V*= reactor volume *(m^3), r_c* = rate of the reaction and k = rate of kinetic *(/d)*.

The mass balance model was developed in *Microsoft Excel 2016* and the workbook consisted of several spreadsheets based on the datasets that assisted into identifying the systematic errors in the trace metal reduction and to quantify the overall removal and fate of these compounds in biological treatment plants.

5.5.2 Speciation of the trace metals

The sources of trace metals included the discharge from the industrial activities, products, products used in the residential applications such as personal care products and cleaning agents, groundwater infiltration and commercial discharge. The concentration of trace metals in wastewater varied with time. Daily, weekly and monthly variations concentration was observed as a function of industrial production patterns. The variation was important in the operation, control and redesign of the treatment plant. The trace metals diurnal patterns are indicated in ***Figure 5.2*** and ***Figure 5.3***.

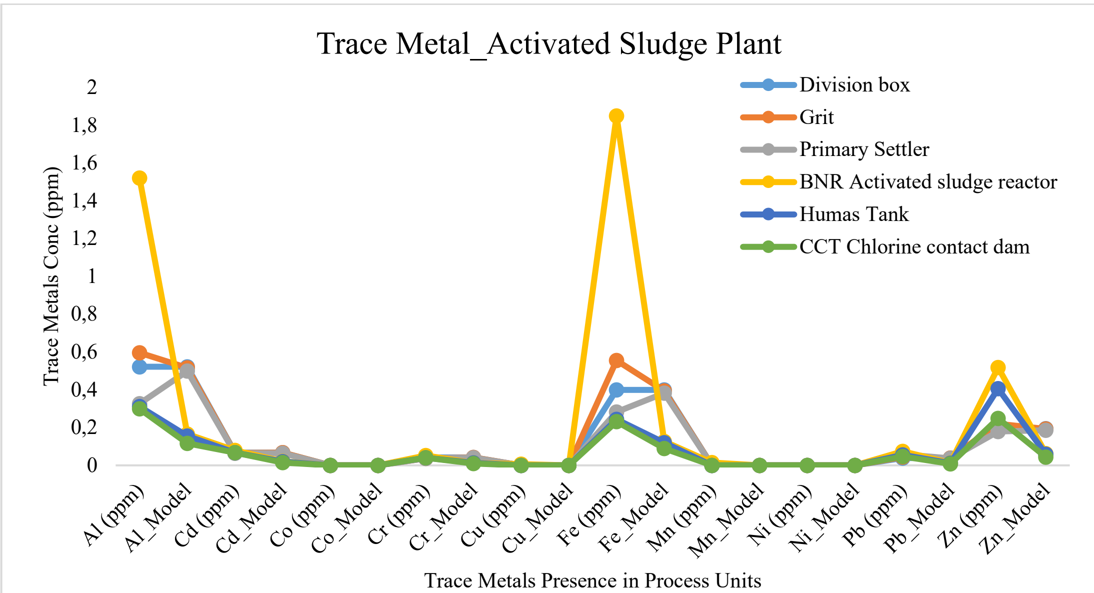


Figure 5.2: *Speciation of the trace metals in the activated sludge plant*

High concentration of *Al*, *Fe* and *Zn* was observed in the all the process units. The highest concentration of *Al* was observed in the biological nutrient removal *(BNR)* unit due to the recycling of the sludge that maintains the concentration followed by the influent in the primary pretreatment units.

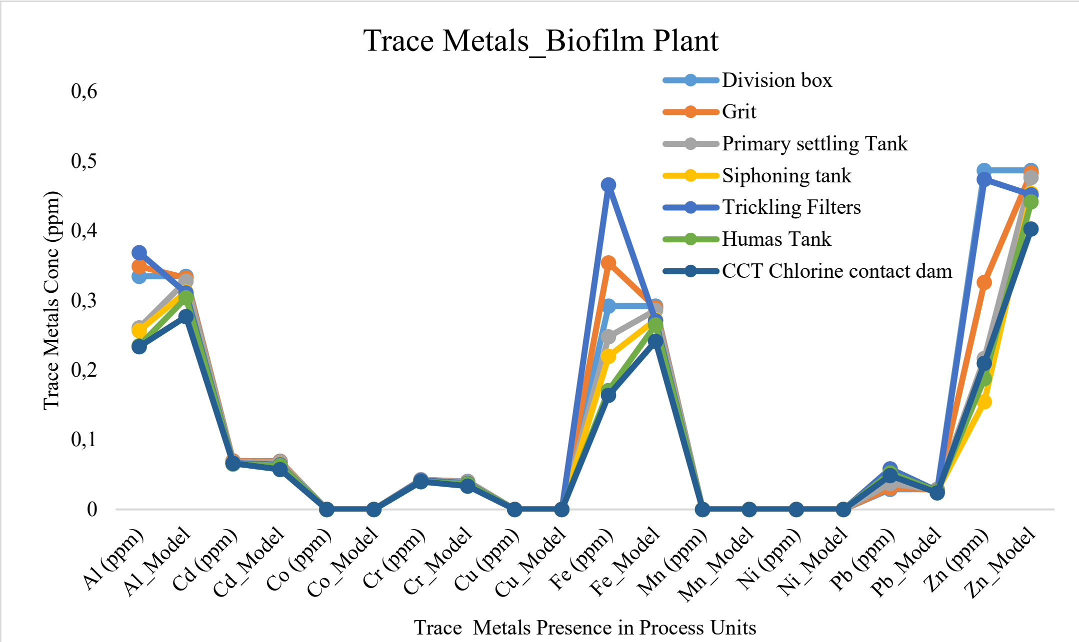


Figure 5.3: *Speciation of the trace metals in the biofilm plant*

High *Al*, *Fe* and *Zn* concentration was observed in the all the process units in the biofilm *WWTP.* The highest concentration of the trace metals, in general, was observed in the primary pretreatment unit due to the high concentration of the trace metals in the influent. The *Zn* was in dominance followed by *Fe* and *Al.* All the other trace metals contributed to metabolism and growth of micro-organism while other were accumulated either with the microbes and sludge discharge. According to Metcalf *et al.,* 2010, trace metals *(micro)* of importance in the biological wastewater treatment, reuse and disposal of biosolids included: irons, copper, lead, manganese, molybdenum, nickel, selenium, vanadium, zinc, Aluminium, zinc, cobalt, chromium. The macro metals that were of importance to the metabolism and in the biological wastewater treatment included; calcium, sodium, iron, potassium and magnesium. Removal of metals from biological treatment processes was mainly by complexation of the metals with microorganisms, precipitation and adsorption. The raw wastewater inflow in the biofilters and activated sludge *WWTP* shows variation in a dominance of *Fe* and *Al* respectively as shown in ***Figure 5.4*** and ***Figure 5.5*** with raw wastewater inflow dominating with respective effluent. The mass balance models showed smooth curve that was consistency with the overall analysis.

Mass balance model allowed detection of inconsistencies within the trace metals datasets and assisted in identifying the systematic errors in the metal reduction.

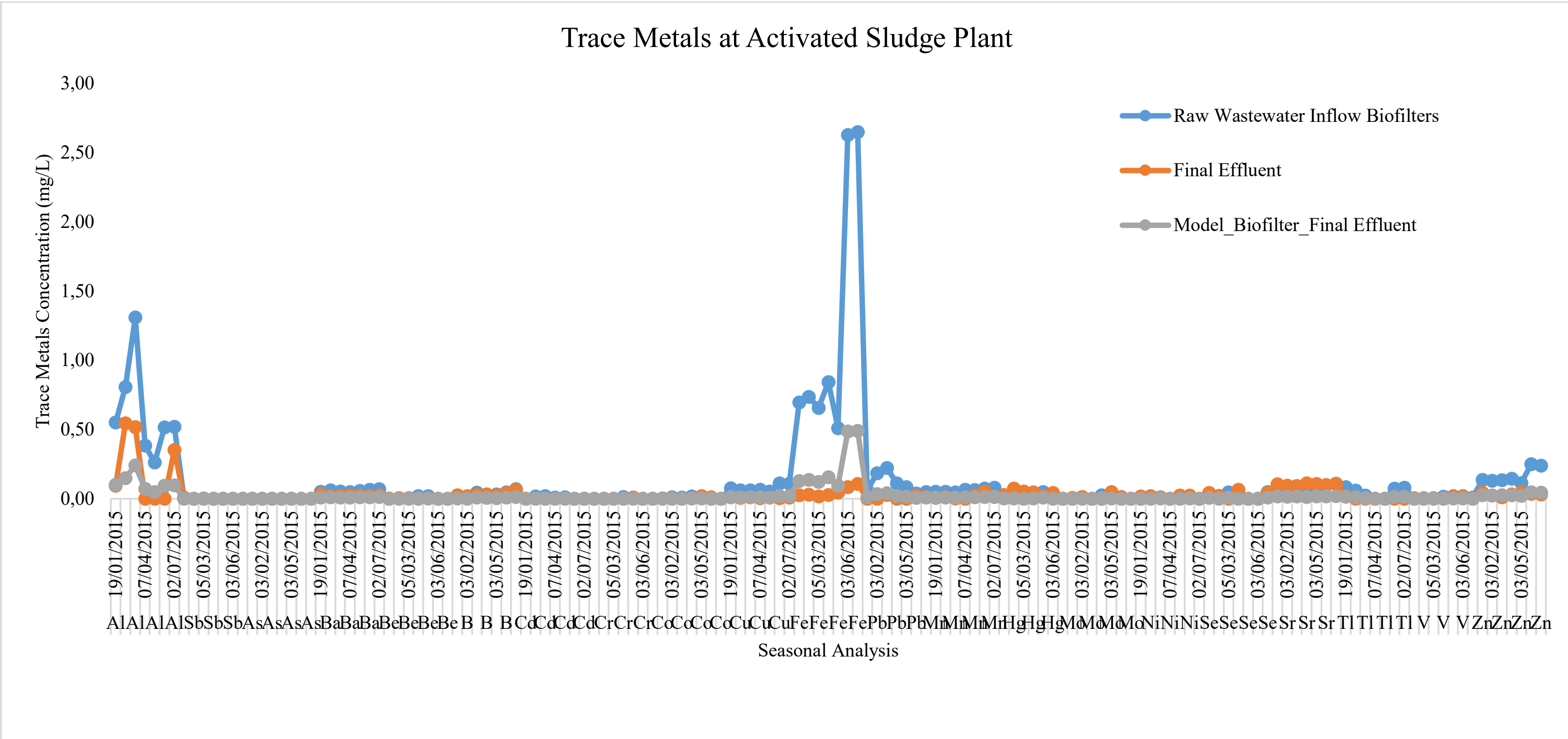


Figure 5.4: *Daily variation of trace metals contents in the influence of the biofilm wastewater treatment plants*

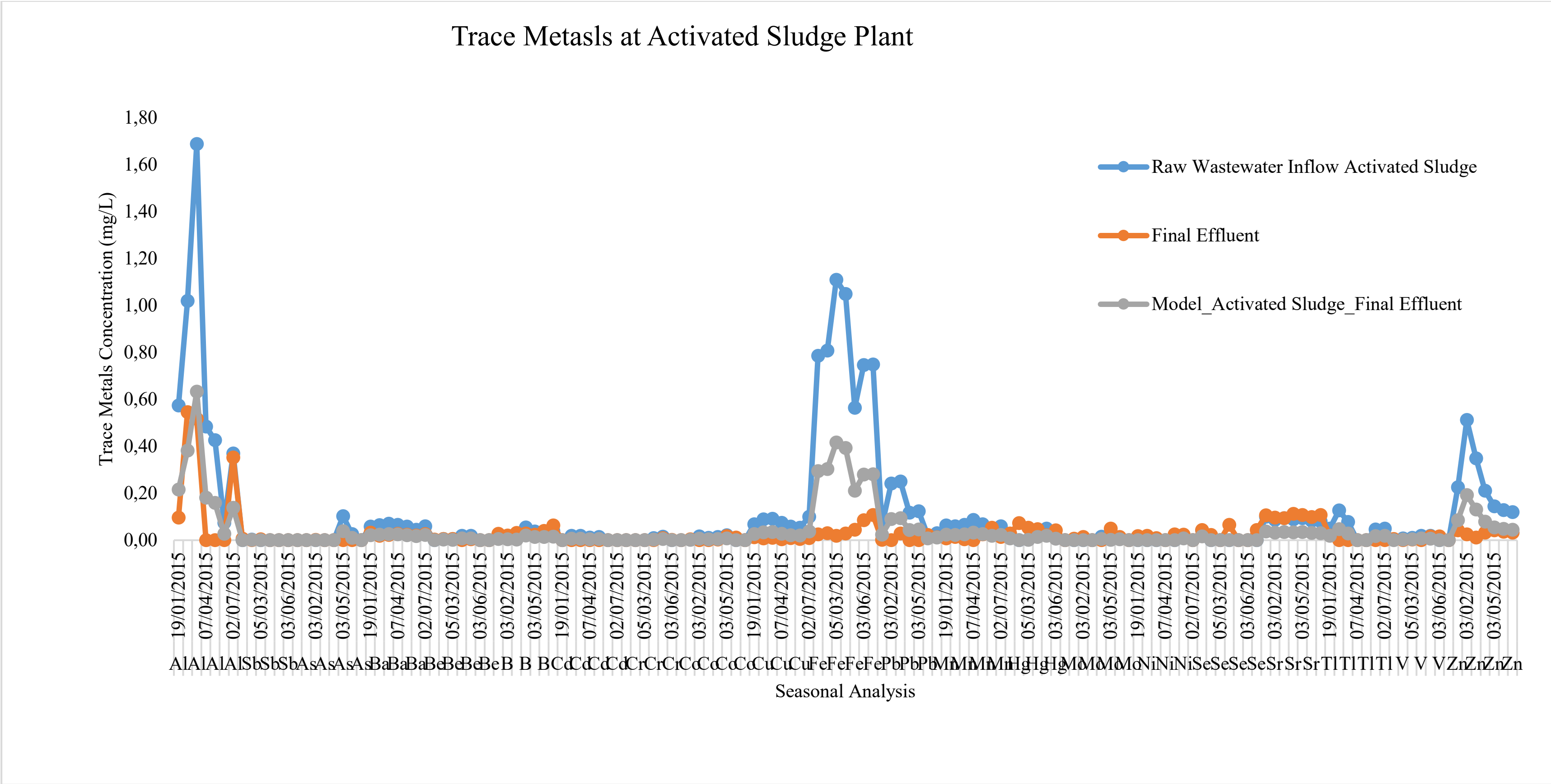


Figure 5.5: *Daily variation of trace metals contents in the influence of the activated sludge wastewater treatment plants*

All the treatment plants showed a distinctly marked profile with a high concentration of trace metals independence of the high load. The trace metals in the wastewater could influence the possibilities for reuse of the wastewater treatment sludge to the agriculture sector by providing the nutrients to the soil. Trace metals in wastewater have a benefactor in metabolism, the growth of biological life and absence of sufficient quantities that lead to micro-pollution, toxicity and limit the growth of algae. According to Metcalf *et al.,* 2010, microbes combine with metals ions and negatively discharge to the surface. The precipitation works under addition of chlorides for the formation of metal sulfides in anaerobic digestion. Trace metals are said to be complexed by carboxyl group found in microbial polysaccharides and other polymers or absorbed by protein materials in the biological cells (Metcalf *et al.,* 2010). According to Mullen *et al.* (1989) and Ahluwalia & Goyal (2007) Freundlich isotherm models, the removal of metals in biological processes were found to fit into the adsorption characteristics. All the trace metals were below the threshold *20 mg/L* and compiled with the wastewater treatment plant license and international standards *(see Appendix D)* (Abdel-Shafy & Mansour, 2014; Department of Water and Sanitation, [Accessed June 2016]; Mackenzie, 2011; Raval *et al.,* 2016). According to Pomiès *et al. (2013)*, the removal efficiency depends on physio-chemical of the trace metals, *WWTP* operating conditions *(parameters),* hydraulic retention time *(HRT),* sludge retention time *(SRT)* and temperature. Another study by Luo *et al.,* 2014 suggested regardless of the technology employed, the trace metal removal depends on physio-chemical properties of the micropollutants and the treatment conditions, and it is essential for the effectively predicting of the impact on the receiving environment.

5.6 Conclusion

The effective operation of wastewater treatment plants played an important role in minimalizing the release of trace metals into the aquatic environment. The predicted fate of transport of the trace metals in the wastewater treatment plant was modelled using mass balance concept. This show a speciation of the trace metals in multiple units associated with water, air, microbes, biosolids and biomass, with biological treatment systems with the quantitative dependent upon physical-chemical and biological properties. Using the mass balance model made the integrated design process friendly and easier especially in data-entry and making results of the analysis process easy and understandable. The mass balance showed removal performance and treatment efficiency of the wastewater treatment plant.

CHAPTER 6:
AI-BASED BASED PREDICTION MODEL FOR TRACE METALS AND COD IN THE WASTEWATER TREATMENT USING ARTIFICIAL NEURAL NETWORKS

6.1 Summary

Artificial intelligence *(AI)* applications are finding their ways into the mainstream lifestyles in our day to day operations. Novel *AI* application techniques such as the artificial neural network *(ANN),* expert systems *(ES),* fuzzy logic *(FL)* and genetic algorithms *(GA)* have gain popularity and space program in the fourth industrial revolution *(FIR).* The goal of the wastewater treatment process is the reduction of the level of pollutants prior to discharge to the environment. The interrelationship between *COD* and *pH* was studied using *AI*-based prediction model *(data-driven modelling)* with *ANNs (universal approximators)* incorporated in *MATLAB (neural network toolbox).* Supervised learning algorithm was adopted for training the *ANNs* and to relate input data to output data. The appropriate architecture of the *ANNs* was determined using several steps of training and testing of the models. The training aimed at estimating, validating, predicting the parameters by an error function minimization. The *ANN* model provided accurate predictions of the effluent stream, in terms of *COD* and trace metals speciation. The goodness of the prediction *(prediction performance)* was attained with the coefficient of determination *(R^2)* of 0.98-0.99, sum of square error *(SSE) 0.00029-0.1598,* room mean-square error *(RMSE) of 0.0049-0.8673,* mean squared error *(MSE) 2.7059e-14 to 2.3175e-15.* The *ANN*-based models were found to be a robust tool for predicting *WWTP* performance. This revealed that the influent indices could be applied to the prediction of the effluent quality *(EQ).* The approach can also be used to handle many other types of waste treatment plants, environmental management, and emerging technologies so as to meet the cost-effectiveness, environmental, technical criteria and wide range of big data support in the implementation of the sustainable development goals *(SDGs).*

6.2 Introduction

The increasing rhythm of urbanization, industrialization, and population increase has created uncertainty on the environmental problems with the uncertainty of knowledge and multiplicity of scales in the *FIR* (Poch, Comas, Rodríguez, Sanchez & Cortés, 2004). Improper maintenance of wastewater treatment plant (*WWTP),* the wide range of operating conditions, can trigger serious public health problem and ecological that affects the flora and fauna (Manu & Thalla, 2017). Due to complex interactions between biological reaction mechanisms, physical, chemical reaction, kinetics, catalysis, separation, transport phenomena, emerging micropollutants, multi-variables aspects of the wastewater treatment process*,* highly non-linear, highly time-varying, the diagnosis of the *WWTP* practice, heterogeneity, incompleteness, and imprecision of the *WWTP's* data, *etc.* makes *WWTP* to have a unique characteristic as compared to other environmental and biotechnological industrial processes (Hong, Rosen & Bhamidimarri, 2003; Poch *et al.,* 2004; Zeng *et al.,* 2003). The biological *WWTP* often receive variation in raw wastewater composition that can pose substantial quality environmental imbalance and a high cost of operation if not well control and predicted, strength and flow rates because of the complex nature of the treatment process (Belanche, Valdés, Comas, Roda & Poch, 1999; Nasr, Moustafa, Seif & El Kobrosy, 2012; Qing, Wang & Meng, 2005). Missing data *(datasets)* due to error handling systems, has been reported to affect the learning and classification accuracies in data analysis, prediction and modelling (Duma, Marwala, Twala & Nelwamondo, 2013). The successful management of these systems requires multidisciplinary approaches from different engineering, big data, *AI,* machine learning *(ML),* deep learning *(DL),* data science, data mining, advanced analytics, automation, blockchain technology, biotechnology, microbiology, data streaming, social science and other scientific fields. *AI* techniques *(data-driven modeling)* have been used in different sectors such as engineering, marine, economics, meteorological, remote sensing, medicine, military, *etc.* to prediction, forecasting, optimization, modeling, identification, and control of complex systems in the quest of implementing and achieving the sustainable development goals (Mellit & Kalogirou, 2008).

The application of the artificial intelligence using multi-dimensional process datasets, visualization techniques can be applied to the prediction and forecast of the *WWTP* (Hong *et al.,* 2003). The complexity of environmental problems makes it necessary to develop and apply to new tools capable of processing data and decision-making processes using tools like environmental decision support systems *(EDSSs). EDSS* can integrate the *AI* techniques, geographical information systems *(GIS),* statistical/numerical methods and environmental tautologies (Poch *et al.,* 2004; Rizzoli & Young, 1997). It is difficult to make most environmental, economic, technical, social and ecological decision without careful forecasting, prediction, modelling and analysis of the development scenarios. This enables the management and stakeholders to choose an option that satisfies a large number of identified conditions and taking into consideration the precaution measure in advance (Palani, Liong & Tkalich, 2008). Various control actions have to be implemented for efficient monitoring of process performed during the operation of *WWTP* (Manu & Thalla, 2017). Most *WWTP* designs are based on waste resources and energy, crisis conditions, and reduce the cost-effectiveness of reaching permissible effluent levels (Wen & Vassiliadis, 1998). The engineers and scientist have extensive experience on the process-based model and data-driven techniques like artificial intelligence with deep learning/machine learning. Process-based models can provide good estimations of the wastewater process parameters or variables but require approximation and estimation of the process variables and lengthy data calibration process. Process-based models require a lot of the input data and a large number of specification model parameters that are unknown unlike the data-driven model techniques that are computational fast, and requires fewer inputs parameters and thus provides alternative to the process-based model (Hong *et al.,* 2003; Palani *et al.,* 2008).

6.3 Hybrid AI Techniques

Artificial intelligent models application tools such as artificial neural network *(ANN),* fuzzy logic *(FL),* expert systems *(ES),* support vector machine *(SVM),* neuro-fuzzy inference systems *(ANFIS),* knowledge-based systems *(KBS),* fuzzy logic control *(FLC),* pattern recognition *(PR),* case-based systems *(CBS),* ruled-based reasoning *(RBR),* ruled based systems *(RBS),* swarm intelligence *(SI),* reinforcement learning *(RL),* hybrid systems *(HS),* expert systems *(ES)* and genetic algorithms *(GA)* have gain popularity and space program in the fourth industrial revolution (Chen, Jakeman & Norton, 2008; Choi & Park, 2001; Dellana & West, 2009; Pai *et al.,* 2009; Poch *et al.,* 2004; Wen & Vassiliadis, 1998). Global development of supervision tools and reliable real-time control was applied to wastewater treatment process. *ANN* has proven to be the universal tool for forecasting and prediction where the desired input-output transformation is usually determined by external, supervised adjustment of the system parameters (Hong *et al.,* 2003). *ANNs* are designed to solve the type of problems where the outputs are required are unknown *(unsupervised learning algorithms)* and known output *(supervised learning algorithms)* (Hong *et al.,* 2003). The basic structures of an *ANN* are: *(1)* input layer where data are introduced to the model and computational of the weighted sum of the input is performed, *(b)* the hidden layer*(s)* where the data are processed and lastly, *(3)* output layer, where the results of the *ANN* are produced (Singh, Basant, Malik & Jain, 2009).

The *ANN* consists of a set of parallel interconnected simple computational units called neurons that resemble the human brain into two ways*: (1)* inter-neuron connection strengths *(weight)* used as storage of knowledge, where the weights are adjusted to particular input datasets leads to a specific target output and *(2)* knowledge acquired by the neurons through learning *(training)* process (Raduly, Gernaey, Capodaglio, Mikkelsen & Henze, 2007).

The research demonstrated the application of the *ANN* to model in forecasting and prediction of the trace metals and chemical oxygen demand (*COD)* in the wastewater treatment plant with the complex and dynamic processes hidden in the monitored datasets.

6.4 Methodology

6.4.1 Concept of deep learning *(machine learning)* with *AI*-modelling using artificial neural network

The interrelationship between *COD* and trace metals were studied using *AI*-based prediction model that allows for the testing/training of *ANNs (tester/creator code)* incorporated and implemented in *MATLAB platform (MATLAB-neural network toolbox)* as described in ***Figure 6.1*** (Raduly *et al.,* 2007). The developed *ANN* was applied to the *Plant A WWTPs*. The treatment processes comprised of bar-rack, aerated grit chamber, primary clarifier, biological nutrient removal *(BNR),* secondary clarifier and lastly, tertiary treatment from the conventional *WWTP*. The influent and effluent datasets were obtained from the year *2015* to *2017.* The period was satisfactory as it covered all seasonal variation in the studied parameters.

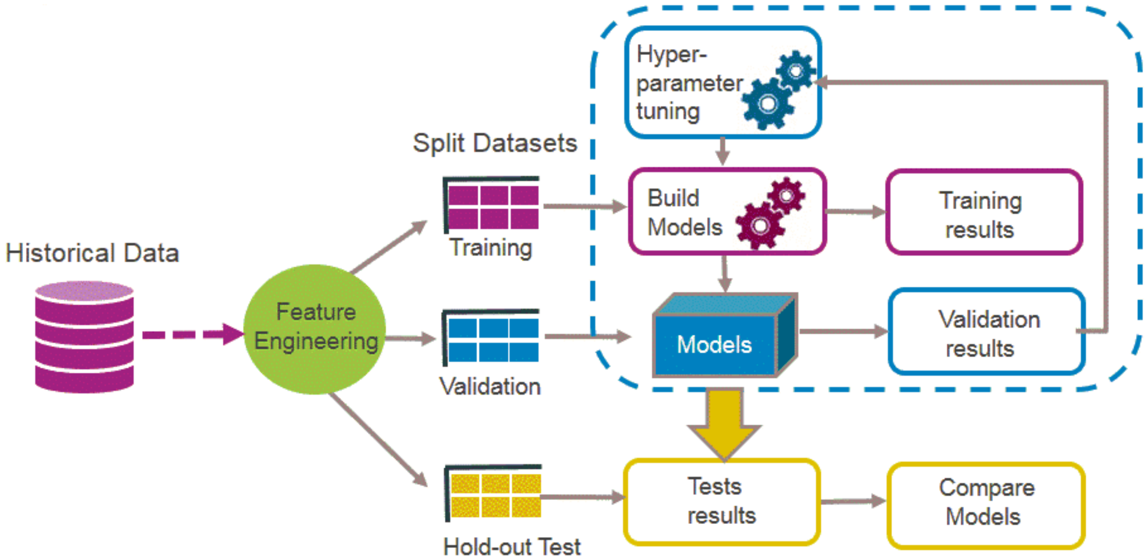


Figure 6.1*: Flow diagram of the concept of deep learning (machine learning) with AI-modelling using artificial neural network*

The datasets used for developing *ANN* was achieved by systematic and efficient sampling and analysis of each process units in the Daspoort *WWTP*. The input variables were seasonal variation series dataset analyzed from the *WWTP*. They included effluent *COD* (COD_{eff}), and effluent trace metals (*trace* $metals_{eff}$) respectively. *21* sets of input dataset training samples used in the train network *(prediction),* and *150* hidden neurons of testing samples were used to test the generalization capability of the train network and lastly data scaling as described by Mingzhi *et al. (2009)*. The training aimed at estimating and predicting the parameters by minimizing an error function with the permissible *WWTP* license limit. The *ANN* employed the model structure of artificial neural networks that were powerful computation technique for modelling complex non-linear relationships. The training, validation and application of *ANN* model for computed of the parameters were undertaken where the appropriate architecture of neurons highly interconnected by synapses *(links)* with weights on a trial basis during testing. ***Figure 6.2*** shows the modelling performance of wastewater plant using artificial neural network concept.

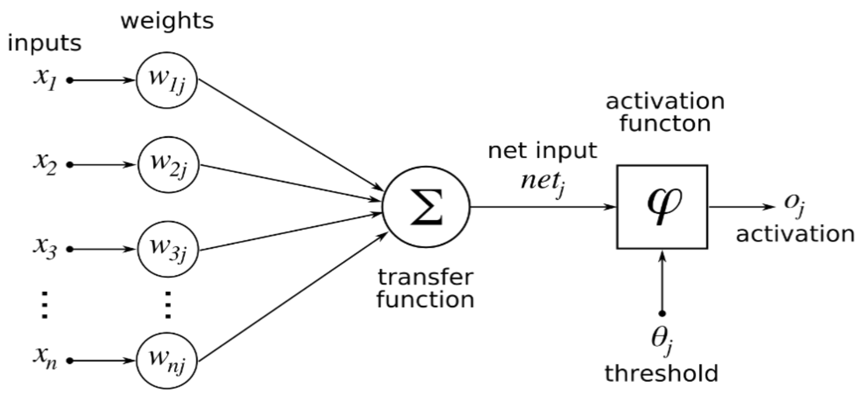


Figure 6.2: *Schematic of the artificial neural network in AI-modelling using deep learning*

The dataset was introduced to the model and computation of the weighted sum of the independent layers of input, the hidden layers introduced to help learn features *(performed an interface to fully interconnect)* from the inputs data, and output determined as described in *(Eq. 6.1*) (Goodfellow, Bengio, Courville & Bengio, 2016).

$$O_i = \sum_{i=1}^{n} (W_{ij} X_i) - \Theta_j \qquad \text{Eq. 6.1}$$

Where: O_i was final output, W_{ij} was input performance, X_j was hidden layers and Θ_j was the residence of prediction practice *(bias)* as hyperparameter for training the process in addition to weight parameters defined in the neural network. The number of the hidden layers *(nodes)* were determined on trial and error basis with a rule of thumb relied on the fact of the number of samples in the training set should at least be greater than the number of the synaptic weights. The node's output determined using a mathematical operation on the node's net input with transfer function operation *(sigmoid, hyperbolic tangent, liner transfer function)* as (Nasr *et al.,* 2012):

- Sigmoid transfer function (Eq. *6.2*:

$$f(x) = \frac{1}{1 + e^{-x}} \qquad 0 \leq f(x) \leq 1 \qquad \text{Eq. 6.2}$$

- Hyperbolic tangent transfer function (Eq. *6.3*:

$$f(x) = tanh\,(x) = \frac{e^{x} - e^{-x}}{e^{x} + e^{-x}} \qquad -1 \leq f(x) \leq 1 \qquad \text{Eq. 6.3}$$

- Linear transfer function (Eq. *6.4*

$$f(x) = x \qquad -\infty < f(x) < +\infty \qquad \text{Eq. 6.4}$$

The train and test data were generated by the probability distribution over datasets called data generating process. To achieve the machine learning *(deep learning)* modern practice goals, a foundational concept such as bias, variance and parameters estimation was useful to formally characterize the notion of overfitting, underfitting and generalization. The prediction problems, a supervised learning algorithm was adopted for training the network. The *MATLAB* opens the network/data manager window *(App Toolbox-Neural Network Fitting Tool-nftool)* that allows the user to import, create, use and export neural networks and data. The networks properties included: network inputs-*COD effluent* and trace metals *effluent*, network output-permissible effluent limits, network type-feed-forward back propagation, training function-*TRAINLM,* adaptation learning function-*LEARNGDM,* number of hidden layers *(neurons)-150* and use of default Levenberg-Marquardt algorithms for training (Mjalli, Al-Asheh & Alfadala, 2007).

6.4.2 Model performance evaluation

This minimized the error *(deviation of the forecasting analysis)* while the model makes the perfectly correct prediction in machine training *(deep learning).* All the computations were done with *Microsoft Excel 2016* and *MATLAB (MathWorks, Inc.*)-deep learning with Levenberg-Marquardt algorithms *(LMA)* for solving generic curve-fitting problems *(non-linear least square problems)* (Mathworks, 1994-2018a, 1994-2018b; Ngia & Sjoberg, 2000) (Mathworks, 2016).

The goodness of the prediction *(prediction performance)* was attained with room mean-square error *(RMSE)-(Eq. 6.5),* mean squared error *(MSE)-(Eq. 6.6),* sum of squared error (*SSE)- (Eq. 6.7)*, coefficient of determination *(R^2)-(Eq. 6.8)* (Mingzhi *et al.,* 2009; Pai *et al.,* 2011; Wan *et al.,* 2011).

$$RMSE = \sqrt{\frac{1}{n}\sum_{t=1}^{n}(Y_a - Y_o)^2} \quad \text{Eq. 6.5}$$

$$MSE = \sum_{t=2}^{n}\frac{(Y_a - Y_o)^2}{n} \quad \text{Eq. 6.6}$$

$$SSE = \sum_{t=2}^{n}(Y_a - Y_o)^2 \quad \text{Eq. 6.7}$$

$$R^2 = 1 - \frac{SS_{Regression}}{SS_{Total}} \quad \text{Eq. 6.8}$$

Where: *n* is the number of data point/training/test samples, Y_a is the target/actual/desired output, Y_o is the network/predict output, SS_{Total} total summed squared error based on the mean, $SS_{Regression}$ is the sum of squared error based off the regression line.

6.5 Results and Discussion

6.5.1 Effect of trace metals and chemical oxygen demand in the wastewater treatment process

Due to the inherent complexity, chemical composition, incoherent flow rate and higher safety factor in the effective operation of the biological wastewater treatment process, the *AI*-based model was extensively tested in managing the wastewater treatment operations. Modelling was accomplished with *ANN (universal approximator)* due to *WWTP* non-uniformity and non-linearity of the biological treatment. The plant input and output data were used to predict the plant without using mechanistic bio-modelling that involves a great degree of complexity and uncertainty. The effect of the *COD* and trace metal in the wastewater treatment processes were explained in ***Figure 6.3*** and ***Figure 6.4*** respectively, where *ANNs* represented complex, non-linear function with parameters adjusted *(trained or calibrated)* against the permissible effluent limits *(big data)*. This involved the network architecture, weights and function for the neurons *(training)* and inputs. The concentration of the effluent trace metals was showed to below *0.05 mg/L*. All the trace metals were below the permissible limit. The concentration of the effluent *COD* was too below permissible limit with evenly distribution outputs due to the source of the wastewater and *WWTPs* parameters/variables that were associated with nutrients removal.

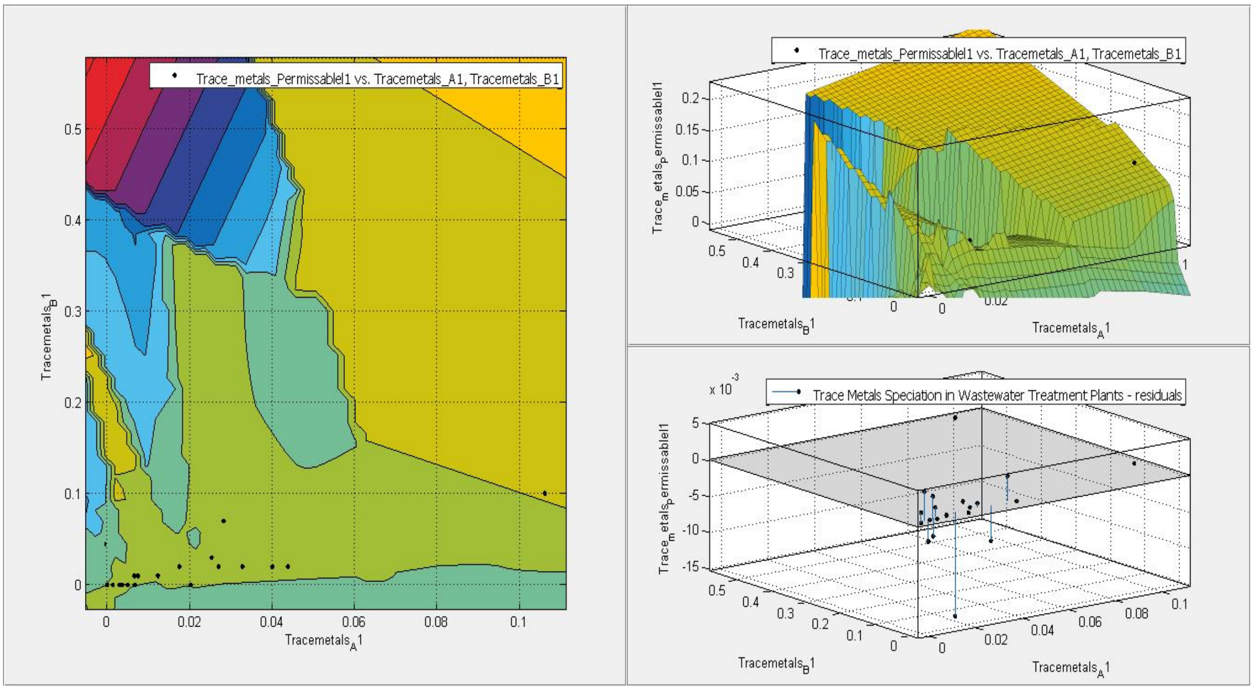


Figure 6.3: *Trace metals speciation in the effluent wastewater treatment process*

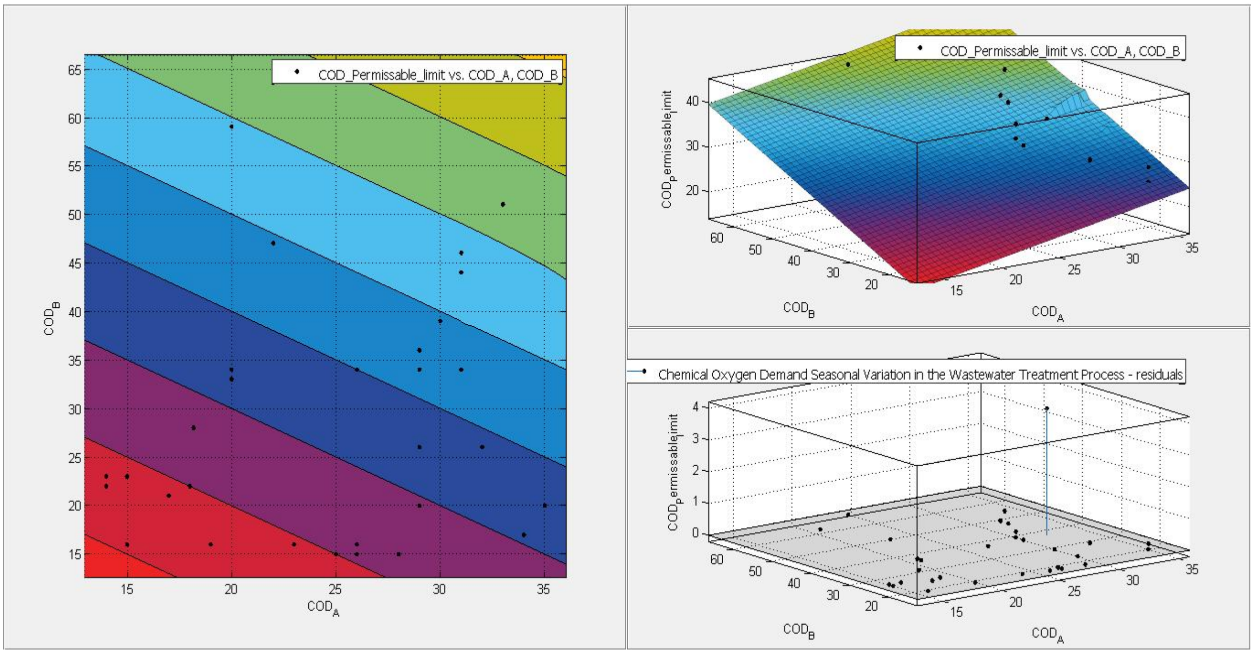


Figure 6.4: *The concentration of the effluent chemical oxygen demand (COD) in the wastewater treatment process*

The interrelationship between *COD* and trace metals was studied using an *AI*-based model with the artificial neural network *(ANN)* incorporated in *MATLAB. ANN* employed a caricature of the way the human brain processes of many units *(nodes and neurons)* working in unison. The prediction problems, a supervised learning algorithm was adopted for training the network to relate input to output data. The *ANN* fitting tool, assisted to select datasets, created and trained a network and evaluated its performance using mean square errors and regression analysis. *21* sample numeric inputs data to present the network and *21* target data defining the desired network output *(set of numeric targets)* was used *(international standard permissible limit for the wastewater treatment compliance).* Training network *(network architecture)* to fit input and targets was undertaken using a training algorithm: Levenberg-Marquardt backpropagation *(Trainlm)* with the *150* hidden neurons. These presented to the network during training, and the network adjusted according to its error. The training aimed at estimating and predicting the parameters by minimizing an error function. The training, validation and application of *ANN* models were computed for the parameters. ***Figure 6.5*** and ***Figure 6.6*** show the prediction of the trace metals and *COD* parameter *(function fit of variation of parameters)* respectively in demonstrating the control performance of the *ANN.* Both showed smooth curve and colorations among training targets, training outputs, validation targets, validation outputs, test targets, test output, low errors and smooth fittings of the datasets. The model developed focused on postulating functional, adaptive, real-time and alternative approach of the removal of the trace metals and *COD.*

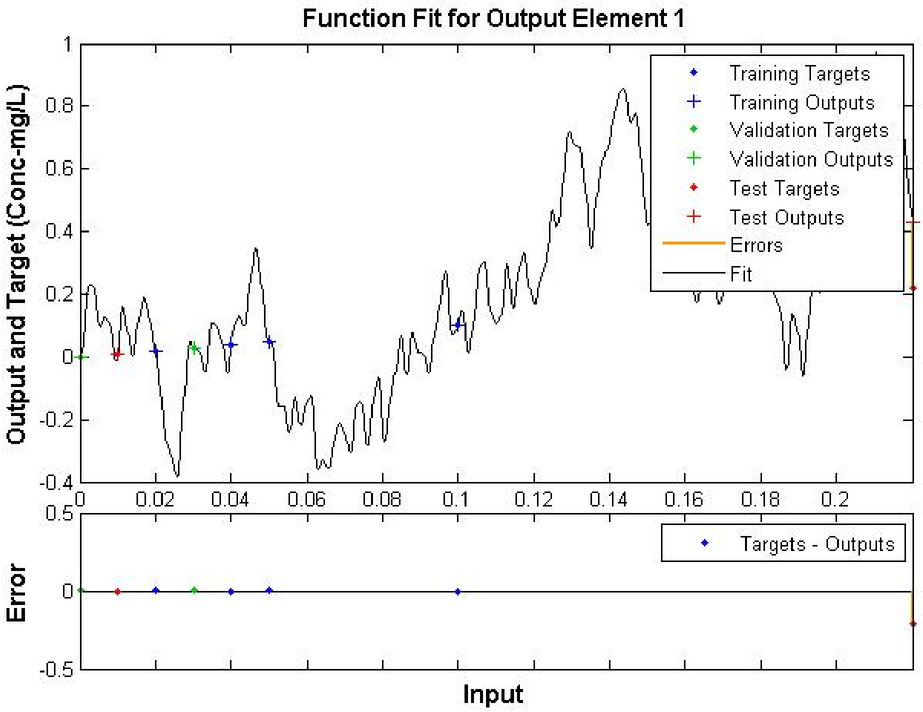


Figure 6.5: *Function fit of the variation of the trace metals*

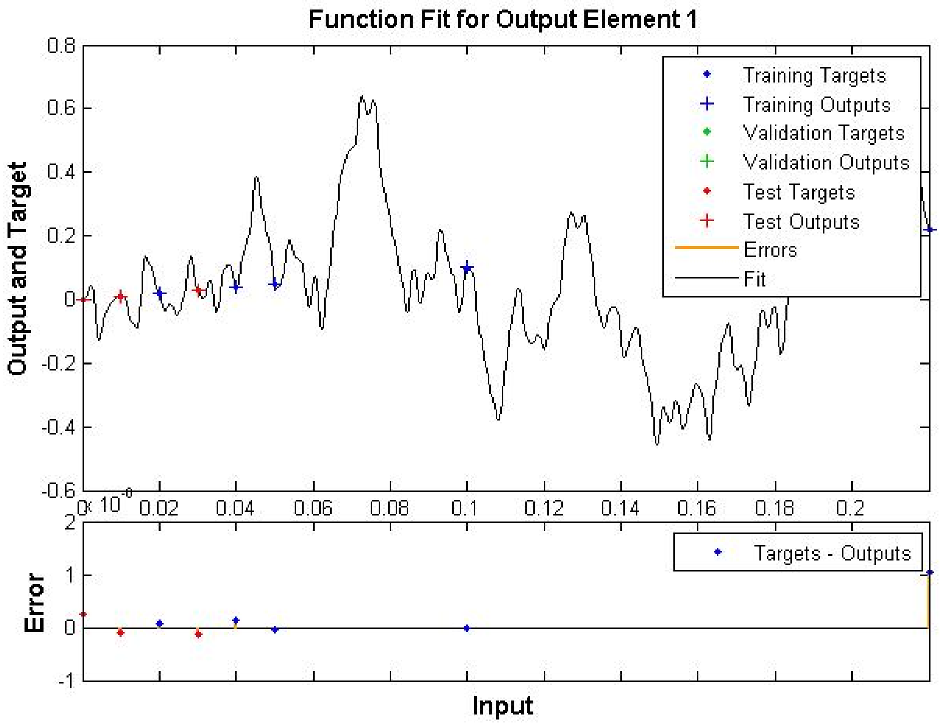


Figure 6.6: *Function fit of the variation of the COD*

The *ANNs* model was used an alternative to the physical model and controller of the complex environmental process, a valuable forecast tool for the wastewater treatment prediction meant to interact with parameters in the real world as same way with the biological nervous system. The *ANN* had a suitable learning capability with a robust, reliable and salient characteristic in capturing the nonlinear relationship between variables *(multi-input and output)*. The data structure and non-linear computation of *ANNs* allow a good fit to complex, multivariable data. The model could be used in parallel with the process-based models as a new prediction tool.

6.5.2 Process performance prediction

The level of confidence over the predictions of developed models was trained and validated using suitable statistical indices as described by Manu & Thalla, 2017 and Wan *et al.,* 2011. A long-term sampling and analysis program was advisable from the year *2015-2017* to ensure the reliability of hybrid control scheme. A train on the training dataset was evaluated by comparing its prediction to the measured values in the overfitting test sets and values calibrated by systematic adjusting various model parameters. The performance of the *ANN* models was assessed through the sum of square error *(SSE),* coefficient of determination *(*R^2*)*, root-mean-square-error *(RMSE),* mean squared error *(MSE),* and the bias computed from the effluent measured data, effluent quality *(EQ)* under permissible effluent limit and model computed values of the dependent variables.

6.5.2.1 Effluent trace metals process performance

Locally weighted smoothing linear regression: *f(x,y)* = lowess *(linear)* smoothing regression computed from *p,* where *x* was normalized by mean *0.023* and std *0.02928,* and where y was normalized by mean *0.0419* and *std 0.1191.,* coefficients *p* was structure. The goodness of fit was found to be: *SSE: 0.000291, R*-square: *0.994,* adjusted *R*-square: *0.9901, RMSE: 0.004924.* ***Figure 6.7*** shows the performance training and overfitting test of the datasets and prediction using network regression for the trace metals.

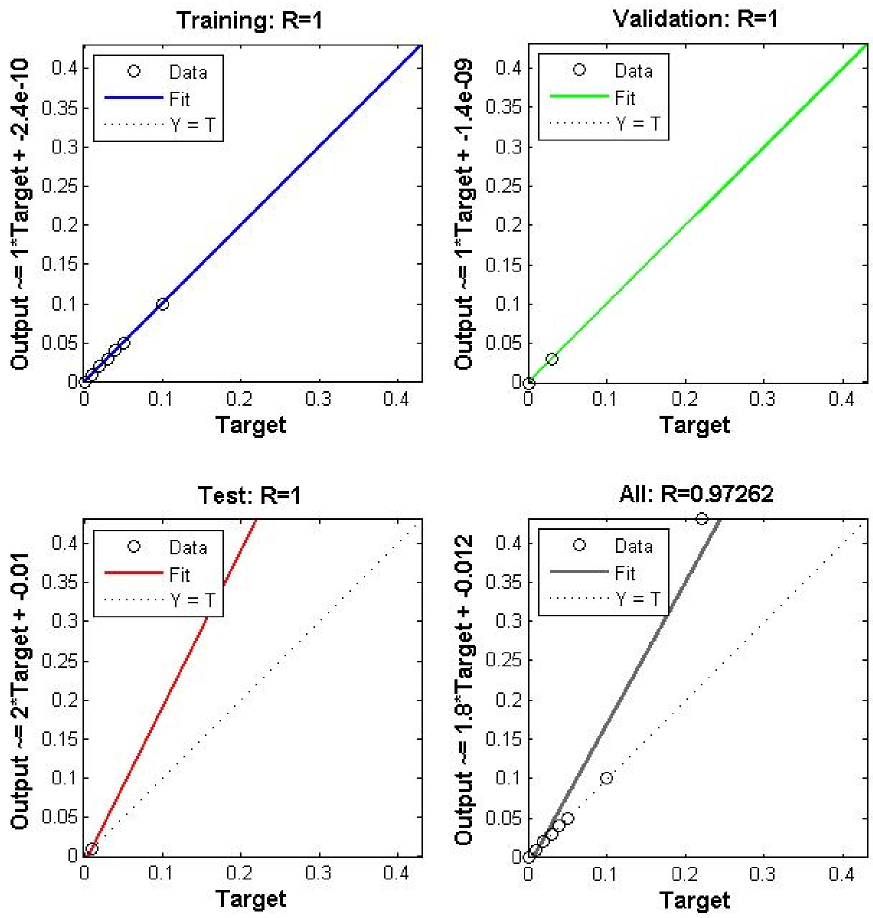


Figure 6.7: *Performance training and overfitting test of the datasets and prediction using regression R for the trace metals (network regression)*

The regression *R* values measured the correlation between outputs and targets. An *R* values of *one (1)* means a close relationship between input and output, and zero (*0)* a random relationship. The correlation coefficient $R^2 > 0.97$ and prediction errors were lower than *10%.* The accuracy of the *ANN* was sufficient for application in *AI*-simulation based *WWTP* design and simulation of the integrated wastewater systems control strategy.

6.5.2.2 Neural network training performance *(Mean Squared Error MSE)* for the trace metals

Even though there was slight uncertainty in the training and overfitting test datasets during model construction, the performance accuracy of the *ANN* trace metals prediction model was shown in ***Figure 6.8***. The best performance was *2.3175e-15* at epoch *3.* The model was successful in simulating the magnitude and patterns measured of the trace metals concentration on seasonal variation.

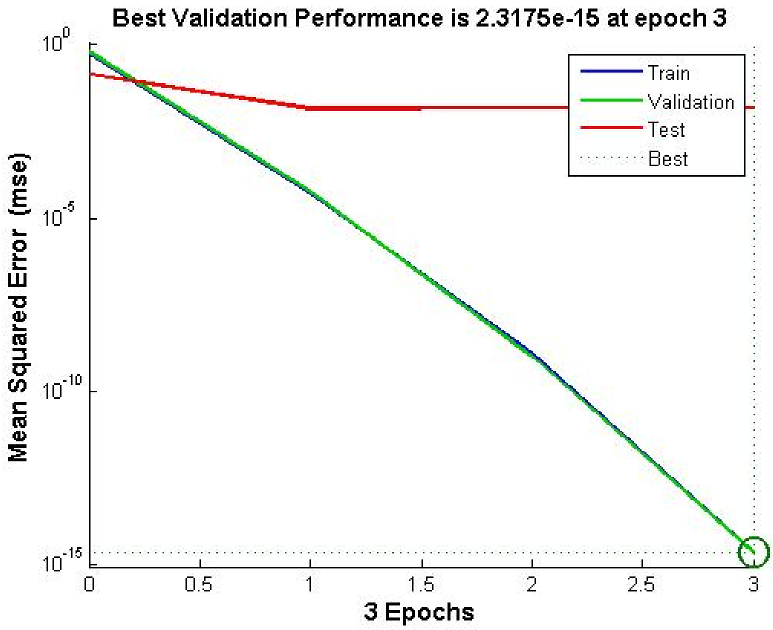


Figure 6.8: *Validation performance of the trace metals using mean squared error*

The *MSE* indicated that average squared difference between outputs and targets. The lower recorded, indicates best fit of the data and high performance with zero meaning no error.

6.5.2.3 Chemical oxygen demand *(COD)* process performance

Locally weighted smoothing linear regression: *f (x, y)* = lowess *(linear)* smoothing regression computed from *p,* where *x* was normalized by *mean 24.62* and *std 6.39,* and where y was normalized by *mean 29.42* and *std 13.58,* coefficients *p* was structure. The goodness of fit was showed as *SSE: 0.1598, R*-square: *0.9919,* adjusted *R*-square: *0.9885* and *RMSE: 0.8673.* ***Figure 6.9*** shows the performance training and overfitting test of the datasets and prediction using regression for the *COD.*

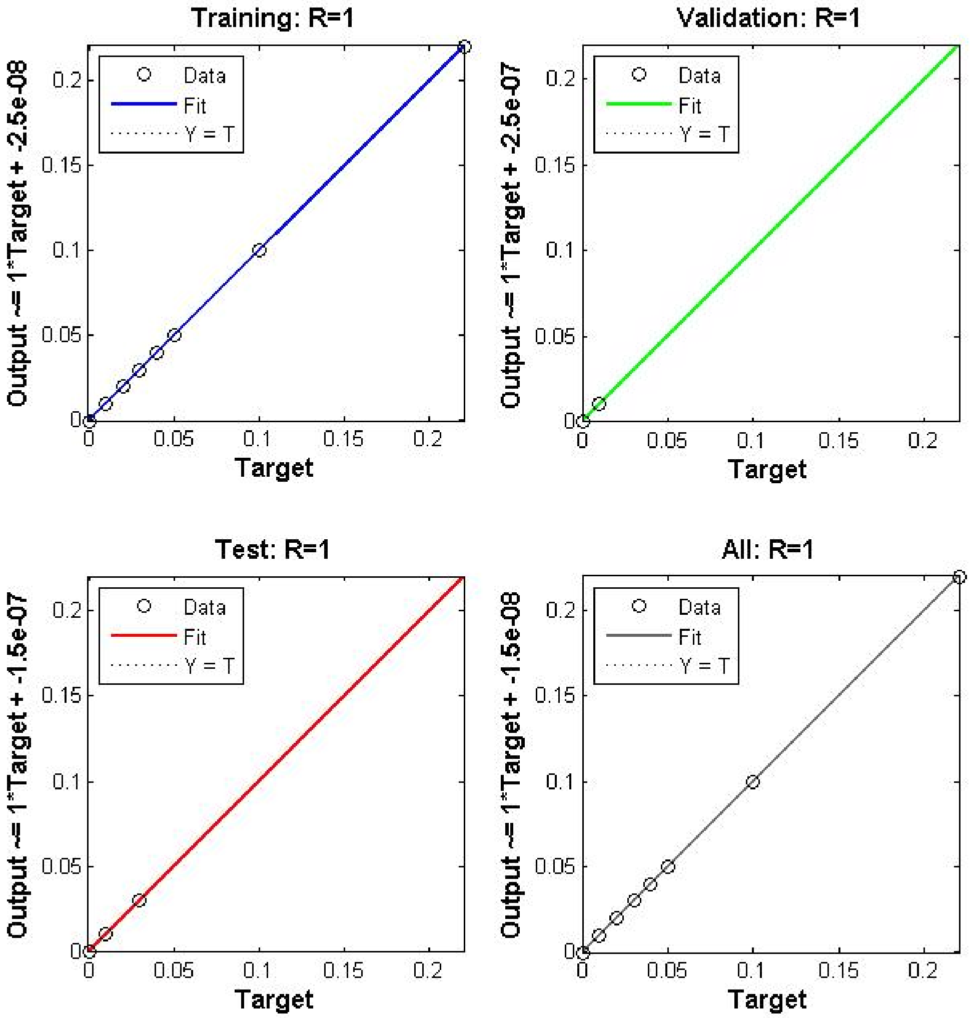


Figure 6.9: *Performance training and overfitting test of the datasets and prediction using regression R for the chemical oxygen demand*

The correlation coefficient $R^2 = 1$ was recorded with no prediction errors and thus was sufficient for application in *AI*-simulation based *WWTP* design and simulation of the integrated wastewater systems control strategy for the *COD* variable.

6.5.2.4 Neural network training performance *(Mean Squared Error-MSE)* for the *COD*

Even though there was slight uncertainty in the training and overfitting test datasets during model construction, the performance accuracy of the *COD* prediction model was shown in ***Figure 6.10***. The best performance was *2.7059e-14* at epoch *3.* The model was successful in simulating the magnitude and patterns measured by the *COD* concentration on seasonal variation.

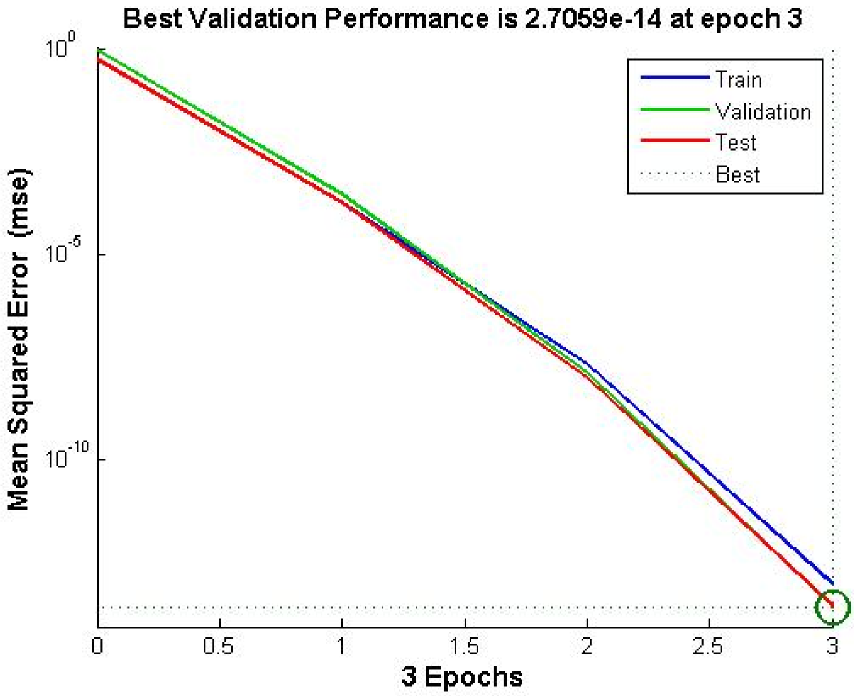


Figure 6.10: *Validation performance of the COD using mean squared error*

The lower value indicated best fit of the data and high performance with zero meaning no error. The error related to the prediction of effluent *(trace metals and COD)* concentration by *ANN* appeared to be more reasonable low on prediction and forecasting. The more the datasets *(big data)* the better the predictions and less the errors.

The *EQ* from *WWTP* met the effluent standard of South Africa and complied with international standard (Abdel-Shafy & Mansour, 2014; Department of Water and Sanitation, [Accessed June 2016]; Mackenzie, 2011; Raval *et al.,* 2016). *ANN* modelling was a useful tool that optimized monitoring networks by identifying essential monitoring stations and time series forecast with acceptable accuracy. The *ANN* solved the interdependency of the effluent and permissible limits variables that showed non-linearity, and non-uniformity. From the performance evaluation, the approach proved capable to define the interrelationship between wastewater quality parameters. According to Raduly *et al.,* 2007, *ANN* simulator can be used to reduce the simulation time constraint that is usually experienced when working with longtime series in real-time. According to Roda, Poch & Bañares-Alcántara, 2000, the wastewater historical data *(big data for dataset)* assist in troubleshooting the *WWTP,* influence changing the weight of the arguments used in the selection of the adequate proposal, automatic evaluate the compliance performance of the *WWTP,* assist in decision making as an alternative design and the process, and to re-use the design records when upgrading an existing *WWTP* or designing a similar *WWTP* capacity. Deep learning with machine learning in *AI*-modelling approach could provide alternatives to a generic framework for the modelling of other treatment processes.

6.6 Conclusion

The widely used artificial intelligence *(AI)*-based prediction models *ANN,* using *MATLAB* platform incorporated with machine learning *(deep learning)* was used to predict the real-life problems of the wastewater treatment processes. Since there was no need to define complex reaction, mathematical and biochemical equation in the use of the *AI*-based models, it was suggested to conduct the simultaneous machine learning with the most appropriate model structure for the specific problems. The deep learning, a new area of a set of algorithms in machine learning principles was efficient and elegant techniques served with a modern paradigm for computing and simulating biological; and environmental design processes with a basic principle of the prediction modelling. The efficiency of operating biological wastewater treatment processes was significantly influenced by an overload in a local community due to varying wastewater source, flow rate and chemical composition. The results presented confirmed that *ANNs* as a good tool for the simulation model of the *WWTP* designs and development of the integrated wastewater systems. The limited time used to train big data *(datasets)* allows faster performance evaluation as compared to conventional modelling. The *ANN* was useful in solving data-intensive problems where algorithm or rules to solve the problem was limited/unknown/difficult to express and can be used as the objective function or constraints in optimization for the best operation or design in the future studies. The goodness of the prediction *(prediction performance)* was attained with the coefficient of determination *(R^2)* of 0.98-0.99, sum of square error *(SSE) 0.00029-0.1598,* room mean-square error *(RMSE) of 0.0049-0.8673,* mean squared error *(MSE) 2.7059e-14 to 2.3175e-15* for the trace metals and COD concentration respectively. The prediction accuracy of the *ANN* was sufficient for the applications envisaged in the simulation of the non-linear behaviour of the plant and valuable performance assessment tool for *WWTP* operations and decision making in troubleshooting. It revealed that the influent indices could be applied to the prediction of the effluent quality.

CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

Wastewater treatment process can be considered as the largest industry in terms of waste management industries. The biological behavior of biotechnological processes occurring in a bioreactor has a complexity unparalleled in the chemistry application principles. The complex systems therefore result in involvement of the models based on mathematical description of the process after the off-line sampling and analysis due to lack of the on-line sensor. The study applied practical knowledge of *IAWQ* Activated Sludge Model *No.1* and mass balance through a database that combines experience from expert knowledge and modelling experience. The basis for the development of reliable mathematical models was a thorough understanding of the process involved. Activated sludge systems was described by mathematical models based on mass balance equations that relate to change of the state variables of the system *(flow rates, concentration and composition)* due to transport and the transformation mechanisms. The authors combine the *ASM1* principles, substrate and microorganisms' kinetics in mass balance, thus resulting in a standardized methodology for expressing nomenclature that is useful for the *WWTP* modelers and other experts. This will enhance coding in programming of the simulation software by eliminating error-prone part of model implementation. The spreadsheet provided corrected matrices with all stoichiometric coefficient for the bio-kinetic models. The presence of emerging micro-pollutants such as *methyparabens, ethylparabens, propylparabens* and the inclusion of water chemistry indicated that the plant has the capability and is effective in removing the fate of micro-pollutants. *COD* mass balance made a lot of sense on prediction of the experimental data that was reliable and accurate. Monitoring the reactor concentration and its changes at a fixed parameter created a long-term change in the loading rate on the *WWTP* and thus increase its efficiency. The structured framework of the models was useful among modellers, operators and management at the *WWTPs* and other wastewater stakeholders. The models provided guidance in identifying the key design parameters and quantify system parameters that ensured optimal performance. The information provided an insight into the wastewater characteristic that included biodegradability, flow distribution, contaminants and potential for the source control. These models provided the quantitative predictions of quality of effluent to be expected from the design of the existing *WWTP* and guidance to the direct attention needed in the system and control response. Use of the *ASM1* facilitated communication of the complex models and enabled a focus on the bio-kinetics models. Mass balance was a powerful tool that allowed detection of inconsistencies within the *WWTP* data sets and assisted to identify the systematic errors. The models were verified by conforming to internal mass balance and adequate validation against the experimental tests. The results contributed to the knowledge transfer on activated sludge and biofilm modelling. No alarm was raised from the Daspoort *WWTP* data analysis efficiency performance and thus the plant met regulatory targets *(permissible effluent limits)*.

The effective operation of wastewater treatment plants played an important role in minimalizing the release of trace metals into the aquatic environment. The predicted fate of transport of the trace metals in the wastewater treatment plant was modelled using mass balance concept. This show a speciation of the trace metals in multiple units associated with water, air, microbes, biosolids and biomass, with biological treatment systems with the quantitative dependent upon physical-chemical and biological properties. Using the mass balance model made the integrated design process friendly and easier especially for data-entry and the ease of understanding results of the analysis process. The mass balance showed removal performance and treatment efficiency of the wastewater treatment plant.

The widely-used artificial intelligence/machine learning/deep learning-based prediction models *ANN,* using *MATLAB* platform was used to predict the real-life problems of the wastewater treatment processes. Since there was no need to define complex reaction, mathematical and biochemical equation in the use of the *AI*-based models, it was suggested to conduct the simultaneous machine learning with the most appropriate model structure for the specific problems. The deep learning, a new area of a set of algorithms in machine learning principles, was efficient and elegant techniques served with a modern paradigm for computing and simulating biological and environmental design processes with a basic principle of the prediction modelling. The efficiency of operating biological wastewater treatment processes was significantly influenced by an overload in a local community due to varying wastewater source, flow rate and chemical composition. The results presented confirmed *ANNs* as a good tool for the simulation model of the *WWTP* designs and development of the integrated wastewater systems. The limited time used to train big data *(datasets)* allows faster performance evaluation as compared to conventional modelling. The *ANN* was useful in solving data-intensive problems where algorithm or rules to solve the problem was limited/unknown/difficult to express and can be used as the objective function or constraints in optimization for the best operation or design in the future studies. The goodness of the prediction *(prediction performance)* was attained with coefficient of determination *(R^2)* of 0.98-0.99, sum of square error *(SSE) 0.00029-0.1598,* room mean-square error *(RMSE) of 0.0049-0.8673* and mean squared error *(MSE) 2.7059e-14 to 2.3175e-15* for the trace metals and *COD* concentration respectively. The prediction accuracy of the *ANN* was sufficient for the applications envisaged in the simulation of the non-linear behavior of the plant and valuable performance assessment tool for *WWTP* operations and decision-making in troubleshooting. It revealed that the influent indices could be applied to the prediction of the effluent quality. The mathematical modelling study developed an effective design for wastewater treatment plant process.

7.2 Recommendations

The initial objectives of this project were as follows:

i. To carry out site reconnaissance and dimension of the WWTPs process unit. This was to assist in getting the complete picture (mass balance) about the occurrence, concentration, fate and transport of trace metals, organic and inorganic compounds.

ii. To carry out in-depth sampling at different intervals (process units) based on retention time from the liquid, mixed sludge, dewatered sludge and analyze organics, inorganics, trace metals and emerging micropollutants.

iii. To analyse thermodynamic and reaction bio-kinetics models that will be used to gain a better understanding of the variable dependency in the wastewater treatment process, biosolids utilization.

iv. To carry out mathematical modelling and simulation of the trace metals, organic, inorganic, micropollutant compounds, physically measured data (operation variables), performance variables in the WWTPs. This will enable a better understanding of each treatment unit and henceforth improved analytical strategies for the pollutant's removal.

v. To optimize parameters and validate empirical results through goodness of the prediction (prediction performance) to ascertain comparability of satisfactory results.

The research project therefore sought to respond to the following questions:

Question1: What are the necessary parameters that need to be considered for an effective mass balance modeling in wastewater treatment plants? Why is the plant design and dimensions important when planning modeling of mass balance?

Question 2: Does sampling time interval impact on modeling results and in what way?

Question 3: Does the choice of mathematical models such as thermodynamics and biokinetics influence the variable dependency during treatment process?

Question 4: What role do parameter simulations play in predicting the efficiency of the wastewater treatment process?

Question 5**:** Why is it important to validate empirical results during optimization of wastewater treatment parameters?

In order to answer the above research questions, we present the following recommendations which address the entire ecosystem of mass balance in a wastewater treatment process, each component indicated as a Unit Operation. The summary table depicting all the crucial aspects of mathematical modelling of WWTP, is hereby presented where the first column lists the unit operation, the second column states the problem being addressed and the third column gives the recommended solution.

Unit Operation	Problem	Solution
Mathematical Models	Why is mathematical modelling crucial in wastewater treatment processes?	The biological behavior of biotechnological processes occurring in a bioreactor has a complexity unparalleled in the application of chemistry principles. The complex systems therefore require the use of models based on mathematical description of the process after the off-line sampling and analysis due to lack of on-line sensors. Mathematical modelling and simulation become essential to describe, predict and control the complicated interaction of the wastewater treatment processes. Mathematical modelling of the activated sludge systems has become a widely accepted tool for plants designs, training of the process operators and engineers, and research tools. The models provided guidance in identifying the key design parameters and quantifying system parameters that ensured optimal performance. The information provided an insight into the wastewater characteristic that included; biodegradability, flow distribution, contaminants and potential for the source control. These models provided the quantitative predictions of quality of effluent to be expected from a design of the

		existing *WWTP* and guidance to the direct attention needed in the system and control response.
Control of the process parameters (concentration, flowrates and composition) in terms of real-time	How does population growth globally, economic development, urbanization impact on wastewater treatment processes?	The global population growth, economic development, urbanization, improvement in living-standards has increased waste generation and introduced emerging contaminants into waste streams that may pose sanitary and environmental risks. These contaminants have increased the demand for new approaches to addressing emerging pollutant removals in wastewater. Therefore, to handle smart wastewater treatment processes, instrumentation, control and automation *(ICA)* is the best approach to enhancing the efficiency of wastewater treatment process. Achieving these process control standards requires the programmable biochemical quantitative-characterization analysis of given waste streams, implementation of innovative integrated waste management systems and reliable waste management data which provides an all-inclusive resource for a comprehensive, critical and informative evaluation of waste management options in waste management programmes. This is due to complex biological reaction mechanisms, lack of reliable on-line instrumentation, unforeseen changes in microbes, organic and inorganic compounds, multivariable aspects of the real wastewater treatment plant *(WWTP)* and highly time-varying process variables that create a need for the intelligent technique for analysis of multi-dimensional process data known as the 'big data' and diagnoses of inter-relationship of the process variables in the *WWTPs.* This reveal that the influent indices could be applied to the prediction of the effluent quality *(EQ)*. The approach can also be used to handle many other types of waste treatment systems, environmental management, carbon capture and emerging technologies so as to meet the cost-effectiveness, environmental, technical criteria and wide range of big data support in the implementation of the national and sustainable development goals *(SDGs)*.
Impact of primary settlement sizing and velocity	Do carbon, nitrogen and phosphorous elements in the primary sedimentation processes have an impact on the primary sedimentation	The quantity and quality of carbon, nitrogen and phosphorus are much affected by primary settling tank due to sludge discharge before the activated sludge reactor. It is important that the primary sedimentation on the wastewater *C, N,* and *P* be determined to enable the settled sewage characterization to be estimated. Sedimentation is characterized by particles that settle discretely at a constant settling velocity and individual particles *(sand and grits)* do not flocculate during settling. High settling velocity give the high efficiency of the wastewater treatment.
Change of design flowrate *(loading)* with the hydraulic retention time	How does sludge age affect the efficiency of wastewater treatment?	The hydraulic control of sludge age revolves a greater responsibility to plant operators and in the redesign of the biological processes to improve effluent quality. This can create a pathogen-free effluent. The dynamics created by the daily flow rate of the inflow could be tapped with the installation of the whirlpool turbines to provide power to run the operations of the *WWTP* and at the same time supply electricity to the local communities.
Effect of the solid retention time in the WWTP	What considerations does one need to take into	The following plant parameters must be considered in the design of the plant: solid retention time *(SRT)*, cell residence time (Θ) or sludge age, net specific bacteria growth rate (μ_{net}) and effluent concentration *(S)* of the biomass

	account when determining the rate of sedimentation of particles in wastewater?	The *SRT* could be controlled by the wasting rate a given percentage of the aeration tank volume on each day. Controlling the *SRT* by sludge wasting affects the net specific biomass growth rate and the reactor substrate concentration. The *SRT* helped control the sludge age and the underflow and overflow. The wasting of solids is required to prevent an accumulation of solids in the oxidation ditch. It is essential that the designer consider the sludge mass more exactly to provide sufficient reactor volume under design organic load that allowed proper concentration at the specified process unit. The increased in *COD* mass load increased the sludge concentration automatically and maintained the sludge age. Maintaining the *COD* mass load constant automatically maintained the sludge concentration constant.
Effect of temperature on microbial growth	What is the significance of temperature in a biological wastewater treatment?	Temperature has a significant effect on the growth rate of the microorganisms in the biological wastewater treatment. The biological reaction rate is directly dependent on the temperature on the assessment of the overall efficiency. The higher mesophilic temperature in the wastewater treatment process creates an enabling environment for the microbial growth and thus influencing the metabolic activities of the microbial population. This has a profound effect on factors such as gas transfer and the settling characteristics of the biological solids. The different temperatures phase that works well are; psychrophilic below *15°C*, mesophilic *15-40°C* and thermophile at *40-70°C*. The increase in temperature shows a gradual increase in growth rate and much higher temperature denature the proteins. When the temperature drops to about *15°C*, methanogen becomes quite inactive and about *5°C*, the autotrophic nitrifying bacteria ease to function. When the temperature rises to *50°C (thermophilic temperature),* aerobic digestion and nitrification stop. The optimum temperature *22°C* of the wastewater treatment process proves to be effective with the other process parameters.
Impact of *pH* and *pH* dependency at the *WWTP*	What is the role of microorganism on the treatment process?	The *pH* range of *7-8* in the wastewater treatment plant suppressed the maximum specific growth rate by increasing the nitrification processes in the conversion of free and saline ammonia to nitrite *(ANOs),* nitrite to nitrate *(NNOs)* and maintaining the balance of food to microorganism conditions that enhance the efficiency of biomass removal. Overloaded WWTPs lack sufficient oxygen supply and the residuals organic acids could lower the reactor *pH.* Lower *pH* below the optimum range of *7-8* for biological growth leads to the formation of acetic acid concentration and this further lowers the *pH* level that reduces the *WWTP* performance.
Seasonal variation of the total alkalinity	What is the significance of total alkalinity in a biological wastewater treatment?	Alkalinity in wastewater resists change in *pH* caused by the addition of acids because wastewater is normally alkalinity from the groundwater, water supply and chemical added to wastewater treatment process. Typically, alkalinity is required to buffer the nitrification reaction. When alkalinity falls below *40 mg/L* as $CaCO_3$, irrespective of CO_2 concentration, the *pH* becomes unstable and decreases low values. The problems associated with fall of *pH* include poor nitrification efficiency, effluents aggressive to concrete and the possibility of development of bulking *(poor settling)* sludges. Alkalinity is introduced to predict the possible *pH* change as it guarantees the continuity in ionic charge of the biological processes in the concentration of $CaCO_3$ where *(50 mg* $CaCO_3/L = 1$ *mg* HCO_3^-/L*).*

		Low alkalinity concentration may lead to unstable *pH that* could reach inhibiting levels. Low alkalinity is always encountered where the source of wastewater is from underlain sandstone area. In such cases, it is advisable to dose with lime or anoxic zone is created to denitrify some, or entire nitrate generated. Nitrate is considered as hydrogen ions that are equivalent to generating alkalinity. Incorporating nitrification and denitrification in a system is said to cause a net loss of alkalinity above *40 mg/L* and consequently the *pH* above *7* as observed in our analysis. To maintain an effluent alkalinity above *50 mg/L,* influent alkalinity was sufficiently put high.
Impact of the electrical conductivity (EC)	What is the significance of electrical conductivity in a biological wastewater treatment?	The EC of water is a measure of the ability to conduct an electrical current as they transport ions in the solution. The conductivity increased with increase in ions. Optimum range of EC anticipate efficiency in the plant performance ND effective removal of the total dissolved solids (TDS) and the ions.
Fate and transport of emerging organic compounds	What processes are involved in the degradation of emerging organic compounds?	The ability of degradation of the emerging micro-pollutants depend on specific microbes and acclimation time. The three principles of emerging micro-pollutant removal are that; i) the compound serves as a growth substrate, with proper environmental conditions; seed source, acclimation time, a wide range of parabens have been found to serve as growth substrate for the heterotrophic bacteria. ii) the compounds are degraded by cometabolic degradation; the compound is degraded but not part of the microorganism metabolism as it has no benefits to the microbe's cell growth and lastly iii) the organic compound provides an electron acceptor.
Degradation of the organic matter inform of chemical oxygen demand	What is the significance of COD in a biological wastewater treatment?	The COD is a powerful tool for checking the results calculated for design from the steady-state model, data measured on experimental systems and the results calculated by dynamic simulation models for the overall plant nutrients removal efficiency. Biomass is mostly organic matter and an increase in biomass measured by particulate COD (total COD minus soluble COD) or volatile suspended solids (VSS). The COD of the sludge particles and effluent COD concentration comprises of the soluble unbiodegradable organics (COD) from the influent that escape with the effluent. Note that the effluent soluble substrate concentration for a complete-mix activated sludge process is the function of solid retention time (SRT) and the biokinetics coefficients for the growth and decay. The effluent *COD* concentration comprised virtually the soluble unbiodegradable organics *(COD)* from the influent plus the *COD* of the sludge particles that escaped with the effluent due to the imperfection of operation of the secondary settling reactor. To ensure nitrification and biological nutrient removal *(BNR)* under normal activated sludge systems operating conditions where sludge age is more than 3 days, the nature of the influent organics in *WWTP* is such that *COD* concentration in the effluent is inconsequential and soluble readily biodegradable organics is completely utilized in a short time of less than *2 hours* while the particulate organics are enmeshed with the sludge mass in the secondary settling tanks.
Effect of the mixed liquor suspended solids	What is the significance of mixed liquor in a biological wastewater treatment?	In the conventional aerobic oxidation process, mixed liquor suspended solids (MLSS) flows from the aeration tank to secondary clarifier where the activated sludge is settled down. The return sludge maintained the concentration of the microorganisms in the aeration tank by the high the population of the microbes that permits rapids breakdown of the organic compounds. The volume of sludge return to the aeration basin typically is 20 to 30 percent of the wastewater flow. A balance to achieve the

		growth of new microbes and their removal by wasting (WAS-waste activated sludge) is instituted by control of the waste portion of the microbes each day to maintain the proper number of microorganisms by efficiency oxidizing the biodegradable COD (bCOD). When too much sludge is wasted, the concentration of the microorganisms in the mixed liquor will become too low for effective treatment and little sludge wasted resulted into a large concentration of microorganism that accumulates and ultimately overflow the secondary tank and flow into the receiving stream.
Impact of total suspended solids in the concentration of suspended solid fraction	What is the significance of total suspended solids in a biological wastewater treatment?	Total suspended solids (TSS) is an important variable in the concentration of the suspended solid fractions. It consisted of volatile suspended solids (VSS) and inorganic suspended solids (ISS): (ISS=TSS-VSS). The mass of total suspended solids (TSS) in the reactor was a function mainly of the daily mass loads of chemical oxygen demand (COD) and inorganic suspended solids (ISS) on the reactor and the sludge age. The choice of treating settled or raw wastewater requires weighing their merits and demerits; for settled sewage smaller reactor volume, reduced secondary sludge and lower oxygen demand, but deals with secondary and primary sludge and their stabilization but for raw sewage and larger reactor volume, higher oxygen demand and increased secondary sludge production, but having no primary sludge to deal with. TSS is used to assess the universal effluent standards by which the performance of treatment plants was judged for the regulatory control purposes.
Effect of dissolved oxygen in the wastewater treatment processes	What is the significance of dissolved oxygen in a biological wastewater treatment?	Dissolved oxygen *(DO)* in the biological treatment is a measure of oxygen dissolved in wastewater to sustain the microbial growth that enhances the breakdown of the organic compounds by the blended biomass and microbes in the aeration reactor. Oxygen is less soluble in the summer time than in winter time. The solubility is enhanced by the change in temperature that is paramount to the chemical reaction, aquatic life and suitability of the water for the beneficial use. Increase in temperature decrease the rate of the dissolved oxygen in the summer time. Temperature influence the oxygen transfer on the bases on saturation DOs. For the COD balance, the more oxygen that is utilized in the system, the lower the sludge production and the lower the active fraction of the sludge observed. An adequate supply of dissolved oxygen enhanced nitrification. The DO level acted as the main diffusion control parameter regulating the extent of simultaneous nitrification and denitrification with different MLSS levels. The variation of DO depend on mixing intensity, sludge settling properties floc size, microbial community, reactor volume due to discrete points of oxygen input (mechanical aeration), and oxygen diffusion rate into the floc. The factors that affect oxygen diffusion in flocs among others included the variation between measured results due to steady-state and dynamic measuring techniques. Lower DO produces sludge with power settling properties but attain lower turbidities of the effluent that high DO. DO deficiency was believed to be one of the most frequent causes responsible for the most filamentous bacteria proliferation in activated sludge processes.

		Energy saving by low DO is feasible if sludge settleability does not become weak to affect the separation of sludge and effluent. It is advisable for nitrification to proceed without inhibition by oxygen limitation though adequately designed aeration equipment to supply the total oxygen demand. The DO above 2 mg/L allow nitrification to proceed with efficiency because the surface aerators, adequate velocity and aerator spacing were well fixed.
Sequence in the biological nitrogen removal	What is the significance of nitrogen in a biological wastewater treatment?	The reasons why it is difficult to obtain the desired level of nitrogen removal efficiency are: *i)* when nitrogen systems are overloaded; the anoxic sludge mass fraction is often reduced to a level that insufficient denitrification capacity remains for proper denitrification; *ii)* At anaerobic digestion, much quantity of nitrogen are released together with solid digested to the liquid phase that returns to the activated sludge systems, this increase the *TKN/COD* ratios of the influent; *iii) TKN* and *COD* ratios are high and that makes nitrogen removal more difficult as nitrate produced is directly related to the *TKN* concentration in the influent, whereas the denitrification capacity is directly linked to the presence of *(biodegradable) COD; iv)* low sludge age enhance the bio-P removal at the expense of nitrogen removal, whereas the opposite is true for a high sludge age; *v)* Primary clarifier or anaerobic pre-treatment units increases the ratio between *COD* and *TKN* in the pre-treated wastewater. The ammonia requirement for synthesis is, however, a negligible fraction of the total ammonia nitrified to nitrate by the nitrifiers at *1%*. The nitrifiers is said to utilize ammonia and nitrite principally for synthesis energy requirements *(catabolism)* but some ammonia uses anabolically for the synthesis of cell mass nitrogen requirement. The temperature increases the maximum specific growth rate of the biomass and increase in half saturation coefficient that enhances the efficiency of the biological processes in *WWTP*. The adequate supply of dissolved oxygen enhanced nitrification.
Effect of biological phosphorus removal	What is the significance of phosphorus in a biological wastewater treatment?	Phosphorus has an influence on the treatment options for the wastewater. This is because most of the nutrients are normally soluble, and hence they cannot be removed by settling, flotation, filtration or other means of solids-liquid separation. Due to higher nitrates concentration or low concentration of volatile fatty acids *(VFAs),* the biological phosphorus removal *(BPR)* is enhanced. High phosphorus in the mixed liquor served as macro-nutrients to the microbes in the wastewater treatment process. The phosphorus requirements decrease as the sludge age increases because net sludge production decreases as sludge age increases. Organic phosphorous models hydrolyze and particulate organic fraction directly to phosphates. It is not possible to transform dissolved *ortho-P* to gaseous form so as to increase the *P* removal from the liquid phase because additional *ortho-P* needs to be incorporated into the sludge mass into two forms; biological and chemically. The demerits of the removal of *P* is noted as; increase in the sludge production due to the inorganic solids formed, increases in salinity of the treated wastewater and increase in the complexity and cost of the wastewater treatment plant.
Impact of chlorine in the disinfection of the wastewater	What is the significance of chlorine in a biological wastewater treatment?	Chlorides are of concern in wastewater as they affect the final reuse of the effluent wastewater. Chlorine reacts with organics constituents in *WWTP* to produce odour compound like carcinogenic and mutagenic. The unconfined rapidly reduction of liquid chlorine in the effluent after dosing is due to vaporization of gas at standard temperature and pressure.

		Chlorine reacts with natural organic matter *(NOM)* to form a number of carcinogenic byproducts that include but not limit to haloacetic acids *(HAAs),* trihalomethanes *(THMs),* haloketones, haloacetonitriles, chloropicrin, chlorophenols, and cyanogen chloride. The wastewater and water bodies have been taken as disposal points for the chlorides, but chlorides are always removed using conventional methods.
Impact of food and microbial *(f/m)* ratio and the efficiency of nutrients removal	What is the significance of food to microbial ratio in a biological wastewater treatment?	The food to microbial ratio *F/M* ratio is related to the system solid retention time (*SRT*). *F/M* ratio is useful to the understanding of the effect of transient loads on the system, i.e. the higher the *COD* loading rate, the faster is the substrate utilization rate and thus higher substrate concentration in the reactor for the wastewater treatment. The *F/M* assist in fixing the sludge age by a means of simple control systems of the mass of sludge in the system by controlling the reactor mixed liquor volatile suspended solids *(MLVSS)* concentration at a specific value. The greater *COD* removal efficiency, the greater the difference between the parameter of settled and raw sewage. The sludge age should replace *F/M* ratio as a control parameter. In particular, nitrification governs the mass of sludge to be wasted daily from the system. This keeps the *MLSS* concentration in the reactor at some specified value of the operation. To keep *F/M* within the desired limit, the reactor *COD* concentration and flow pattern needed to be measured regularly to determine the daily *COD* mass load. During the winter season, the sludge age and *F/M* ratio were lower due to decrease in temperature that lowers endogenous respiration rate. This kept the ammonia concentration low.
Speciation of the trace metals	What is the impact of trace metals in biological wastewater treatment processes?	The sources of trace metals included the discharge from the industrial activities, products, products used in the residential applications such as personal care products and cleaning agents, groundwater infiltration and commercial discharge. Most trace metals contributed to metabolism and growth of micro-organism while others are accumulated either with the microbes and sludge discharge. Trace metals in wastewater are beneficial in terms of in metabolism, the growth of biological life and absence of sufficient quantities that lead to micro-pollution, toxicity and limit the growth of algae. Trace metals *(micro)* of importance in the biological wastewater treatment, reuse and disposal of biosolids included: irons, copper, lead, manganese, molybdenum, nickel, selenium, vanadium, zinc, aluminium, zinc, cobalt, chromium. The macro metals that are of importance to the metabolism and in the biological wastewater treatment included; calcium, sodium, iron, potassium and magnesium. Removal of trace metals from biological treatment processes is mainly by complexation of the metals with microorganisms, precipitation and adsorption. Microbes combine with metals ions and are discharge to the surface. The precipitation works under addition of chlorides for the formation of metal sulfides in anaerobic digestion. Trace metals are said to be complexed by carboxyl group found in microbial polysaccharides and other polymers or absorbed by protein materials in the biological cells. Regardless of the technology employed, the trace metal removal depends on physio-chemical properties of the micropollutants and the treatment conditions.
Bioinformatic	What are bioinformatics tools applied in	Implementation of the bioinformatics tools for mathematical modeling analysis in the intelligent wastewater treatment systems in counter-checking the behaviors of complex biomolecular systems, explanatory,

	mathematical modelling in wastewater treatment processes?	forecasting and predictions that are useful in the decision making and precisely engineering cellular functions, troubleshooting, design of new and upgrade of the existing *WWTPs,* and enhancing the effluent permissible limits on discharge to the environment.
Biomass Utilization and Beneficiations	What are the modern technologies for the biosolid utilization and beneficiation in the wastewater treatment plant?	Utilize biochar produced from sludge as an alternative adsorbent for commercial activated carbon for the removal of trace metal in wastewater treatment processes, tooth whitening and facial cleaning. Adopt blockchain quantitative-characterization of biomass that would contribute to affordable, sustainable, reliable, carbon-neutral form of modern energy and development of adequate waste-to-energy recovery management strategies in bridging the gap of the fourth industrial revolution. Scaling up and commercialization of the waste-to-energy (energy of thing) technologies *(biomethane production)* to cut off the operation cost and adoption of the sewage sludge as adsorbent *(biochar)* for the trace metal reduction in the wastewater treatment. A big-data anaerobic digestion platform by artificial neural network will assist on the comprehensive quantitative-characterization, microbial activities and parameters optimization in the biomethane production. In the renewable energy sector, a sensor attached to energy production equipment would transmit readings on parameters like the current, intake pressure and temperature leading to higher energy efficiency. Accumulated data can be analyzed to produce models correlating parameter changes to equipment problems. These models can be deployed to operations and new sensor data scored against them to flag potential issues for investigation before production is affected. The models can act as a realistic performance benchmark for the wastewater treatment process.
Wastewater to water utilization	What are the modern technologies for the wastewater utilization and beneficiation in the wastewater treatment plant?	Data science tools, big data, visual analytics and real-time stream processing capabilities on intelligence equipment management and production optimization can be used to process historical sensor error to surface patterns that predict process unit equipment efficiency. Making use of the effluent for the zero-soil *(hydroculture)* vertical and horizontal farming *(hydroponic)*, landscaping, cooling systems, hydropower generation, and irrigation that will eventually bring great value to the agribusiness investment.
Artificial Intelligence	What is the impact of Fourth Industrial Revolution (4IR) in the wastewater treatment technologies?	Further evaluation exploration of *AI* will prove beneficial in the WWTPs in developing a system that helps decision makers to arrive at a more transparent and systematics decision. Prioritized the innovative of on-line *(sensor)* in the parameter detection, sample analysis, data analysis and implementation. This will enhance holistic, automation, proactive and continuous monitoring, analysis, accumulation of historical quality data to *WWTP* monitoring risk network, enhance best WWTP practice and management, hotspot identification and increasing performance that meet regulatory *(permissible limits)* target. Embracing and driving fourth wave generation blockchain disruptive technology, robotics, sensors, automation technologies, sharing technologies, dematerialization, mobile ubiquity, advanced data analytics in the revolution of the wastewater systems, water management, renewable energy generation, environmentalism, mitigation of climate change, poverty eradication, improve health care, social and economic aspect in the realization of the National and United Nation sustainable development goals.

Online wastewater treatment	What is modern online technologies for the wastewater treatment?	Embrace innovative suction technology, decentralized intelligent wastewater treatment processes, biodegradable flush-less systems that save water loss in toilet flushing and online wastewater treatment before reaching wastewater treatment plant. This will cut operation cost in the treatment. Tap the inflows dynamics of the wastewater flows and implement the man-made whirlpool/underwater turbine transforming into electric energy for the running wastewater treatment plant and domestic use to the local communities. Online wastewater treatment in providing a renewable, sustainable and neural form of energy *(biomethane)* for implementation fourth industrial revolution: automation, blockchains, artificial intelligence, robotics, hyperloop and other vehicles, electricity generation, home and industrial heat and fire.
Energy-Water-Food nexus	How can we embrace the energy-water-food nexus in realization of the *2030* national goals and *UN* sustainable development goals?	Embracing the principles of the global trend in the energy-water-food nexus, emerging technologies with the *17* sustainable development goals are the world's bold and ambitious plan to end poverty, protect the plant and ensure that all mankind enjoy peace and prosperity. Implementation and policy measures with regards to the water-food-energy exploitation due to disruptive technologies such as *AI,* robotics, blockchain and advanced analytics should be enhanced. Enhance people, process and technology *(PPT),* upskilling to achieve objectives, achieving alternatives, operation cost recovery *(OCR)* and prove of concept *(POC)* implementation. Implement security data network *(security data issue reduction measures)* among the professional service providers *(PSP)*. Embrace decision making through data-driven culture (data economy) in achieving *2030* national goals and *UN* sustainable development goals.

REFERENCES

Abdel-Shafy, H.I. & Mansour, M.S.M. (2014). Biogas production as affected by heavy metals in the anaerobic digestion of sludge. *Egyptian Journal of Petroleum, 23*(4), 409-417.

Acero, J.L., Benítez, F.J., Real, F.J. & González, M. (2008). Chlorination of organophosphorus pesticides in natural waters. *Journal of hazardous materials, 153*(1-2), 320-328. doi: http://dx.doi.org/10.1016/j.jhazmat.2007.08.051

Ahluwalia, S.S. & Goyal, D. (2007). Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresource technology, 98*(12), 2243-2257.

Al-Khatib, I.A., Monou, M., Zahra, A.S.F.A., Shaheen, H.Q. & Kassinos, D. (2010). Solid waste characterization, quantification and management practices in developing countries. A case study: Nablus district – Palestine. *Journal of Environmental Management, 91*(5), 1131-1138.

American Public Health Association (APHA) (2005). Standard methods for the examination of water and wastewater. *American Public Health Association (APHA): Washington, DC, USA*.

Amin, S. (2009). Review on biofuel oil and gas production processes from microalgae. *Energy conversion and management, 50*(7), 1834-1840.

Anagnostopoulos, K.P., Gratziou, M. & Vavatsikos, A.P. (2007). Using the fuzzy analytic hierarchy process for selecting wastewater facilities at prefecture level. *European Water, 19*(20), 15-24.

Andersen, H.R., Lundsbye, M., Wedel, H.V., Eriksson, E. & Ledin, A. (2007). Estrogenic personal care products in a greywater reuse system. *Water Science and Technology, 56*(12), 45.

Angelidaki, I., Hendriksen, H.V., Mathrani, I., Schmidt, J., Sørensen, A. & Ahring, B. (1996). *The biogas process. Lecture notes for: Energy from biomass (6362)*.

Anjum, M., Al-Makishah, N.H. & Barakat, M.A. (2016). Wastewater sludge stabilization using pre-treatment methods. *Process Safety and Environmental Protection, 102*, 615-632.

Annika, K., Julika, P. & Adelphi, R. (Accessed 2016). Guidelines and StandardS for Wastewater Reuse. *EM-Learning-Berlin*.

Antoniou, P., Hamilton, J., Koopman, B., Jain, R., Holloway, B., Lyberatos, G. & Svoronos, S.A. (1990). Effect of temperature and pH on the effective maximum specific growth rate of nitrifying bacteria. *Water research, 24*(1), 97-101.

Association., (American Public Health Association), A.W.W., Federation., W.P.C. & Federation., W.E. (1915). *Standard methods for the examination of water and wastewater* (Vol. 2): American Public Health Association.

Barakat, M.A. (2011). New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry, 4*(4), 361-377.

Barker, P.S. & Dold, P.L. (1997). General model for biological nutrient removal activated-sludge systems: model application. *Water Environment Research, 69*(5), 985-991.

Barnabé, S., Brar, S.K., Tyagi, R.D., Beauchesne, I. & Surampalli, R.Y. (2009). Pre-treatment and bioconversion of wastewater sludge to value-added products − Fate of endocrine disrupting compounds. *Science of the Total Environment, 407*(5), 1471-1488.

Barron, F.H. & Barrett, B.E. (1996). The efficacy of SMARTER − Simple multi-attribute rating technique extended to ranking. *Acta Psychologica, 93*(1), 23-36.

Bavcon, M., Trebše, P. & Zupančič-Kralj, L. (2003). Investigations of the determination and transformations of diazinon and malathion under environmental conditions using gas chromatography coupled with a flame ionisation detector. *Chemosphere, 50*(5), 595-601. doi: http://dx.doi.org/10.1016/S0045-6535(02)00643-4

Beamish, F.E. (2012). *Analysis of noble metals: Overview and selected methods*: Elsevier.

Bedoux, G., Roig, B., Thomas, O., Dupont, V. & Le Bot, B. (2012). Occurrence and toxicity of antimicrobial triclosan and by-products in the environment. *Environmental Science and Pollution Research, 19*(4), 1044-1065.

Belanche, L.A., Valdés, J.J., Comas, J., Roda, I.R. & Poch, M. (1999). Towards a model of input-output behaviour of wastewater treatment plants using soft computing techniques. *Environmental modelling & software, 14*(5), 409-419.

Belgaied, J.E. & Trabelsi, H. (2003). Determination of cisapride, its oxidation product, propyl and butyl parabens in pharmaceutical dosage form by reversed-phase liquid chromatography. *Journal of Pharmaceutical and Biomedical Analysis, 33*(5), 991-998. doi: http://dx.doi.org/10.1016/S0731-7085(03)00421-7

Belton, V. (1986). A comparison of the analytic hierarchy process and a simple multi-attribute value function. *European Journal of Operational Research, 26*(1), 7-21.

Berkun, M. & Onal, A. (2004). Effects of inorganic metals on respirometric oxygen uptake and related Sag curve formations in streams. *Water S. A., 30*(2), 273-278.

Biller, D.V. & Bruland, K.W. (2012). Analysis of Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in seawater using the Nobias-chelate PA1 resin and magnetic sector inductively coupled plasma mass spectrometry (ICP-MS). *Marine Chemistry, 130*, 12-20.

Blanco, E., Casais, M.d.C., Mejuto, M.d.C. & Cela, R. (2009). Combination of off-line solid-phase extraction and on-column sample stacking for sensitive determination of parabens and p-hydroxybenzoic acid in waters by non-aqueous capillary electrophoresis. *Analytica Chimica Acta, 647*(1), 104-111. doi: http://dx.doi.org/10.1016/j.aca.2009.05.024

Błędzka, D., Gromadzińska, J. & Wąsowicz, W. (2014). Parabens. From environmental studies to human health. *Environment International, 67*, 27-42. doi: http://dx.doi.org/10.1016/j.envint.2014.02.007

Boleda, M.R., Galceran, M.T. & Ventura, F. (2011). Behavior of pharmaceuticals and drugs of abuse in a drinking water treatment plant (DWTP) using combined conventional and ultrafiltration and reverse osmosis (UF/RO) treatments. *Environmental Pollution, 159*(6), 1584-1591. doi: http://dx.doi.org/10.1016/j.envpol.2011.02.051

Bolong, N., Ismail, A.F., Salim, M.R. & Matsuura, T. (2009). A review of the effects of emerging contaminants in wastewater and options for their removal. *Desalination, 239*(1-3), 229-246. doi: http://dx.doi.org/10.1016/j.desal.2008.03.020

Bond, T., Huang, J., Graham, N.J.D. & Templeton, M.l.R. (2014). Examining the interrelationship between DOC, bromide and chlorine dose on DBP formation in drinking water − A case study. *Science of the Total Environment, 470-471*, 469-479. doi: http://dx.doi.org/10.1016/j.scitotenv.2013.09.106

Bottero, M., Comino, E. & Riggio, V. (2011). Application of the analytic hierarchy process and the analytic network process for the assessment of different wastewater treatment systems. *Environmental modelling & software, 26*(10), 1211-1224.

Bożym, M., Florczak, I., Zdanowska, P., Wojdalski, J. & Klimkiewicz, M. (2015). An analysis of metal concentrations in food wastes for biogas production. *Renewable energy, 77*, 467-472.

Brausch, J.M. & Rand, G.M. (2011). A review of personal care products in the aquatic environment: environmental concentrations and toxicity. *Chemosphere, 82*(11), 1518-1532.

Burgess, J.E., Quarmby, J. & Stephenson, T. (1999). Role of micronutrients in activated sludge-based biotreatment of industrial effluents. *Biotechnology advances, 17*(1), 49-70.

Canosa, P., Rodríguez, I., Rubí, E., Negreira, N. & Cela, R. (2006). Formation of halogenated by-products of parabens in chlorinated water. *Analytica Chimica Acta, 575*(1), 106-113. doi: http://dx.doi.org/10.1016/j.aca.2006.05.068

Chai, J., Liu, J.N.K. & Ngai, E.W.T. (2013). Application of decision-making techniques in supplier selection: A systematic review of literature. *Expert Systems with Applications, 40*(10), 3872-3885.

Chang, B.V., Wang, T.H. & Yuan, S.Y. (2007). Biodegradation of four phthalate esters in sludge. *Chemosphere, 69*(7), 1116-1123.

Chang, N.-B. & Davila, E. (2008). Municipal solid waste characterizations and management strategies for the Lower Rio Grande Valley, Texas. *Waste management, 28*(5), 776-794.

Chang, T.C., You, S.J., Damodar, R.l.A. & Chen, Y.Y. (2011). Ultrasound pre-treatment step for performance enhancement in an aerobic sludge digestion process. *Journal of the Taiwan Institute of Chemical Engineers, 42*(5), 801-808.

Chen, S.H., Jakeman, A.J. & Norton, J.P. (2008). Artificial intelligence techniques: an introduction to their use for modelling environmental systems. *Mathematics and computers in simulation, 78*(2-3), 379-400.

Cheng, S., Grosse, W., Karrenbrock, F. & Thoennessen, M. (2002). Efficiency of constructed wetlands in decontamination of water polluted by heavy metals. *Ecological Engineering, 18*(3), 317-325.

Chmielewski, A.G., Owczarczyk, A. & Palige, J. (1998). Radiotracer investigations of industrial waste water equalizer-clarifiers. *Nukleonika, 43*(2), 185-194.

Choi, D.J. & Park, H. (2001). A hybrid artificial neural network as a software sensor for optimal control of a wastewater treatment process. *Water research, 35*(16), 3959-3967.

Chowdhury, S. (2012). Associated cancer risks and medical expenses. Journal of Hazardous Materials 187: 574-584). *Journal of hazardous materials, 237*, 384-385. doi: 10.1016/j.jhazmat.2011.09.047

Clarke, B.O. & Smith, S.R. (2011). Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids. *Environment International, 37*(1), 226-247. doi: http://dx.doi.org/10.1016/j.envint.2010.06.004

Committee, W.T.p. (2013). *Wastewater Treatment Process Modelling* (Vol. Second Edition).
Crites, R. & Tchobanoglous, G. (1998). Small and Decentralized Wastewater Treatment Systems. *Boston/London, WCB/McGraw-Hill*.
Dabrowski, J.M., Shadung, J.M. & Wepener, V. (2014). Prioritizing agricultural pesticides used in South Africa based on their environmental mobility and potential human health effects. *Environment international, 62*, 31-40.
Danckwerts, P.V. (1953). Continuous flow systems: distribution of residence times. *Chemical Engineering Science, 2*(1), 1-13.
Das, N., Vimala, R. & Karthika, P. (2008). Biosorption of heavy metals-An overview. *Indian journal of Biotechnology, 7*(2), 159-169.
Davis, T.A., Volesky, B. & Mucci, A. (2003). A review of the biochemistry of heavy metal biosorption by brown algae. *Water research, 37*(18), 4311-4330.
De Souza Jr, L.R. & Lorenz, L. Residence Time Distribution for Tubular Reactors.
Dellana, S.A. & West, D. (2009). Predictive modeling for wastewater applications: Linear and nonlinear approaches. *Environmental modelling & software, 24*(1), 96-106.
Department of Water Affairs (DWA) (Accessed 2016). Wastewater treatment Plants in Gauteng. *https://www.dwa.gov.za/documents/gd/gdgt.pdf*.
Department of Water and Sanitation (DWS) (Accessed June 2016). General and Special Standards for the Wastewater Treatment, Requirements for The Purification of Waste Water or Effluent, Water Act 54 of 1984, South Africa.
Designs, T. (Accessed 2016). Application Note: Fluorescent Tracer Studies (www.turnerdesigns.com). *998-5121*, pp2-2.
Dimpe, K.M., Ngila, J.C., Mabuba, N. & Nomngongo, P.N. (2014). Evaluation of sample preparation methods for the detection of total metal content using inductively coupled plasma optical emission spectrometry (ICP-OES) in wastewater and sludge. *Physics and Chemistry of the Earth, Parts A/B/C, 76*, 42-48.
Dimpe, K.M. & Nomngongo, P.N. (2016). Current sample preparation methodologies for analysis of emerging pollutants in different environmental matrices. *TrAC Trends in Analytical Chemistry, 82*, 199-207.
Dipl-lng. M. & Schon, B.W. (2009). ”Numerical modeling of anaerobic digestion processes in Agricultural Biogas plants”. 4-26.
Dodgson, J.S., Spackman, M., Pearman, A. & Phillips, L.D. (2009). *Multi-criteria analysis: a manual*: Department for Communities and Local Government: London.
Driouich, R., Takayanagi, T., Oshima, M. & Motomizu, S. (2000). Separation and determination of haloperidol, parabens and some of their degradation products by micellar electrokinetic chromatography. *Journal of Chromatography A, 903*(1-2), 271-278. doi: http://dx.doi.org/10.1016/S0021-9673(00)00869-4
Duma, M., Marwala, T., Twala, B. & Nelwamondo, F. (2013). Partial imputation of unseen records to improve classification using a hybrid multi-layered artificial immune system and genetic algorithm. *Applied Soft Computing, 13*(12), 4461-4480.
DWS. (2016). Department of Water and Sanitation, Wastewater treatment Plants in Gauteng. https://www.dwa.gov.za/documents/gd/gdgt.pdf.

Edokpayi, J.N., Odiyo, J.O., Popoola, O.E. & Msagati, T.A.M. (2016). Assessment of Trace metals contamination of surface water and sediment: A case study of Mvudi River, South Africa. *Sustainability, 8*(2), 135.

Eelke, L.B. (2014). 'Building an explorative model of Biogas production process in an anaerobic digester,'. *Wageningen University*, 2-3.

Environmental Protection Agency (EPA) (2011). Principles of Design and Operations of Wastewate, Treatment Pond Systems for Plant Operators, Engineers, and Managers. *National Risk Management Research Laboratory – Land Remediation and Pollution Control Division*.

EPA (Environmental Protection Agency) (Accessed 2016). Standards and Potential Health effects of the Contaminants regulated under National Safe Drinking Water Act (SDWA) *Environmental Protection Agency (EPA)-USA, Act 1974*.

Eva, E. (2010). Workshop 3 Modelling of Biogas production http://www.mrtc.mdh.se/han/FoPlan/ass3-eva_ericson.

Farooq, M., Khan, I., Gul, S., Palige, J. & Dobrowolski, A. (2003). Radiotracer investigations of municipal sewage treatment stations. *Nukleonika, 48*(1), 57-61.

Farré, M.L., Pérez, S., Kantiani, L. & Barceló, D. (2008). Fate and toxicity of emerging pollutants, their metabolites and transformation products in the aquatic environment. *TrAC Trends in Analytical Chemistry, 27*(11), 991-1007. doi: http://dx.doi.org/10.1016/j.trac.2008.09.010

Fein, J.B., Daughney, C.J., Yee, N. & Davis, T.A. (1997). A chemical equilibrium model for metal adsorption onto bacterial surfaces. *Geochimica et Cosmochimica Acta, 61*(16), 3319-3328.

Ferretto, N., Tedetti, M., Guigue, C., Mounier, S., Redon, R. & Goutx, M. (2014). Identification and quantification of known polycyclic aromatic hydrocarbons and pesticides in complex mixtures using fluorescence excitation-emission matrices and parallel factor analysis. *Chemosphere, 107*, 344-353. doi: http://dx.doi.org/10.1016/j.chemosphere.2013.12.087

Filipe, C.D.M., Meinhold, J., Jørgensen, S.B., Daigger, G.T. & Grady, C.P. (2001). Evaluation of the potential effects of equalization on the performance of biological phosphorus removal systems. *Water Environment Research, 73*(3), 276-285.

Fischer, K., Fries, E., Korner, W., Schmalz, C. & Zwiener, C. (2012). New developments in the trace analysis of organic water pollutants. *Appl Microbiol Biotechnol, 94*(1), 11-28. doi: 10.1007/s00253-012-3929-z

Fu, F. & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: a review. *Journal of Environmental Management, 92*(3), 407-418.

Fytili, D. & Zabaniotou, A. (2008). Utilization of sewage sludge in EU application of old and new methods − a review. *Renewable and Sustainable Energy Reviews, 12*(1), 116-140.

Gallego, A., Hospido, A., Moreira, M.T. & Feijoo, G. (2008). Environmental performance of wastewater treatment plants for small populations. *Resources, Conservation and Recycling, 52*(6), 931-940.

Gans, N., Mobini, S. & Zhang, X.N. Appendix E. Mass and Energy Balances at the Gaobeidian Wastewater Treatment Plant in Beijing, China.

Gawdzik, J. & Gawdzik, B. (2012). Mobility of Heavy Metals in Municipal Sewage Sludge from Different Throughput Sewage Treatment Plants. *Polish Journal of Environmental Studies, 21*(6).

Geissen, V., Mol, H., Klumpp, E., Umlauf, G., Nadal, M., Van der Ploeg, M., . . . Ritsema, C.J. (2015). Emerging pollutants in the environment: A challenge for water resource management. *International Soil and Water Conservation Research, 3*(1), 57-65. doi: http://dx.doi.org/10.1016/j.iswcr.2015.03.002

George, D. & Mallery, P. (2016). *IBM SPSS Statistics 23 step by step: A simple guide and reference*: Routledge.

Gerber, M. & Span, R. (2008). An analysis of available mathematical models for anaerobic digestion of organic substances for production of biogas. *Proc. IGRC, Paris*.

Gernaey, K.V., Van Loosdrecht, M.C.M., Henze, M., Lind, M. & Jørgensen, S.B. (2004). Activated sludge wastewater treatment plant modelling and simulation: state of the art. *Environmental modelling & software, 19*(9), 763-783.

Goodfellow, I., Bengio, Y., Courville, A. & Bengio, Y. (2016). *Deep learning* (Vol. 1): MIT press Cambridge.

Gujer, W., Henze, M., Mino, T. & Van Loosdrecht, M. (1999). Activated sludge model no. 3. *Water science and technology, 39*(1), 183-193.

Guo, J., Peng, Y., Wang, S., Zheng, Y., Huang, H. & Wang, Z. (2009). Long-term effect of dissolved oxygen on partial nitrification performance and microbial community structure. *Bioresource technology, 100*(11), 2796-2802.

H., H.K. Design of an Activated Sludge Simulation Plant for the Treatment of Wastewater Using ChemCAD Simulation Software. *Water & Air Enterprises Ltd., Vancouver, BC. Canada*.

Haman, C., Dauchy, X., Rosin, C. & Munoz, J.-F. (2015). Occurrence, fate and behavior of parabens in aquatic environments: A review. *Water Research, 68*, 1-11. doi: http://dx.doi.org/10.1016/j.watres.2014.09.030

Haritash, A.K. & Kaushik, C.P. (2009). Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): a review. *Journal of hazardous materials, 169*(1), 1-15.

Hauduc, H., Rieger, L., Takács, I., Héduit, A., Vanrolleghem, P.A. & Gillot, S. (2010). A systematic approach for model verification: application on seven published activated sludge models. *Water science and technology, 61*(4), 825-839.

Health., N.Y.S.D. o. “Manual of Instruction for Water Treatment Plant Operators “.

Heidler, J. & Halden, R.U. (2007). Mass balance assessment of triclosan removal during conventional sewage treatment. *Chemosphere, 66*(2), 362-369.

Hellinga, C., Schellen, A.A.J.C., Mulder, J.W., Van Loosdrecht, M.C.M. & Heijnen, J.J. (1998). The SHARON process: an innovative method for nitrogen removal from ammonium-rich waste water. *Water science and technology, 37*(9), 135-142.

Henze, M. (2000). *Activated sludge models ASM1, ASM2, ASM2d and ASM3* (Vol. 9): IWA publishing.

Henze, M. (2008). Biological wastewater treatment: principles, modelling and design. *London: IWA Publ*, 401-437.

Henze, M. & Comeau, Y. (2008). Wastewater characterization. *Biological wastewater treatment: principles, modelling and design. IWA Publishing, London*, 33-52.

Henze, M., Grady, C.P.L., Gujer, W., Marais, G.V.R. & Matsuo, T. (1987). Activated sludge model No. 1. IAWPRC Task group on mathematical modelling for design and operation of biological wastewater treatment. *IAWPRC Scientific and Technical Reports, London*.

Henze, M., Gujer, W., Mino, T., Matsuo, T., Wentzel, M.C., vR Marais, G. & Van Loosdrecht, M.C.M. (1999). Activated sludge model no. 2d, ASM2d. *Water science and technology, 39*(1), 165-182.

Henze, M., Gujer, W., Takashi, M. & Van Loosdrecht, M. (2002). Activated Sludge Models ASM1, ASM2, ASM2D and ASM3; IWA Task group on Mathematical Modelling for Design and Operation of Biological Wastewater Treatment. *IWA Publisher*.

Henze, M., Van Loosdrecht, M.C.M., Ekama, G.A. & Brdjanovic, D. (2008). *Biological wastewater treatment*: IWA publishing.

Hernández, F., Portolés, T., Pitarch, E.A. & López, F.O.J. (2007). Target and nontarget screening of organic micropollutants in water by solid-phase microextraction combined with gas chromatography/high-resolution time-of-flight mass spectrometry. *Analytical Chemistry, 79*(24), 9494-9504.

Herselman, J.E. & Moodley, P. (2009). Guideline for the utilization and disposal of wastewater sludge. *Water Research Commission Report No. TT 350/09, 4 and 5*.

Hocaoglu, S.M., Insel, G., Cokgor, E.U. & Orhon, D. (2011). Effect of low dissolved oxygen on simultaneous nitrification and denitrification in a membrane bioreactor treating black water. *Bioresource technology, 102*(6), 4333-4340.

Hong, Y.T., Rosen, M.R. & Bhamidimarri, R. (2003). Analysis of a municipal wastewater treatment plant using a neural network-based pattern analysis. *Water research, 37*(7), 1608-1618.

Hu, Z., Wentzel, M.C. & Ekama, G.A. (2007). A general kinetic model for biological nutrient removal activated sludge systems: Model development. *Biotechnology and Bioengineering, 98*(6), 1242-1258.

Huang, H.-Y., Lai, Y.-C., Chiu, C.-W. & Yeh, J.-M. (2003). Comparing micellar electrokinetic chromatography and microemulsion electrokinetic chromatography for the analysis of preservatives in pharmaceutical and cosmetic products. *Journal of Chromatography A, 993*(1-2), 153-164. doi: http://dx.doi.org/10.1016/S0021-9673(03)00395-9

Hyland, K.C., Dickenson, E.R.V., Drewes, J.E. & Higgins, C.R.P. (2012). Sorption of ionized and neutral emerging trace organic compounds onto activated sludge from different wastewater treatment configurations. *Water research, 46*(6), 1958-1968.

IAEA (International Atomic Energy Agency) (2011a). Radioactive applications in wastewater treatment plants. *International Atomic Energy Agency., Training course series 46*.

IAEA (2011b). Radioactive applications in wastewater treatment plants. International Atomic Energy Agency. *Training course series 46.*

IWA (International Water Association ((Accessed February 2018). International Water Association (IWA) Task Group on Benchmarking of Control Strategies for WWTPs. *http://apps.ensic.inpl-nancy.fr/benchmarkWWTP/*.

Jenkins, D., Richard, M G. & Daigger, G.T. (1993). Manual on the causes and control of activated sludge bulking and foaming. 2 *Manual on the causes and control of activated sludge bulking and foaming. 2. ed*: Lewis.

Jeppsson, U. (1996). *Modelling aspects of wastewater treatment processes*: IEA, LTH, Box 118, SE-221 00 Lund, Sweden.

Kamika, I., Coetzee, M., Mamba, B.B., Msagati, T. & Momba, M.B.N. (2014). The impact of microbial ecology and chemical profile on the enhanced biological phosphorus removal (EBPR) process: a case study of Northern Wastewater Treatment Works, Johannesburg. *International journal of environmental research and public health, 11*(3), 2876-2898.

Kanchanamayoon, W. & Tatrahun, N. (2008). Determination of polycyclic aromatic hydrocarbons in water samples by solid-phase extraction and gas chromatography. *World J Chem*, p. 51-54.

Kang, J.H., Katayama, Y. & Kondo, F. (2006). Biodegradation or metabolism of bisphenol A: from microorganisms to mammals. *Toxicology, 217*(2), 81-90.

Karimi, A.R., Mehrdadi, N., Hashemian, S.J., Bidhendi, G.R.N. & Moghaddam, R.T. (2011). Selection of wastewater treatment process based on the analytical hierarchy process and fuzzy analytical hierarchy process methods. *International Journal of Environmental Science & Technology, 8*(2), 267-280.

Karlsson, A., Einarsson, P., Schnürer, A., Sundberg, C., Ejlertsson, J. & Svensson, B.H. (2012). Impact of trace element addition on degradation efficiency of volatile fatty acids, oleic acid and phenyl acetate and on microbial populations in a biogas digester. *Journal of bioscience and bioengineering, 114*(4), 446-452.

Karvelas, M., Katsoyiannis, A. & Samara, C. (2003). Occurrence and fate of heavy metals in the wastewater treatment process. *Chemosphere, 53*(10), 1201-1210.

Kigozi, R., Aboyade, A.O. & Muzenda, E. (2014). Technology selection of biogas digesters for OFMSW via multi-criteria decision analysis.

Köck-Schulmeyer, M., Villagrasa, M., de Alda, M.L., Céspedes-Sánchez, R., Ventura, F. & Barceló, D. (2013). Occurrence and behavior of pesticides in wastewater treatment plants and their environmental impact. *Science of the Total Environment, 458*, 466-476.

Langergraber, G., Rieger, L., Winkler, S., Alex, J., Wiese, J., Owerdieck, C., . . . Maurer, M. (2004a). A guideline for simulation studies of wastewater treatment plants. *Water Science & Technology, 50*(7), 131-138.

Leake, D.B. (1996). *Case-Based Reasoning: Experiences, lessons and future directions*: MIT press.

Lee, H.-B., Peart, T.E. & Svoboda, M.L. (2005). Determination of endocrine-disrupting phenols, acidic pharmaceuticals, and personal-care products in sewage by solid-phase extraction and gas chromatography-mass spectrometry. *Journal of Chromatography A, 1094*(1-2), 122-129. doi: http://dx.doi.org/10.1016/j.chroma.2005.07.070

Lee, M.-R., Lin, C.-Y., Li, Z.-G. & Tsai, T.-F. (2006). Simultaneous analysis of antioxidants and preservatives in cosmetics by supercritical fluid extraction combined with liquid chromatography-mass spectrometry. *Journal of Chromatography A, 1120*(1-2), 244-251. doi: http://dx.doi.org/10.1016/j.chroma.2006.01.075

Lemoine, F., Maupin, I., Lemée, L., Lavoie, J.-M., Lemberton, J.-L., Pouilloux, Y. & Pinard, L. (2013). Alternative fuel production by catalytic hydroliquefaction of solid municipal wastes, primary sludges and microalgae. *Bioresource technology, 142*, 1-8.

Levenspiel, O. (1972). Chemical reaction engineering. *Wiley, New York, 2nd*. Ed

Liu, Y S., Ying, G.G., Shareef, A. & Kookana, R.S. (2012). Occurrence and removal of benzotriazoles and ultraviolet filters in a municipal wastewater treatment plant. *Environmental pollution, 165*, 225-232. doi: http://dx.doi.org/10.1016/j.envpol.2011.10.009

Lubliner, B., Redding, M. . & Ragsdale, D. (2010). *Pharmaceuticals and personal care products in municipal wastewater and their removal by nutrient treatment technologies*: Washington State Department of Ecology.

Luo, Y., Guo, W., Ngo, H.H., Nghiem, L.D., Hai, F.I., Zhang, J., . . . Wang, X.C. (2014). A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Science of The Total Environment, 473*, 619-641.

Ma, J. *et al.* (2009). Determination of organophosphorus pesticides in underground water by SPE-GC-MS. . *Journal of chromatographic science, 47(2)*, p. 110-115.

Mackenzie, L.D. (2011). Water and wastewater engineering, design principles and practice. *McGraw-Hill International Edition*.

Madikizela, L.M., Muthwa, S.F. & Chimuka, L. (2014). Determination of Triclosan and Ketoprofen in river water and wastewater by solid phase extraction and high performance liquid chromatography. *South African Journal of Chemistry, 67*, 0-0.

Mamais, D. & Jenkins, D. (1992). The effects of MCRT and temperature on enhanced biological phosphorus removal. *Water science and technology, 26*(5-6), 955-965.

Manu, D.S. & Thalla, A.K. (2017). Artificial intelligence models for predicting the performance of biological wastewater treatment plant in the removal of Kjeldahl Nitrogen from wastewater. *Applied Water Science*, 1-9.

Marlene, M.B. & Leonardo, M. (Accessed 2016). Operational monitoring and management procedures for municipal wastewater treatment operations. *Water Research Commission, Report TT489/11*.

Márquez-Sillero, I., Aguilera-Herrador, E., Cárdenas, S. & Valcárcel, M. (2010). Determination of parabens in cosmetic products using multi-walled carbon nanotubes as solid phase extraction sorbent and corona-charged aerosol detection system. *Journal of Chromatography A, 1217*(1), 1-6. doi: http://dx.doi.org/10.1016/j.chroma.2009.11.005

Martínez Vidal, J. L., Plaza-Bolaños, P., Romero-González, R. & Garrido Frenich, A. (2009). Determination of pesticide transformation products: A review of extraction and detection methods. *Journal of Chromatography A, 1216*(40), 6767-6788. doi: http://dx.doi.org/10.1016/j.chroma.2009.08.013

Matheri, A.N., Mbohwa, C., Belaid, M., Seodigeng, T. & Ngila, J.C. (2016). Multi-criteria analysis of different technologies for the bioenergy recovery from OFMSW.

Matheri, A.N., Mbohwa, C., Ntuli, F., Belaid, M., Seodigeng, T., Ngila, J.C. & Njenga, C.K. (2018). Waste to energy bio-digester selection and design model for the organic fraction of municipal solid waste. *Renewable and Sustainable Energy Reviews, 82*, 1113-1121.

Mathworks, I. (1994-2018a). Deep learning, https://www.mathworks.com/discovery/deep-learning.html.

Meena, P., Peter, H.G., Lucy, A., Michael, J.C., Juliet, C.S. & Courtne, Y.S. (2010). Clearing the Waters A focus on the water quality solutions. 1-91.

Mellit, A. & Kalogirou, S.A. (2008). Artificial intelligence techniques for photovoltaic applications: A review. *Progress in energy and combustion science, 34*(5), 574-632.

Meng, X.Z., Wang, Y., Xiang, N., Chen, L., Liu, Z., Wu, B., . . . Ebinghaus, R. (2014). Flow of sewage sludge-borne phthalate esters (PAEs) from human release to human intake: implication for risk assessment of sludge applied to soil. *Science of the Total Environment, 476*, 242-249.

Metcalf, E. (1979). ”Wastewater Engineering Treatment, Disposal “Reuse, McGraw-Hill 2nd Edition

Metcalf, E. “Wastewater Engineering Treatment, Disposal and Reuse”, McGraw-hill International Editions 3rd Edition.

Metcalf, L., Eddy, H.P. & Tchobanoglous, G. (2010). Waste Water Engineering: Treatment, Disposal, and Reuse. *McGraw-Hill*.

Miezah, K., Obiri-Danso, K., Kádár, Z., Fei-Baffoe, B. & Mensah, M.Y. (2015). Municipal solid waste characterization and quantification as a measure towards effective waste management in Ghana. *Waste management, 46*, 15-27.

Mingzhi, H., Jinquan, W., Yongwen, M., Yan, W., Weijiang, L. & Xiaofei, S. (2009). Control rules of aeration in a submerged biofilm wastewater treatment process using fuzzy neural networks. *Expert Systems with Applications, 36*(7), 10428-10437.

Mjalli, F.S., Al-Asheh, S. & Alfadala, H.E. (2007). Use of artificial neural network black-box modeling for the prediction of wastewater treatment plants performance. *Journal of Environmental Management, 83*(3), 329-338.

Mogolodi, D., Ngila, J.C. & Mabuba, N. (2015). Sample preparation techniques for determination of total metal content in wastewater treatment plants in Gauteng province. *https://ujdigispace.uj.ac.za/bitstream/handle/10210/13709/Dimpe%20MsC%20Thesis%2817-02-15%29-Finale.pdf?sequence=1&isAllowed=y*.

Mohan, D. & Pittman Jr, C.U. (2007). Arsenic removal from water/wastewater using adsorbents − a critical review. *Journal of hazardous materials, 142*(1-2), 1-53.

Moja, S.J. & Mtunzi, F. (2013). Application of solid phase extraction (SPE) method in determining polycyclic aromatic hydrocarbons (PAHs) in river water samples. *Journal of environmental chemistry and ecotoxicology, 5*(11), 278-283.

Mullen, M.D., Wolf, D.C., Ferris, F.G., Beveridge, T.J., Flemming, C.A. & Bailey, G.W. (1989). Bacterial sorption of heavy metals. *Applied and environmental microbiology, 55*(12), 3143-3149.

Murthy, R.C. (Accessed 2016). Analysis of heavy metals in the water and wastewater. *Metal analysis laboratory Industrial Toxicology Research Centre, Lucknow, Chapter 6*.

Nalli, S., Cooper, D.G. & Nicell, J.A. (2006). Metabolites from the biodegradation of di-ester plasticizers by Rhodococcus rhodochrous. *Science of the Total Environment, 366*(1), 286-294.

Nalli, S., Horn, O.J., Grochowalski, A.R., Cooper, D.G. & Nicell, J.A. (2006). Origin of 2-ethylhexanol as a VOC. *Environmental pollution, 140*(1), 181-185.

Nasr, M.S., Moustafa, M.A.E., Seif, H.A.E. & El Kobrosy, G. (2012). Application of Artificial Neural Network (ANN) for the prediction of EL-AGAMY wastewater treatment plant performance-EGYPT. *Alexandria engineering journal, 51*(1), 37-43.

Neves, E.R., Schäfer, S., Phillips, A., Canejo, J. & Macedo, M.F. (2009). Antifungal effect of different methyl and propyl paraben mixtures on the treatment of paper biodeterioration. *International Biodeterioration & Biodegradation, 63*(3), 267-272. doi: http://dx.doi.org/10.1016/j.ibiod.2008.07.011

Ngia, L.S.H. & Sjoberg, J. (2000). Efficient training of neural nets for nonlinear adaptive filtering using a recursive Levenberg-Marquardt algorithm. *IEEE Transactions on Signal Processing, 48*(7), 1915-1927.

Oishi, S. (2002). Effects of propyl paraben on the male reproductive system. *Food and Chemical Toxicology, 40*(12), 1807-1813. doi: http://dx.doi.org/10.1016/S0278-6915(02)00204-1

Ojeda-Benítez, S., Armijo-de Vega, C. & Marquez-Montenegro, M.Y. (2008). Household solid waste characterization by family socioeconomic profile as unit of analysis. *Resources, Conservation and Recycling, 52*(7), 992-999.

P.S., V. (2001). Exemption granted in terms of section 21 (4) of the water act, 1956 in respect of the purificaton or treatment of water used for industrial purposes. *Department of Water Affairs and Forestry-South Africa*.

Pai, T.Y., Wan, T.J., Hsu, S.T., Chang, T.C., Tsai, Y.P., Lin, C.Y., . . . Yu, L.F. (2009). Using fuzzy inference system to improve neural network for predicting hospital wastewater treatment plant effluent. *Computers & Chemical Engineering, 33*(7), 1272-1278.

Pai, T.Y., Yang, P.Y., Wang, S.C., Lo, M.H., Chiang, C.F., Kuo, J.L., . . . Hu, H.C. (2011). Predicting effluent from the wastewater treatment plant of industrial park based on fuzzy network and influent quality. *Applied Mathematical Modelling, 35*(8), 3674-3684.

Paíga, P., Lolić, A., Hellebuyck, F., Santos, L.H., Correia, M. & Delerue-Matos, C. (2015). Development of a SPE-UHPLC-MS/MS methodology for the determination of non-steroidal anti-inflammatory and analgesic pharmaceuticals in seawater. *Journal of pharmaceutical and biomedical analysis, 106*, 61-70.

Palani, S., Liong, S. & Tkalich, P. (2008). An ANN application for water quality forecasting. *Marine pollution bulletin, 56*(9), 1586-1597.

Parawira, W. (2004). *Anaerobic Treatment of Agricultural Residues and Wastewater-Application of High-Rate Reactors*: Lund University.

Pedrouzo, M., Borrull, F., Marcé, R.M. & Pocurull, E. (2011). Analytical methods for personal-care products in environmental waters. *TrAC Trends in Analytical Chemistry, 30*(5), 749-760. doi: http://dx.doi.org/10.1016/j.trac.2011.01.009

Perlovich, G.L., Rodionov, S.V. & Bauer-Brandl, A. (2005). Thermodynamics of solubility, sublimation and solvation processes of parabens. *European Journal of Pharmaceutical Sciences, 24*(1), 25-33. doi: http://dx.doi.org/10.1016/j.ejps.2004.09.007

Peter, L. & Freese, S. (2009). A Simple Guide to the Chemistry Selection and Use of Chemicals for Water and Wastewater Treatment (pp. 1-136). Pretoria: Water Research Commission.

Pietrogrande, M.C. & Basaglia, G. (2007). GC-MS analytical methods for the determination of personal-care products in water matrices. *TrAC Trends in Analytical Chemistry, 26*(11), 1086-1094. doi: http://dx.doi.org/10.1016/j.trac.2007.09.013

Pitarch, E., Portoles, T., Marin, J.M., Ibanez, M., Albarran, F. & Hernandez, F. (2010). Analytical strategy based on the use of liquid chromatography and gas chromatography with triple-quadrupole and time-of-flight MS analyzers for investigating organic contaminants in wastewater. *Analytical and Bioanalytical Chemistry, 397*(7), 2763-2776. doi: 10.1007/s00216-010-3692-x

Poch, M., Comas, J., Rodríguez-R.I., Sanchez-M.M. & Cortés, U. (2004). Designing and building real environmental decision support systems. *Environmental modelling & software, 19*(9), 857-873.

Pohekar, S.D. & Ramachandran, M. (2004). Application of multi-criteria decision making to sustainable energy planning − a review. *Renewable and Sustainable Energy Reviews, 8*(4), 365-381.

Pomiès, M., Choubert, J.M., Wisniewski, C. & Coquery, M. (2013). Modelling of micropollutant removal in biological wastewater treatments: a review. *Science of The Total Environment, 443*, 733-748.

Porubova, J., Bazbauers, G. & Markova, D. (2011). Modeling of the Adiabatic and Isothermal Methanation Process. *Scientific Journal of Riga Technical University. Environmental and Climate Technologies, 6*(1), 79-84.

Prusakiewicz, J. J., Harville, H. M., Zhang, Y., Ackermann, C. & Voorman, R. L. (2007). Parabens inhibit human skin estrogen sulfotransferase activity: Possible link to paraben estrogenic effects. *Toxicology, 232*(3), 248-256. doi: http://dx.doi.org/10.1016/j.tox.2007.01.010

Qing, X.X., Wang, B. & Meng, D. (2005). Applications of artificial intelligence technology to wastewater treatment fields in China. *Journal of Chongqing University, 4*(4), 213-217.

Raduly, B., Gernaey, K.V., Capodaglio, A.G., Mikkelsen, P.S. & Henze, M. (2007). Artificial neural networks for rapid WWTP performance evaluation: Methodology and case study. *Environmental modelling & software, 22*(8), 1208-1216.

Ramos, S., Homem, V., Alves, A. & Santos, L. (2016). A review of organic UV-filters in wastewater treatment plants. *Environment international, 86*, 24-44.

Rathnayake, R.M.L.D., Oshiki, M., Ishii, S., Segawa, T., Satoh, H. & Okabe, S. (2015). Effects of dissolved oxygen and pH on nitrous oxide production rates in autotrophic partial nitrification granules. *Bioresource technology, 197*, 15-22.

Raval, N. P., Shah, P.U. & Shah, N.K. (2016). Adsorptive removal of nickel (II) ions from aqueous environment: a review. *Journal of Environmental Management, 179*, 1-20.

Richardson, S.D., Plewa, M.L.J., Wagner, E.D., Schoeny, R. & DeMarini, D.M. (2007). Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research. *Mutation Research/Reviews in Mutation Research, 636*(1), 178-242.

Richardson, S.D. & Ternes, T.A. (2011). Water Analysis: Emerging Contaminants and Current Issues. *Analytical Chemistry, 83*(12), 4614-4648. doi: 10.1021/ac200915r

Rieger, L., Gillot, S., Langergraber, G., Ohtsuki, T., Shaw, A., Takacs, I. & Winkler, S. (2012). *Guidelines for using activated sludge models*: IWA publishing.

Rieger, L., Koch, G., Kühni, M., Gujer, W. & Siegrist, H. (2001). The EAWAG Bio-P module for activated sludge model No. 3. *Water research, 35*(16), 3887-3903.

Rivera, F., Pinzón, R., Barragán, M., Arjona, I., Broce, K., Deago, E., . . . Brisset, P. (2012). radiotracer test performed at Howard Waste Water Treatment Plant in Panamá City, Panamá. *Tracer 7 – Seventh International Conference Tracers and Tracing Methods*.

Rizzoli, A.E. & Young, W.J. (1997). Delivering environmental decision support systems: software tools and techniques. *Environmental modelling & software, 12*(2-3), 237-249.

Roda, I.R., Poch, M. & Bañares-Alcántara, R. (2000). Application of a support system to the design of wastewater treatment plants. *Artificial Intelligence in Engineering, 14*(1), 45-61.

Rudi, S. & Marlene, V.M. (2013). "Wastewater treatment plants in South Africa''.

Russ, K. (2009). A Review of the Evidence: Health Effects of Personal Care Products. *Nursing for Women's Health, 13*(5), 392-401.

Saaty, T.L. (2004). Decision making − the analytic hierarchy and network processes (AHP/ANP). *Journal of systems science and systems engineering, 13*(1), 1-35.

Sanders, W.T.M., Veeken, A.H.M., Zeeman, G. & Van Lier, J.B. (2003). Analysis and optimization of the anaerobic digestion of the organic fraction of municipal solid waste. *Biomethanization of the organic fraction of municipal solid wastes. IWA, London*, 63-90.

Sasi, S., Rayaroth, M.P., Devadasan, D., Aravind, U.K. & Aravindakumar, C.T. (2015). Influence of inorganic ions and selected emerging contaminants on the degradation of Methylparaben: A sonochemical approach. *Journal of Hazardous Materials, 300*, 202-209. doi: http://dx.doi.org/10.1016/j.jhazmat.2015.06.072

Schattauer, A., Abdoun, E., Weiland, P., Plöchl, M. & Heiermann, M. (2011). Abundance of trace elements in demonstration biogas plants. *Biosystems Engineering, 108*(1), 57-65.

Scientific, T.F. (2009). iTEVA software manual.

Scientific, T.F. (2009). ICP emission spectrometer. *ICAP 6000 series*.

Semblante, G.U., Hai, F.I., Huang, X., Ball, A.S., Price, W.E. & Nghiem, L.D. (2015). Trace organic contaminants in biosolids: impact of conventional wastewater and sludge processing technologies and emerging alternatives. *Journal of hazardous materials, 300*, 1-17.

Shamuyarira, K.K. & Gumbo, J.R. (2014). Assessment of heavy metals in municipal sewage sludge: A case study of Limpopo Province, South Africa. *International journal of environmental research and public health, 11*(3), 2569-2579.

Shanmugam, G., Ramaswamy, B.R., Radhakrishnan, V. & Tao, H. (2010). GC-MS method for the determination of paraben preservatives in the human breast cancerous tissue. *Microchemical Journal, 96*(2), 391-396. doi: http://dx.doi.org/10.1016/j.microc.2010.07.005

Shaw, S. (2010). Halogenated flame retardants: do the fire safety benefits justify the risks? *Reviews on environmental health, 25*(4), 261-306.

Sheoran, A.S. & Sheoran, V. (2006). Heavy metal removal mechanism of acid mine drainage in wetlands: a critical review. *Minerals engineering, 19*(2), 105-116.

Singanan, M. & Peters, E. (2013). Removal of toxic heavy metals from synthetic wastewater using a novel biocarbon technology. *Journal of Environmental Chemical Engineering, 1*(4), 884-890.

Singh, K.P., Basant, A., Malik, A. & Jain, G. (2009). Artificial neural network modeling of the river water quality − a case study. *Ecological Modelling, 220*(6), 888-895.

Skoczyńska, E., Korytár, P. & Boer, J.d. (2008). Maximizing chromatographic information from environmental extracts by GCxGC-ToF-MS. *Environmental science & technology, 42*(17), 6611-6618.

Smolders, G.J.F., Van der Meij, J., Van Loosdrecht, M.C.M. & Heijnen, J.J. (1995). A structured metabolic model for anaerobic and aerobic stoichiometry and kinetics of the biological phosphorus removal process. *Biotechnology and Bioengineering, 47*(3), 277-287.

Soni, M.G., Carabin, I.G. & Burdock, G.A. (2005). Safety assessment of esters of p-hydroxybenzoic acid (parabens). *Food and Chemical Toxicology, 43*(7), 985-1015. doi: http://dx.doi.org/10.1016/j.fct.2005.01.020

Sötemann, S.W., Van Rensburg, P., Ristow, N.E., Wentzel, M.C., Loewenthal, R.E. & Ekama, G.A. (2005). Integrated chemical/physical and biological processes modeling Part 2-Anaerobic digestion of sewage sludges. *Water Sa, 31*(4), 545-568.

Sötemann, S.W., Wentzel, M.C. & Ekama, G.A. (2006). Mass balance-based plant-wide wastewater treatment plant models – Part 4: Aerobic digestion of primary and waste activated sludges. *Water Sa, 32*(3), 297-306.

SPSS, I. (2016). Statistical analysis software package – IBM SPSS Statistics.

Sreekrishnan, T.R., Kohli, S. & Rana, V. (2004). Enhancement of biogas production from solid substrates using different techniques – a review. *Bioresource technology, 95*(1), 1-10.

Srivastava, N.K. & Majumder, C.B. (2008). Novel biofiltration methods for the treatment of heavy metals from industrial wastewater. *Journal of hazardous materials, 151*(1), 1-8.

Stack, M. M., Huang, W., Wang, G. & Hodge, C. (2011). Some views on the construction of bio-tribo-corrosion maps for Titanium alloys in Hank's solution: Particle concentration and applied loads effects. *Tribology International, 44*(12), 1827-1837.

Stamatelatou, K., Pakou, C. & Lyberatos, G. (2011). Occurrence, Toxicity, and Biodegradation of Selected Emerging Priority Pollutants in Municipal Sewage Sludge. Comprehensive Biotechnology . M. Moo-Young: Burlington, Academic Press.

Stamou, I. & Antizar-Ladislao, B. (2016). A life cycle assessment of the use of compost from contaminated biodegradable municipal solid waste with silver and titanium dioxide nanoparticles. *Journal of cleaner production, 135*, 884-891.

Stenstrom, M.K. & Poduska, R.A. (1980). The effect of dissolved oxygen concentration on nitrification. *Water research, 14*(6), 643-649.

Stenstrom., M.K. (2003). Fundamentals of Chemical Reactor Theory. . *Civil & Environmental Engineering Department, University of California, Los Angeles*.

Steter, J.R., Rocha, R.S., Dionísio, D., Lanza, M.R.V. & Motheo, A.J. (2014). Electrochemical oxidation route of methyl paraben on a boron-doped diamond anode. *Electrochimica Acta, 117*, 127-133. doi: http://dx.doi.org/10.1016/j.electacta.2013.11.118

Stevens-Garmon, J., Drewes, J. E., Khan, S.J., McDonald, J.A. & Dickenson, E.R.V. (2011). Sorption of emerging trace organic compounds onto wastewater sludge solids. *Water research, 45*(11), 3417-3426.

Sundararajan, R., Jayanthi, S. & Elango, R. (1997). Anaerobic digestion of organic fractions of municipal solid waste and domestic sewage of Coimbatore. *Indian Journal of Environmental Health, 39*(3), 193-196.

Takács, I. & Vanrolleghem, P.A. (2006). *Elemental balances in activated sludge modelling.* Paper presented at the Proceedings of IWA World Water Congress.

Terasaki, M., Yasuda, M., Makino, M. & Shimoi, K. (2015). Aryl hydrocarbon receptor potency of chlorinated parabens in the aquatic environment. *Environmental Science: Water Research & Technology, 1*(3), 375-382. doi: 10.1039/C5EW00047E

Thomaidi, V.S., Stasinakis, A.S., Borova, V.L. & Thomaidis, N.S. (2015). Is there a risk for the aquatic environment due to the existence of emerging organic contaminants in treated domestic wastewater? Greece as a case-study. *J Hazard Mater, 283*, 740-747. doi: 10.1016/j.jhazmat.2014.10.023. S0304-3894(14)00844-9 [pii]

Trenholm, R.A., Vanderford, B.J., Drewes, J.E. & Snyder, S.A. (2008). Determination of household chemicals using gas chromatography and liquid chromatography with tandem mass spectrometry. *Journal of Chromatography A, 1190*(1-2), 253-262. doi: http://dx.doi.org/10.1016/j.chroma.2008.02.032

USEPA (U.S Environmental Protection Agency) (1986). Design Manual: Municipal Wastewater Disinfection, U.S Environmental Protection Agency Publication EPA 625/1-86/021, Washington, D.C.

USEPA (1991). (1991) Guidance Manual for Compliance with Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Sources. *U.S. Environmental Protection Agency, Washington, D.C.*

USEPA (1994). National Primary Drinking Water Regulations; Disinfectants and Disinfection Byproducts: Proposed. *Federal Register, 59*, 38,668-638,829.

Vahdani, B. & Naderi-Beni, M. (2014). A mathematical programming model for recycling network design under uncertainty: an interval-stochastic robust optimization model. *The International Journal of Advanced Manufacturing Technology, 73*(5-8), 1057-1071.

Van der Merwe-Botha, M. (2009). Water quality: A vital dimension of water security. *Development Planning Division Working Paper No, 14*.

Van Eeden, P.H. & Schoonbee, H.J. (1996). Metal concentration in liver, kidney, bone and blood of three species of birds from metals polluted wetland. *Water SA*.

Van Haandel, A. & Van Der Lubbe, J. (2012). *Handbook of biological wastewater treatment*: Iwa Publishing.

Van Veldhuizen, H.M., Van Loosdrecht, M.C.M. & Heijnen, J.J. (2015). Model development and full-scale testing. *Applications of Activated Sludge Models*, 69.

Van Wyk, C.S. (2011). Removal of heavy metals from metal-containing effluent by yeast biomass. *African Journal of Biotechnology, 10*(55), 11557-11561.

Vega, P., Alawneh, F., Gonzalez, L., Francisco, M. & Perez, B. A Computer Based Tool for the Simulation, Integrated Design and Advanced Control of Wastewater Treatment Processes.

Veglio, F. & Beolchini, F. (1997). Removal of metals by biosorption: a review. *Hydrometallurgy, 44*(3), 301-316.

Verlicchi, P. & Zambello, E. (2015). Pharmaceuticals and personal care products in untreated and treated sewage sludge: occurrence and environmental risk in the case of an application on soil − a critical review. *The science of the Total Environment, 538*, p. 750-767.

Volesky, B. (2001). Detoxification of metal-bearing effluents: biosorption for the next century. *Hydrometallurgy, 59*(2-3), 203-216.

Wan, J., Huang, M., Ma, Y., Guo, W., Wang, Y., Zhang, H., . . . Sun, X. (2011). Prediction of effluent quality of a paper mill wastewater treatment using an adaptive network-based fuzzy inference system. *Applied Soft Computing, 11*(3), 3238-3246.

Wang, F., Lu, X. & Li, X. (2016). Selective removals of heavy metals (Pb2+, Cu2+, and Cd2+) from wastewater by gelation with alginate for effective metal recovery. *Journal of hazardous materials, 308*, 75-83.

Wang, S., Wang, Y., Zhang, R., Wang, W., Xu, D., Guo, J., . . . Yu, K. (2015). Historical levels of heavy metals reconstructed from sedimentary record in the Hejiang River, located in a typical mining region of Southern China. *Science of The Total Environment, 532*, 645-654.

WEF (Water Environment Federation) (2006). Biological Nutrient Removal (BNR) Operation in Wastewater Treatment Plants (pp. 25, 105-226.): American society of civil Engineers, Enviromental and water resource Institute, and Water Environment Federation. Alexandria, Virginia: McGraw-Hill.

WEF (Water Environment Federation) (2011). Information Technology in Water and Wastewater Utilities. *Prepared by the Information Technology in Water and Wastewater Utilities Task Force of the Water Environment Federation®. Alexandria, Virginia: McGraw-Hill, 33*.

Wen, C.H. & Vassiliadis, C.A. (1998). Applying hybrid artificial intelligence techniques in wastewater treatment. *Engineering Applications of Artificial Intelligence, 11*(6), 685-705.

Wentzel, M.C. & Ekama, G.A. (1997). Principles in the design of single-sludge activated-sludge systems for biological removal of carbon, nitrogen, and phosphorus. *Water Environment Research, 69*(7), 1222-1231.

Wiel, H.J.V.d. (2003). Determination of elements by ICP-AES and ICP-MS. *National Institute of Public Health and the Environment (RIVM), Horizontal-19*.

Wijekoon, K.C., Hai, F.I., Kang, J.H., Price, W.E., Guo, W., Ngo, H.H. & Nghiem, L.D. (2013). The fate of pharmaceuticals, steroid hormones, phytoestrogens, UV-filters and pesticides during MBR treatment. *Bioresource technology, 144*, 247-254.

Yamamoto, H.W.M., Hirata, Y., Nakamura, Y., Nakamura, Y., Kitani, C., Sekizawa, J., Uchida, M., Nakamura, H., Kagami, Y., Koshio, M., Hirai, N., Tatarazako, N. (2007a). Preliminary ecological risk assessment of butylparaben and benzylparaben -1. Removal efficiency in wastewater treatment, acute/chronic toxicity for aquatic organisms, and effects on medaka gene expression. *Environmental Sciences : an International Journal of Environmental Physiology and Toxicology*, 14 Suppl:73-87.

Yang, S., Hai, F.I., Price, W.E., McDonald, J.A., Khan, S.J. & Nghiem, L.D. (2016). Occurrence of trace organic contaminants in wastewater sludge and their removals by anaerobic digestion. *Bioresource technology, 210*, 153-159.

Ying, G.G. & Kookana, R.S. (2007). Triclosan in wastewaters and biosolids from Australian wastewater treatment plants. *Environment international, 33*(2), 199-205.

Yu, Y., Huang, Q., Wang, Z., Zhang, K., Tang, C., Cui, J., . . . Peng, X. (2011). Occurrence and behavior of pharmaceuticals, steroid hormones, and endocrine-disrupting personal care products in wastewater and the recipient river water of the Pearl River Delta, South China. *Journal of Environmental Monitoring, 13*(4), 871-878. doi: 10.1039/C0EM00602E

Zazouli, M.A., Nasseri, S., Mahvi, A.H., Mesdaghinia, A.R., Younecian, M. & Gholami, M. (2007). Determination of hydrophobic and hydrophilic fractions of natural organic matter in raw water of Jalalieh and Tehranspars water treatment plants (Tehran). *J Appl Sci, 7*(18), 2651-2655.

Zeng, G., Jiang, R., Huang, G., Xu, M. & Li, J. (2007). Optimization of wastewater treatment alternative selection by hierarchy grey relational analysis. *Journal of Environmental Management, 82*(2), 250-259.

Zeng, G.M., Qin, X.S., He, L., Huang, G.H., Liu, H.L. & Lin, Y.P. (2003). A neural network predictive control system for paper mill wastewater treatment. *Engineering Applications of Artificial Intelligence, 16*(2), 121-129.

Zhang, D., Chen, Y.Y., Zhao, Y. & Zhu, X. (2010). New sludge pretreatment method to improve methane production in waste activated sludge digestion. *Environmental Science & Technology, 44*(12), 4802-4808.

Zhang, L., Ouyang, W. & Lia, A. (2012). Essential role of trace elements in continuous anaerobic digestion of food waste. *Procedia Environmental Sciences, 16*, 102-111.

Zhao, X. & Hwang, H.-M. (2009). A Study of the Degradation of Organophosphorus Pesticides in River Waters and the Identification of Their Degradation Products by Chromatography Coupled with Mass Spectrometry. *Archives of Environmental Contamination and Toxicology, 56*(4), 646-653. doi: 10.1007/s00244-008-9220-8

Zolfaghari, M., Drogui, P., Seyhi, B., Brar, S.K., Buelna, G. & Dubé, R. (2014). Occurrence, fate and effects of Di (2-ethylhexyl) phthalate in wastewater treatment plants: A review. *Environmental pollution, 194*, 281-293.

Zuloaga, O., Navarro, P., Bizkarguenaga, E., Iparraguirre, A., Vallejo, A., Olivares, M. & Prieto, A. (2012). Overview of extraction, clean-up and detection techniques for the determination of organic pollutants in sewage sludge: a review. *Analytica chimica acta, 736*, 7-29.

APPENDICES

Appendix A: Questionnaire on Selection of the Wastewater Treatment Plants

Questionnaire on Selection of the Wastewater Treatment Plants *(WWTPs)* and Technologies used in Gauteng Province, South Africa

Stakeholders are: Services, Management and Consultants

My name is Anthony Njuguna Matheri, a *PhD* student in the department of Chemical Engineering, University of Johannesburg *(UJ)*

This project is a collaboration between Water Research Commission (*WRC)* and *UJ*

The questionnaire is addressed to key institutions and organisations in the Gauteng Province, South Africa, with competences on the safe discharge of wastewater. Your organisation has been identified as one of these institutions.

This study aims to collect basic information *(questionnaire survey)* from wastewater treatment plants operations and management, stakeholders, Department of Water and Sanitation *(DWS),* Water Research Commission *(WRC).* The aim is to help in the identification, selection of appropriate wastewater treatment technologies, optimisation of operational parameters and hence effective plant design and efficient plant operation. This will also assist municipalities in achieving green drop certification of wastewater treatment plants for the removal of organic compounds and inorganics *(trace elements).* This questionnaire will take into account the plant design and general conditions of wastewater treatment plants; economic, environmental, social-cultural, and technologies/technical criteria.

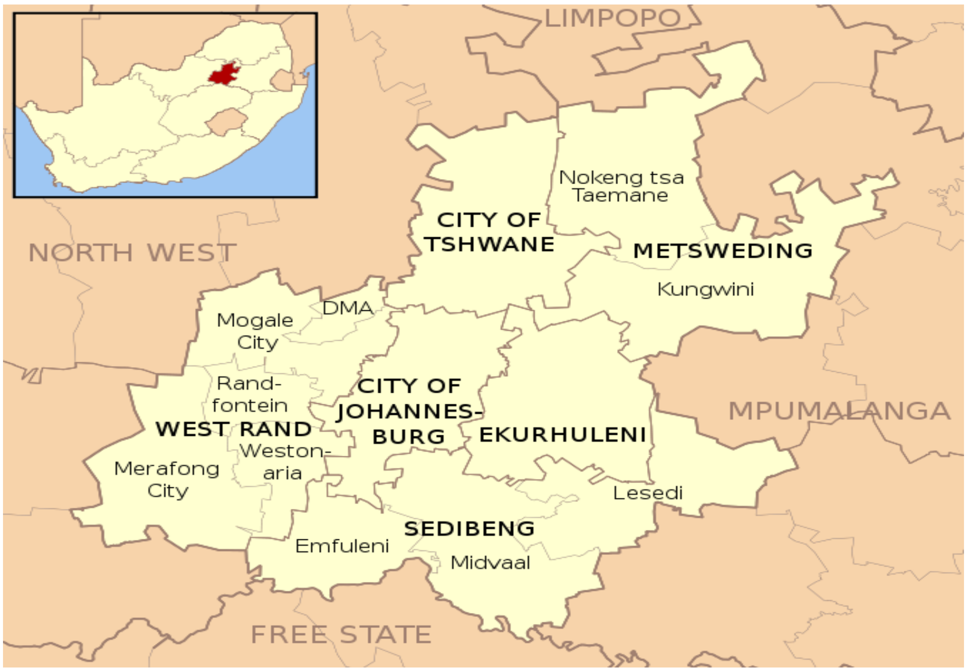
Prepared by: *Mr* Anthony Njuguna Matheri *(UJ), Prof* Freeman Ntuli *(UJ), Prof* Jane Catherine Ngila *(UJ), Dr* Tumisang Seodigeng *(VUT),* Dr John Zvimba *(WRC),* Dr Zvinowanda Caliphs *(UJ), Dr* Geoffrey Orina Bosire *(UJ),* and *Dr* Van Staden Juliana *(UJ).* Correspondence: Department of Chemical Engineering, University of Johannesburg, +27616686335, anthonym@uj.ac.za or tonynjuguna22@gmail.com

Filling out this questionnaire will take not more than *20* minutes. Please, complete as accurately as possible. We kindly and highly appreciate your support in this academic project and look forward to receiving your reply. Please provide full contact information in the relevant section.

Contacts Details:

Company/Institution

Address	Contact Person
Street	Title
Postcode/Town	Surname
Province	First names
Municipality	Position
Phone	Phone
Fax	Fax



Map of Gauteng Province as case study for selection of WWTPs

Plant Design

1. What is the latest **green drop score** for the WWTP? [ ]
2. What is the latest WWTP cumulative risk rating ***(CRR)****?* [ ]
3. What is the average design capacity of WWTP in ***ML/day*** in the past *12* months? [ ]
4. What is the daily inflow of the WWTP in ***ML/day*** the last *12* months? [ ]
5. Is your plant designed to Nitrify or De-nitrify? ***(indicate appropriate answer with 'X')***
   a) Nitrify [ ] b) De-nitrify [ ]
6. What is the type of treated wastewater? ***(indicate appropriate answer with 'X')***
   Domestic [ ]
   Industrial [ ]
   Combined [ ]
7. Do you ever receive wastewater from the following sources? ***(indicate appropriate answer with 'X')***
   i. Abattoir [ ]
   ii. Food processing plants [ ]
   iii. Landfill [ ]
   iv. Septic tanks [ ]
   v. Mining plants [ ]
   vi. Sources high in fats and oil [ ]
   vii. Sources of soaps and surfactants [ ]
   viii. Health care [ ]
   ix. Cosmetics Plants [ ]
8. How much sludge is hauled off-site on a daily basis ***(m^3)*** [ ]
9. Please specify if there are anoxic or anaerobic stages and the stage/zone ***(Before, after or within the aeration tank)?***
   Anoxic Stage/zone ____
   Anaerobic Stage/zone ____

10. Do organic and hydraulic loads exceed theoretical plant design capacities? Y es ☐ N o ☐

11. What is the typical ***MLSS*** that the sludge digester is run at? ______ mg/l

12. What is the typical sludge age that the sludge digester is run at? ______ days

13. Are chemicals dosed for phosphate removal? Yes ☐ No ☐

14. Are chemicals dosed for Nitrates removal? Yes ☐ No ☐

15. Are anti-forming agents used? Yes ☐ No ☐

16. Are chemicals dosed directly into the aeration basins? Yes ☐ No ☐
(Please state what and approximately how much)

____

____

17. Does the plant have chemical enhanced primary treatment *(CEPT)?* Yes ☐ No ☐

18. What is the average dissolved oxygen ***(DO)*** within the aeration basin? ______

19. Does the level of dissolved oxygen in the basin ever get as low as *1.0* mgO_2/l? Yes ☐ No ☐

20. What is the average ***pH*** of the settled sewage? ______

21. Does the plant have different inflows*? (If the answer is Yes, kindly specify the number of inflows)*

____

____

21. What type/s is the secondary treatment unit for nutrients removal in the *WWTP?*

[Indicate appropriate answer with X in the first column and the corresponding hydraulic retention time (HRT)]:

		HRT (hours)
Biological nutrients removal (BNR)		
Aeration tanks		
Settling ponds		
Trickling filters		
Rotating biological contactors *(RBC)*		
Membrane bioreactor *(MBR)*		
Sequencing batch reactor *(SBR)*		

22. Which process/es is used to treat the sludge in your *WWTP?*

[Indicate appropriate answer with X in the first column and the corresponding hydraulic retention time (HRT):

		HRT (hours)
Anaerobic digestion		
Biogas production		
Gasification		
Pyrolysis		
Sludge thickening		
Sludge combustion		
Sludge draining		
Sludge drying		
Sludge processing		

23. Are you aware of the **waste *(sludge)* to energy technology *(WtE)*-renewable energy** as a source of green *(clean)* energy? Yes ☐ No ☐

24. Does the plant use **renewable energy technologies**? Ye s ☐ No ☐

25. How do you rate the *COD* removal as recommended by Department of Water and Sanitation *(Water/Waste Act 49)?* ***[Indicate appropriate answer with X]***

i.	Poor	
ii.	Excellent	

26. What is the major source of *COD* in the *WWTP?*

____

____

27. How do you rate the inorganic *(Heavy metals)* compounds removal as recommended by *DWS (Water/Waste Act 49)? [Indicate appropriate answer with X]*

i.	Poor	
ii.	Excellent	

28. What is the major source of trace elements in the *WWTP?*

____

____

29. Choose the measuring instruments used in your laboratory and on-site in the *WWTP.* You can tick more than one instrument/technique if applicable *[Indicate appropriate answer with X on either Laboratory or on-site]*

	Laboratory	On-site
Automatic analysers		
Microbial load test		
Chlorine measuring test		
COD measuring device		
BOD measuring device		
Densitometers		
ICP for inorganic *(heavy metals)* analyser		
Flow meters, current meters, level meters		
Gas analysers		
Gas indicators, gas detectors		
Gas chromatograph mass spectrometry *(GC-MS)*		
Liquid chromatograph mass spectrometry *(LC-MS)*		
High-performance liquid chromatograph *(HPLC)*		
Atomic absorption spectrometry *(AAS)*		

Ion chromatography		
Carbon measuring instrument		
Calorimeter		
Conductimeters		
Flow meter		
Ozonometers		
Organic and inorganic tracer		
pH-value measuring devices		
Photometers		
Refractometers		
Oxygen content measuring devices		
Sludge measuring devices *(Characterization of sludge: VFA, VOC, etc.)*		
Spectrometers		
Thermometer		
Automatic titration		
Turbidimeters		
Other measuring instruments		

30. The questions are about the **environmental impacts** of *WWT* technologies/processes in your plant ***[Indicate appropriate answer with X].***

i) Does the plant have geological impact on groundwater pollution?	Yes		No	
ii) Does the plant experience strong odour generation?	Yes		No	
iii) Does the plant experience large amount of water evaporation?	Yes		No	
iv) Does the plant conduct a health safety environment *(HSE)* audit?	Yes		No	

31. What are the requirements of the personal in the *WWTP?*

____

____

____

____

32. Specify occupational health risk in the *WWTP*

____

____

33. The following questions are about the **technological/technical aspect** of *WWT* technologies/processes in your plant. ***[Please indicate appropriate answer with X]***

i) Is the plant performing efficiently and meeting regulatory standards in terms of percentage removals of parameters such as *COD, BOD,* Total Suspended Solid *(TSS),* Total Phosphorus *(TP),* Total Nitrogen *(TN),* Faecal Coliforms and Heavy Metals? Yes ☐ No ☐

ii) Does the plant have an efficient routine sampling program? Yes ☐ No ☐

iii) Does the plant have specialized and skilful personnel to handle the WWT technologies? Yes ☐ No ☐

iv) Does the plant have a training program for staff capacity building? Yes ☐ No ☐

v) Does the plant have the capacity to handle the average organic loading rates? Yes ☐ No ☐

vi) Does the plant accommodate excess inflow from storm water e.g. flooding? Yes ☐ No ☐

34. The following questions are about the **economic aspect** of *WWT* technologies/processes in your plant?

i) Does the plant have the ability to accommodate additional operational facilities and future expansions? Yes ☐ No ☐

ii) Does the plant have sufficient funds for operation and maintenance costs? Yes ☐ No ☐

iii) Does the plant have sludge disposal facilities? Yes ☐ No ☐

35. Describe any approach that you think would improve the efficiency of the plant and lower the cost of the wastewater treatment.

____

____

36. Identify any policy hindrance in the development plan, plant efficiency and regulatory standards.

____

____

Please email the electronic copies to anthonym@uj.ac.za , tonynjuguna22@gmail.com or
Send hard copies to:

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If you would like to be kept informed of the progress of the project, then please ensure that you provide a contact name and email address at the beginning of the questionnaire.

Place, Date

Signature

Appendix B1: The Activated Sludge Model *(ASM) No. 1* under International Association of Water Quality *(IAWQ)*

***Table B1:** Process Kinetics and Stoichiometry for Carbon Oxidation, Nitrification, and Denitrification*

j	Components → i Process ↓	1 S_I	2 S_S	3 X_I	4 X_S	5 $X_{B,H}$	6 $X_{B,A}$	7 X_P	8 S_O	9 S_{NO}	10 S_{NH}	11 S_{ND}	12 X_{ND}	13 S_{ALK}	Process Rate $\rho_J[ML^{-3}T^{-1}]$
1	Aerobic growth of heterotrophs		$-\frac{1}{Y_H}$			1			$-\frac{1-Y_H}{Y_H}$		$-i_{XB}$			$-\frac{i_{XB}}{14}$	$\mu_H(\frac{S_S}{K_S-S_S})(\frac{S_O}{K_{O,H}-S_O})]X_{B,H}$
2	Anoxic growth of heterotrophs		$-\frac{1}{Y_H}$			1				$-\frac{1-Y_H}{2.86Y_H}$	$-i_{XB}$			$\frac{1-Y_H}{14-2.86Y_H}-\frac{i_{XB}}{14}$	$\mu_H(\frac{S_S}{K_S-S_S})(\frac{K_{O,H}}{K_{O,H}-S_O})]*(\frac{S_{NO}}{K_{NO}+S_{NO}})\eta_g X_{B,H}$
3	Aerobic growth of autotrophs				$1-f_p$		1	f_p	$-\frac{4.57-Y_A}{Y_A}$	$\frac{1}{Y_A}$	$-i_{XB}-\frac{1}{Y_A}$			$-\frac{i_{XB}}{14}-\frac{1}{7Y_A}$	$\mu_A(\frac{S_{NH}}{K_{NH}-S_{NH}})(\frac{S_O}{K_{O,A}-S_O})]X_{B,A}$
4	Decay of heterotrophs					-1							$i_{XB}-f_P i_{XP}$		$b_H X_{B,H}$
5	Decay of autotrophs				$1-f_p$			f_p					$i_{XB}-f_P i_{XP}$		$b_A X_{B,H}$
6	Ammonification of soluble organic nitrogen										1	-1		$\frac{1}{14}$	$k_a S_{ND} X_{B,H}$
7	Hydrolysis of entrapped organics		1		-1										$k_h\frac{\frac{X_s}{X_{B,H}}}{K_X+(\frac{X_S}{X_{B,H}})}[\frac{S_O}{K_{O,H}+S_O})$ $+(\eta_h\frac{K_{O,H}}{K_{O,H}-S_O})(\frac{S_{NO}}{K_{NO}-S_{NO}})]X_{B,H}$
8	Hydrolysis of entrapped nitrogen											1	-1		$P_7(X_{ND}/X_S$
Observed Conversion Rate $[ML^{-3}T^{-1}]$		$r_i=\sum_j v_{ij}p_j$													
Stoichiometry parameters: Heterotrophic yield: Y_H Autotrophic yield: Y_A Fraction of biomass yielding particulate products: f_p Mass N/Maas COD in biomass: i_{XB} Mass N/Maas COD in product from biomass: i_{XP}		Soluble inert organic matter $[M(COD)L^{-3}]$	Readily biodegrable substrate $[M(COD)L^{-3}]$	Particulate inert organic matter $[M(COD)L^{-3}]$	Slowly biodegrable substrate $[M(COD)L^{-3}]$	Active heterotrophic biomass $[M(COD)L^{-3}]$	Active autotrophic biomass $[M(COD)L^{-3}]$	Particulate products arising from biomass decay $[M(COD)L^{-3}]$	Oxygen (negative COD) $[M(-COD)L^{-3}]$	Nitrate and nitrite nitrogen $[M(N)L^{-3}]$	$NH_4^+ + NH_3$ nitrogen $[M(N)L^{-3}]$	Soluble biodegradable organic nitrogen $[M(N)L^{-3}]$	Particulate biodegradable organic nitrogen $[M(N)L^{-3}]$	Alkalinity-Molar units	Kinetics Parameters: Heterotrophic growth and decay: μ_H, K_S, $K_{O,H}$, K_{NO}, b_H Autotrophic growth and decay: μ_A, K_{NH}, $K_{O,A}$, b_A Correction factor for anoxic gowth of heterotrophs: η_g Ammonication: k_a Hydrolysis: k_h, K_x Correction factor for anoxic hydrolysis: η_h

Appendix B2: Activated Sludge Model *No.1* Spreadsheet

Municipal influent

Exercise: Please fill out all cells marked with

Step 1: Available measurements in blue

	Symbol	Value	Unit
COD_{tot}	T_{COD}	723.0	mgCOD/L
Collodial	C_{COD}	141.0	mgCOD/L
Particulate COD	X_{COD}	245.0	mgCOD/L
Filtered COD	SC_{COD}	478.0	mgCOD/L
Floc-filtered COD	S_{COD}	337.0	mgCOD/L
Effluent floc-filtered COD	S_I	30.0	mgCOD/L
TKN	TKN	39.0	mgN/L
$NH_{x\text{-}N}$	S_{NHx}	28.0	mgN/L
VSS	VSS	218.8	mgVSS/L
TSS	TSS	251.0	mgTSS/L
BOD	BOD	350.0	mgO_2/L
Alkalinity	S_{ALK}	250.0	$mgCaCO_3/L$

Step 2: calculated fractions (for data quality check)

	Symbol	Value	Evaluation	typical
Filtered COD fraction	SC_{COD}/T_{COD}	0.66	478	0.4
Floc-filtered COD fraction	S_{COD}/T_{COD}	0.47	337	
▸ Ammonia fraction	NH_x/TKN	0.72		0.6-0.8
▸ COD/VSS ratio	$C_{COD}+XC_{COD}$/VSS	1.76		1.5-1.8
▸ VSS/TSS ratio	VSS/TSS	0.87		0.8-0.9
▸ COD/BOD ratio	T_{COD}/BOD	2.07		2.0-2.5

green easy to measure, **yellow** requires some assumptions but not so important, **red** is important and difficult to measure

Step 3: Resulting model state variables

Soluble Species	Symbol old	Symbol new	Value	Unit	Calculation	Fraction of COD_{tot}
Oxygen, O_2	S_O	S_{O2}	0.0	gO_2/m^3		
Inert COD	S_I	S_U	30.0	$gCOD/m^3$		0.04
Substrate COD	S_S	S_B	307.0	$gCOD/m^3$	$(S_{COD}-S_I)$	0.42
Ammonium N	S_{NH}	S_{NHx}	28.0	gN/m^3		
Nitrate N	S_{NO}	S_{NOx}	0.0	gN/m^3		
Organic N	S_{ND}	$S_{B,N}$	5.5	gN/m^3	(TKN-SNH)/2	
Alkalinity mmol	S_{ALK}	S_{Alk}	5.0	mol/m^3	divide value in mgCaCO3/L by 50	

Particulate Species	Symbol old	Symbol new	Value	Unit	Calculation	Fraction of COD_{tot}
Inert COD	X_I	$X_{U,Inf}$	94.0	$gCOD/m^3$	X_I = 13% of T_{COD}	0.13
Substrate COD	X_S	X_B	255.9	$gCOD/m^3$		0.4
Het BM COD	X_{BH}	X_{OHO}	36.2	$gCOD/m^3$	X_{BH} = 5% of T_{COD}	0.05
Aut BM COD	X_{BA}	X_{ANO}	0.0	$gCOD/m^3$	X_{BA} = 0% of T_{COD}	0
Part XP COD	X_P	$X_{U,E}$	0.0	$gCOD/m^3$		0
Org Nitrogen	X_{ND}	$XC_{B,N}$	5.5	gN/m^3	(TKN-SNH)/2	
Inorg. Suspended Solids	ISS	X_ISS	32.3	$g\ ISS/m^3$	TSS-VSS	

Step 4: Comparing model predicted combined variables with measurements

	Symbol		Model	Measured	Comment	Evaluation
Biodegradable COD	bCOD		599.0		All biodegradable COD	
Carbonaceous BOD5	BOD		399.3	350.0	Approx. 2/3rd of bCOD	
VSS	VSS		218.8	218.8	All particulate COD divided by COD/VSS ratio.	
TSS	TSS		251.0	251.0	VSS divided by measured VSS/TSS ratio.	
COD	COD		723.0	723.0	All COD states.	

Appendix B3: Wastewater Treatment Plant Simulator

GREENTECH BIOLOGICAL WASTEWATER TREATMENT SIMULATOR (Anthony Njuguna Matheri @ Copyright)

INPUT DATA

Physical Measured Data (Operation Variables)

Parameter	Symbol	Value	Units
Tank/Reactor/Digester Volume	V	2833	m^3
Depth and Layouts	H	5	m
Fluid Flow rates	Q	17000	m^3/h
Sludge Flow rates (Return)	Q_w	4545	m^3/h
hydraulic Retention Time	t	0.16665	h

Performance Measured Influent

Parameter	Symbol	Value	Units
Effluent Organics	So	141	mg/L
Biomass Concentration in Aeration Tank	X	278	mg/L
Effluent Nutrients	Xe	19	mg/L
Dissolved Oxygen	DO	7.5	
Temperature	T	20	^oC
pH	pH	7.5	
Alkalinity		268	mg/L
Effluent Nutrients Return line	X_R	2670	mg/L
Biomass Conc Influent	X_o	254	mg/L
Ortho phosphate	X_{ve}	241	mg/L
Chlorine	Cl	51	mg/L
Electrical Conductivity	E	58	mS/m

Measured Influent (Organic and Inorganics)

Parameter	Symbol	Value	Units
Total COD	T_{COD}	495.00	mgCOD/L
Particulate COD	X_{COD}	245.00	mgCOD/L
Colloidal COD	C_{COD}	141.00	mgCOD/L
Filtered COD	SC_{COD}	250.00	mgCOD/L
Floc-filtered COD	S_{COD}	109.00	mgCOD/L
Effluent floc-filtered COD	S_I	25.00	mgCOD/L
Total Kjeldahkl Nitrogen	TKN	40.00	mgN/L
Ammonia Nitrogen	S_{NHx}	30.00	mgN/L
Volatile Suspended Solids	VSS	218.75	mgVSS/L
Total Suspended Solids	TSS	254.36	mgTSS/L
Biochemical Oxygen Demand	BOD	271.35	mgO_2/L
Alkalinity	S_{ALK}	220.00	$mgCaCO_3/L$
Total Phosphate	PO_4^{-3}	241.00	$mgPO4^{-3}/L$
Chlorine	Cl	51.00	mgCl/L

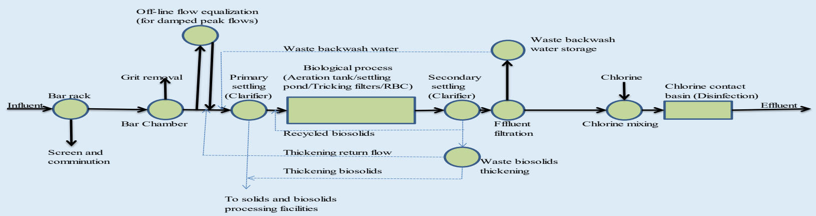
Measured Influent (Trace Metals)

Parameter	Symbol	Value	Units
Aluminium	Al	1.69	mg/L
Arsenic	As	0.10	mg/L
Cadmium	Cd	0.02	mg/L
Cobalt	Co	0.02	mg/L
Chromium	Cr	0.01	mg/L
Copper	Cu	0.09	mg/L
Iron	Fe	0.84	mg/L
Manganese	Mn	0.07	mg/L
Mercury	Hg	0.01	mg/L
Molybdenum	Mo	0.03	mg/L
Nickel	Ni	0.01	mg/L
Lead	Pb	0.12	mg/L
Silver	Ag	0.01	mg/L
Selenium	Se	0.05	mg/L
Titanium	Ti	0.01	mg/L
Zinc	Zn	0.25	mg/L

KINETIC CONSTANTS

Kinetic Coefficients

Coeffient	Unit	Value	Range	Typical
k	*g bsCOD/g VSS.d*	*4*	4.0-12.0	6
Ks	*mg/L BOD*		20-60	30
	mg/L bsCOD		5.0-30.0	15
Y	*mg VSS/mg BOD*	*0.45*	0.4-0.8	0.6
	mg VSS/mg COD		0.4-0.6	0.45
μ_m *(max specific growth rate)*	d^{-1}	*1.07*	1.0-8.0	3
b	*g bsCOD/g VSS.d*	*1.04*	0.06-0.15	0.1
K_S, K_{NH4}, K_{NO2}	*mg/L*	9		9
fv (VSS residual)		0.7	0.7-0.85	
fp		0.001		
fd	*unitless*	0.15		0.15
K_{O2}	*mg/L*	0.2		0.2
K_{max}		9.5		9.5
K_o (halfsaturation constant, oxygen)	mg/L	0.2	*0.3-2*	
k_d			0.0011-1	
k_n		0.3		
b_{AT} (endogenous respiration rate)		0.04		
k_{nT} (half saturation coefficient)		1.23		
fp (phosphous removal)		0.025		
K_s *(micropollutant)*		8		
b (micropollutant)		0.1		
μ_m *(micropollutant)*		3		
k (trace metals)		12		
k_d *(first order decay rate constant-Disinfectant)*		6		
t (disinfectant)		0.027		
Number of reactors		3		
Constant		2		
Constant		1000		
Constant		7.2		
Constant		100		
Constant		1.42		
Constant		2.35		
Constant		1		



EFFLUENT SIMULATION

Parameter	Symbol	Value	Units	Limits
Primary Settlement Sizing	V	2833.00	m^3	
Primary Settlement Velocity	V	30.00	m/h	
Organic Volumetric Loading Rate	L_{org}	0.85	kg $COD/m^3.d$	
Sludge Retention Time/Sludge Age	SRT	5.04	d	
Specific Organic Loading Rate	L	1.11	h^{-1}	
Temperature	T	20.00	^oC	44
pH	pH	7.50		5.5-7.5
Substrate Concentration	S	16.66	mg/L	30
Biomass Concetration	X	271.13	mg/L	30
Mixed Liquor	$P_{XT,VSS}$	1500.16	mg/L	
Nitrogen Concentration	N_{ae}	0.35	mg/L	1.5
Phosphorus Concentration	P_r	4.22	mg/L	10
Oxygen Required	R_o	2111.57	kd/d	
Food/Microbial Ratio	F/M	0.00	bsCOD/gVSS.d	
Organics Removal Efficiency	E	88.18	%	
Micro-pollutants Concentration	MP	0.88	mg/L	30
Disinfectants *(i.e. Chlorine)*	Cl	43.37	mg/L	0.25

Parameter	Symbol	Value	Units	Limits
Aluminium	Al	0.61	mg/L	0.05
Arsenic	As	0.04	mg/L	5
Cadmium	Cd	0.01	mg/L	10
Cobalt	Co	0.01	mg/L	20
Chromium	Cr	0.00	mg/L	10
Copper	Cu	0.03	mg/L	20
Iron	Fe	0.30	mg/L	20
Manganese	Mn	0.03	mg/L	20
Mercury	Hg	0.00	mg/L	5
Molybdenum	Mo	0.01	mg/L	20
Nickel	Ni	0.00	mg/L	20
Lead	Pb	0.04	mg/L	5
Selenium	Se	0.00	mg/L	5
Titanium	Ti	0.02	mg/L	20
Zinc	Zn	0.00	mg/L	20

Appendix C: Daspoort Wastewater Treatment Plant: Site Survey, Tracer Application and Sampling Program

Appendix D: Local and International Effluent Discharge Standards and the Specification

Table D1: *Standard and the Specification of the Effluent Discharge in South Africa*

VARIABLES A. GENERAL	TARGET VALUE	MAXIMUM
pH		6-10.0
Temperature °*C*	38	44
Electric conductivity-*EC (mS/m)*	150	300
Total dissolved solids *(TDS)*	1000	2000
Bio-degradable chemical oxygen demand *(COD)*	2000	5000
Oxygen demand *(PV Strength)*	1000	1400
Suspended solids *(Organic)*		2000
Suspended solids *(Non-organic)*	50	100
Caustic alkalinity as *CaCO*		2000
Substance soluble in petroleum ether	50	300
Anionic surface-active agents	50	300
Substance from which hydrogen Cyanide can be liberated *(as HCN)*	5	20
Formaldehydes *(HCHO)*		50
All sugars and/or starch *(as glucose)*	1000	1500
Available chlorine *(as Cl_2)*	50	100
Sulphates *(as SO_4)*	200	1500
Sulphides, hidrosulphides, polisulphides	200	1500
Fluorine containing compounds *(as F)*	2	5
Chloride *(as Cl)*	200	500
Sodium *(as Na)*		500
Phosphate *(as P)*		10
Free and saline *(as NH_4)*		100
Calcium carbides		400
Phonetic compounds	0	1
B. METALS: GROUP *1*		
Total threshold concentration of metal group *1* shall not exceed *50 mg/L*		
Iron *(Fe)*		20
Cobalt *(Co)*		20
Chromium *(Cr)*		10
Silver *(Ag)*		20
Copper *(Cu)*		20
Titanium *(Ti)*		20
Nickel *(Ni)*		20
Tungsten *(W)*		20
Zinc *(Zn)*		20
Cadmium *(Cd)*	1	10
Manganese *(Mn)*		20
Molybdenum *(Mo)*		20

B. METALS: GROUP

Total threshold concentration of metal group 2 shall not exceed 20 mg/L

Arsenic *(As)*		5
Boron *(B)*		5
Lead *(Pb)*	1	5
Selenium *(Se)*		5
Mercury *(Hg)*	1	5

C. Radioactive Wastes

Any waste of radioactive isotopes shall not exceed the concentration of radioactive as laid down by the National Nuclear Regulation.

D. Regardless of above, any substance that might have the ability to have a severe effect on the biological or chemical treatment process of a sewage treatment plant, shall not be discharge into the sewer system.

APPENDIX E: LOCAL AND INTERNATIONAL EFFLUENT DISCHARGE STANDARDS AND THE SPECIFICATION

Table E1: Trace elements and organics compounds permissible concentration worldwide (Annika, Julika & Adelphi, Accessed 2016; EPA, Accessed 2016; Herselman & Moodley, 2009; Marlene & Leonardo, Accessed 2016; Murthy, Accessed 2016; P.S., 2001)

Substance/Parameters	*SA* Section *39* of the National Water Act no *36 pf 1998* — General limits	Special limits	European Union	International Standard *ISO 11466*	*WHO*	South Africa WWTP	American water works association	*SDWA*
Faecal coliforms *(cfu/per 100 mL)*	1000	0	<1000			150 *CFU*/100ml		0
Biological oxygen demand *(mg/L)*			30					
Chemical Oxygen Demand *(mg/L)*	75	30	10-30.			50		
Turbidity *(Turbidity units TU)*							<0.1	
Colour *(colour units)*							<3	
Odor							none	
pH	5.5-9.5	5.5-7.5	6.5-8.4		6.8	6.5-8.5	6.5-8.5	
Ammonia *(ionised and un-ionised)* as Nitrogen *(mg/L)*	3	2				1		
Nitrate/Nitrite as Nitrogen *(mg/L)*	15	1.5	10-30.		45	6		10
Chlorine as free Chlorine *(mg/L)*	0.25	0				0.2		
Total dissolved solid TDS *(mg/L)*			450-2000				200	
Suspended Solids *(mg/L)*	25	10	<1 to 30			10		
Electrical Conductivity *(ms/m)*	70-150	50-100				80		
Phenols *(mg/L)*					0.001			
Ortho-Phosphate as Phosphorous *(mg/L)*	10	1-2.5	0.1-30			0.9		
Fluoride *(mg/L)*	1	1						
Soap, oil or grease *(mg/L)*	2.5	05	8					
Aluminium							<0.05	
Dissolved Arsenic *(mg/L)*	0.02	0.01	0.1		0.05			0.1
Beryllium			0.1		1			2

Dissolved Cadmium *(mg/L)*	0.005	0.001	0.01	0.01		0.005
Dissolved Chromium *(mg/L)*	0.05	0.02	0.1	0.05		0.1
Dissolved Copper *(mg/L)*	0.01	0.002	0.2	0.05	<0.2	1.3
Cobalt			0.05			
Dissolved Cyanide *(mg/L)*	0.02	0.01	0.01	0.01		0.2
Fluoride *(mg/L)*			1.5			4
Dissolved Iron *(mg/L)*	0.3	0.3	5	0.3	<0.05	
Dissolved Lead *(mg/L)*	0.01	0.006	5			
Lithium			2.5			
Dissolved Manganese *(mg/L)*	0.1	0.1	0.2	0.1	<0.01	
Molybdenum			0.01			
Lead *(mg/L)*			5	0.05		0
Nickel			0.2			
Mercury and its compound *(mg/L)*	0.005	0.001	0.002	0.001		0.002
Dissolved Selenium *(mg/L)*	0.02	0.02	0.02	0.01		0.05
Silver				0.05		
Thallium						0.0005
Vanadium			0.1			
Dissolved Zinc *(mg/L)*	0.1	0.04	2	5	<1.0	
Boron *(mg/L)*	1	0.5	1.12-2.0			

APPENDIX F: ANALYTICAL TECHNIQUES FOR MONITORING WATER POLLUTANTS

F1: Introduction

F1.1 Analytical techniques for monitoring water pollutants

Development and validation of novel analytical techniques for preconcentration and determination of organic contaminants was considered. To test the robustness of the analytical system for monitoring of organics in wastewater, three compounds in the class of parabens were studied, namely, methylparaben, ethylparaben and propylparaben. Sample preparation methods (extraction of analyte compounds) using solid phase extraction (SPE) methods were studied. Analyte detection techniques based on ultra-high performance liquid chromatography hyphenated to tandem mass spectrometry (UHPLC-MS/MS) was investigated. Experimental factors such as sample pH, sample volume and eluent volume, were optimized using a two-level (2k) full factorial design in conjunction with response surface methodology (RSM). The chemometric approach is advantageous in that it decreases the number of experimental runs resulting in reduced analysis times, reagent consumption, sample volume as well as the cost of analysis [1]. Various extraction techniques either conventional or newly developed, were employed for the determination of parabens in wastewater. They include dispersive liquid-liquid microextraction (DLLME) [2], solid phase microextraction (SPME) [3], dispersive ionic liquid (IL)-DLLME [4], magnetic solid phase extraction (MSPE) [5], rotating disk sorptive extraction (RDSE) [1], among many others. However, the most common and robust extraction and pre-concentration method, for extraction of parabens is solid phase extraction (SPE) [6,3]. This is largely due to its versatility in retaining these compounds and the availability of a wide array of adsorbents, chemistries and sizes of the SPE cartridges, making it a robust and selective extraction technique [7]. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) is the most frequently used method for determination of parabens due to its sensitivity, selectivity and very low detection levels (µg L^{-1} to ng L^{-1}) [8]. In addition, no derivatization is required as is the case with gas chromatograhy (GC) analysis [1,9]. The UHPLC technique uses sub-2-µm particle size columns which makes it more favourable over the traditional HPLC, as it tremendously improves resolution with increased peak capacity and shortened analysis times [10].

F2. Sample collection for analytical techniques

The analytical procedures used for sample preparation for quantification of the organic contaminants in wastewater included sample collection; solid phase extraction (SPE), experimental design, application of carbon nanodots in SPE. The quantification techniques included liquid chromatography and gas chromatography hyphenated to tandem mass spectrometry. Chemometric techniques were used for the optimization of sample extraction procedures as per Muckoya *et al.* [11]. The collection of samples from WWTP in Gauteng was done from two locations in the east and west of the plant. There were 7 sampling sites from the east plant and 6 sampling sites on the west plant. Two samples were collected per sampling site while observing the retention times calculated by the use of the tracer [12]. Solid phase extraction procedure: Extraction of parabens from the wastewater samples was performed using Oasis HLB cartridges (6 mL, 200 mg). Prior to the extraction, the samples were filtered on a Millipore filtration unit using 0.45 µm filter paper to remove any suspended matter that may otherwise interfere with the SPE extraction due to clogging. A multivariate experimental design was employed for optimization of SPE experimental conditions [12]. The parameters studied were sample volume, elution volume and sample pH. Solid phase extraction of parabens with packed carbon nanodots (CNDs). Characterization of synthesized was done with TEM, SEM, FTIR, XRD techniques. The carbon nanodots were synthesized according to previous literature [13] with slight modification as per Muckoya *et al.* [14]. The application of the CNDs for extraction of methyl-, ethyl- and propyl paraben (MePB, EthPB, ProPB), azinphos-methyl and parathion-methyl from the wastewater samples, was performed using pre-packed SPE cartridges with the CNDs. Chromatographic-mass spectrometry experimental runs were conducted using Nexera Ultra High-Performance Liquid Chromatography (UHPLC Shimadzu, Japan). Separation of the analytes was obtained using a pinnacle DB biphenyl column of 100 x 2.1 mm and 3 µm particle size (RESTEK, USA). The mass spectrometry detection was acquired in multiple reaction monitoring (MRM) mode. The detailed procedures are given in [15].

F3. Summary Results on Analytical Techniques for Water Sample Preparation and Analyte Detection

The WWTP East side (E1-E7) is the trickling unit and West (W1-W6) is the biological nutrients removal (BNR) unit. The various sampling points are as shown in **Table F1** where sampling codes (E1-E7 and W1-W6) refer to influent system as it progresses to effluent with sampling code from 1 to 7. The concentrations obtained for the three parabens in this study are also shown in **Table F1**. The highest concentration was found in the samples corresponding to methylparaben and propylparaben. This is in line with what is expected as the two types of compounds are the commonly used parabens in personal care products such as toothpaste, body creams, shampoos, etc., typically found in domestic sewage [16,17]. In addition, due to their synergistic effects, these compounds are formulated together and hence the observed high concentrations as compared to ethylparaben [18,19].

The SPE extraction procedures were optimized using two-level factorial design to obtain the optimum conditions of the extraction parameters which resulted in high extraction yield. This multivariate optimization approach revealed that sample pH and sample volume had the most significant effect on the analytical response (recovery) of the analytes (the three parabens). The results obtained provided high recoveries (78-120%) with minimal sample extraction volume (50 mL). The efficiency (accuracy) of the developed CNDs based SPE procedure was validated by spiking effluent wastewater samples containing none of the parabens orthe organo-phosphorous pesticides (OPPs). The spiking was performed at two concentration levels, 10 and 100 µg L^{-1} in four replicates (n=4) or each level. The spiking procedure was adopted due to unavailability of certified reference material with the organic contaminants in the study. The recoveries obtained for the two spike levels ranged between 62.9-102% and 71.3-123% for influent and effluent wastewater samples respectively with <10% RSDs for all the analytes (MePB, EthPB, ProPB, Azinphos-methyl and methyl-parathion). These results are a proof that developed CNDs-SPE method achieved remarkable quantitative recoveries with good repeatability making it suitable for routine analysis and monitoring of these organic contaminants in wastewater simultaneously. The developed method based on CNDs was applied to real wastewater samples obtained from a domestic municipal WWTP analyzed in four replicates (n=4). The concentrations obtained are as shown in **Table F2**. The three parabens (MePB, EthPB and ProPB) were found in the studied wastewater samples albeit at low concentrations (0.13-3.51 µg L^{-1}). This is similar to what has been reported by other studies in the literature [18,19]. The OPP pesticides studied were not detected in both the influent and effluent wastewater samples. The presence of trace amounts of MePB, EthPB and ProPB can be attributed to the fact the WWTP in study mostly treats domestic wastewater. Parabens are preservatives in consumer products used on daily basis such as shampoos, body lotion toothpaste. They are therefore easily susceptible to be washed off down the drainage systems that are connected to the WWTPs.

The levels of parabens observed were very low, e.g 3.3 µg/L. The level concentrations obtained for the two plants (East and West) do not show much difference in the parabens concentration which is indicative of adequate removal of the parabens. These findings are comparable with other studies that reported the determination of parabens from WWTP elsewhere [19]. The limit of detection (LOD) and limit of quantification (LOQ) obtained were 0.04-0.12 µgL−1 and 0.14-0.40 µgL−1 respectively. The method was properly validated with real wastewater samples obtained from the local WWTP, suggesting its suitability and applicability in the determination of three parabens namely Methylparaben (MePB), Ethylparaben (EthPB) and Propylparaben (ProPB), in wastewater samples. In general, the percentage recoveries obtained using the synthesized CNDs for SPE were better than the commercial based oasis HLB SPE cartridges. Moreover, only 170 mg of the CNDs was employed compared to the 200 mg in the commercial based cartridges. These results indicate the applicability of the synthesized CNDs in extraction of multi-class organic compounds in wastewater water samples. In addition, the results obtained showcase the viability of using UHPLC-MS/MS coupled with chemometric optimization approach in determining the occurrence of the organic contaminants in wastewater systems.

Table F1: Application of SPE (Oasis HLB) In extraction of MePB, EthPB and PropB in wastewater samples (n=6)

		Methylparaben		**Ethylparaben**		**Propylparaben**	
Sampling code	**Sampling point**	**Conc (µg/L)**	**RSD %**	**Conc (µg/L)**	**RSD %**	**Conc (µg/L)**	**RSD %**
E1	Division box	2.33	1.63	0.40	0.17	1.82	0.96
E2	Grit	2.86	6.39	0.54	4.88	1.48	2.42
E3	Primary setting tank	1.98	3.83	ND		0.82	3.36
E4	Siphoning tank	1.85	0.12	ND		0.47	2.54
E5	Trickling filters	ND		ND		ND	
E6	Humas tank	ND		ND		ND	
E7	CCT chlorine contact dam	ND		ND		ND	
W1	Division box	2.97	2.95	<LOQ		2.17	2.62

W2	Grit	2.30	1.86	ND		1.58	0.95
W3	Primary setter	2.56	2.25	ND		1.54	0.28
W4	BNR activated sludge reactor	ND		ND		ND	
W5	Humas tank	ND		ND		ND	
W6	CCT chlorine contact dam	ND		ND		ND	

ND: not detected, Conc: concentration, E: East, W: West, BNR: biological nutrients removal

Table F2: Application of proposed method on unspiked wastewater samples (n=4)

	Influent water		**Effluent water**
	Conc (µg/L)	**RSD %**	**Conc (µg/L)**
Methylparaben	3.51	2.63	<LOD
Ethylparaben	0.13	3.36	<LOD
Propylparaben	1.46	5.44	<LOD
Azinphos-Methyl	<LOD		<LOD
Parathion-methyl	<LOD		<LOD

F4. Conclusions

The results obtained from optimized analytical techniques showed that, the percentage analyte recoveries obtained using the synthesized carbon nanodots (CNDs) packing of SPE were better than the commercial based oasis HLB SPE cartridges. Only 170 mg of the CNDs was employed compared to the 200 mg in the commercial based cartridges. These results indicate the applicability of the synthesized CNDs in extraction of multi-class organic compounds in wastewater samples. For analyte quantification, UHPLC-MS/MS coupled proved to be highly efficient when combined with chemometric optimization method in determining the presence of the organic contaminants in wastewater systems.

F5. References

[1] Becerra-Herrera M, Miranda V, Arismendi D, Richter P (2018) Chemometric optimization of the extraction and derivatization of parabens for their determination in water samples by rotating-disk sorptive extraction and gas chromatography mass spectrometry. Talanta 176:551-557

[2] Xue Y, Chen N, Luo C, Wang X, Sun C (2013) Simultaneous determination of seven preservatives in cosmetics by dispersive liquid-liquid microextraction coupled with high performance capillary electrophoresis. Analytical Methods 5 (9):2391-2397

[3] López-Darias J, Pino V, Meng Y, Anderson LJ, Afonso MA (2010) Utilization of a benzyl functionalized polymeric ionic liquid for the sensitive determination of polycyclic aromatic hydrocarbons; parabens and alkylphenols
in waters using solid-phase microextraction coupled to gas chromatography-flame ionization detection. Journal of Chromatography A 1217:7189-7719. doi:10.1016/
[4] Ma T, Li Z, Jia Q, Zhou W (2016) Ultrasound-assisted temperature-controlled ionic liquid emulsification microextraction coupled with capillary electrophoresis for the determination of parabens in personal care products. Electrophoresis 37 (12):1624-1631
[5] Chen Y, Cao S, Zhang L, Xi C, Chen Z (2017) Modified QuEChERS combination with magnetic solid-phase extraction for the determination of 16 preservatives by gas chromatography-mass spectrometry. Food Analytical Methods 10 (3):587-595
[6] González-Mariño I, Quintana JB, Rodríguez I, Cela R (2009) Simultaneous determination of parabens, triclosan and triclocarban in water by liquid chromatography/electrospray ionisation tandem mass spectrometry. Rapid Communications in Mass Spectrometry 23 (12):1756-1766. doi:10.1002/rcm.4069
[7] Piao C, Chen. L, Wang Y (2014) A review of the extraction and chromatographic determination methods for the analysis of parabens. Journal of chromatograpy B 969:139-148
[8] Pedrouzo M, Borrull F, Marcé RM, Pocurull (2009) Ultra-high-performance liquid chromatography-tandem mass spectrometry for determining the presence of eleven personal care products in surface and wastewaters. Journal of Chromatography A 1216 (42):6994-7000. doi:10.1016/j.chroma.2009.08.039
[9] Zgoła-Grześkowiak A, Jeszka-Skowron M, Czarczyńska-Goślińska B, Grześkowiak T (2016) Determination of parabens in polish river and lake water as a function of season. Analytical Letters 49 (11):1734-1747.
[10] Jaume A, Danie lR, Bozo Z, Sandra P, Damià B (2015) Liquid Chromatography-Mass Spectrometry quantification and confirmation aspects.
[11] Vallerie AM, Philiswa NN, Ngila* JC (2018) Factorial Design Optimisation of Solid Phase Extraction for Preconcentration of Parabens in Wastewater Using Ultra-High Performance Liquid Chromatography Triple Quadrupole Mass Spectrometry. Current Analytical Chemistry 14:1-10. doi:http://dx.doi.org/10.2174/1573411014666180627150854
[12] Kunkel U, Radke M (2011) Reactive tracer test to evaluate the fate of pharmaceuticals in rivers. Environmental science & technology 45 (15):6296-6302
[13] Leardi R (2009) Experimental design in chemistry: A tutorial. Analytica chimica acta 652 (1-2):161-172. doi:10.1016/j.aca.2009.06.015

[14] Shi L, Li X, Li Y, Wen X, Li J, Choi MM, Dong C, Shuang S (2015) Naked oats-derived dual-emission carbon nanodots for ratiometric sensing and cellular imaging. Sensors and Actuators B: Chemical 210:533-541
[15] Albero B, Pérez RA, Sánchez-Brunete Co, Tadeo JL (2012) Occurrence and analysis of parabens in municipal sewage sludge from wastewater treatment plants in Madrid (Spain). Journal of hazardous materials 239-240:48-55. doi:10.1016/j.jhazmat.2012.05.017
[16] Núñez L, Tadeo JL, García-Valcárcel AI, Turiel E (2008) Determination of parabens in environmental solid samples by ultrasonic-assisted extraction and liquid chromatography with triple quadrupole mass spectrometry. Journal of Chromatography A 1214 (1-2):178-182. doi:10.1016/j.chroma.2008.10.105
[17] Canosa P, Rodríguez I, Rubí E, Bollaín MH, Cela R (2006) Optimisation of a solid-phase microextraction method for the determination of parabens in water samples at the low ng per litre level. Journal of Chromatography A 1124 (1-2):3-10. doi:10.1016/j.chroma.2006.03.045
[18] Regueiro J, Becerril E, Garcia-Jares C, Llompart M (2009) Trace analysis of parabens, triclosan and related chlorophenols in water by headspace solid-phase microextraction with in situ derivatization and gas chromatography-tandem mass spectrometry. Journal of Chromatography A 1216 (23):4693-4702
[19] Mashile G, Mpupa A, Nomngongo P (2018) In-Syringe Micro Solid-Phase Extraction Method for the Separation and Preconcentration of Parabens in Environmental Water Samples. Molecules 23 (6):1450

APPENDIX G:

PHOTOCATALYTIC DEGRADATION OF WATER CONTAMINANTS USING NANOMATERIALS

G1. Introduction

Photocatalysis is considered as one of the most promising technique in water treatment since it has a great potential utilizing green and sustainable solar energy in removing organic pollutants and harmful bacteria present in polluted water systems [31]. The photocatalytic technology uses light and a photocatalyst (e.g metal oxide) in the decomposition of organic pollutants. Semiconductors have been used in photocatalysis for decomposing the organic pollutants rapidly and in an environmentally friendly manner [32-35]. Tungsten trioxide (WO_3) is a promising n-type semiconductor photocatalyst with an optical band gap (Eg) of 2.8 eV that has received attention in recent times [36,37]. Doping of photocatalysts plays an important role in modifying the catalyst properties. Iron (Fe) was used for doping WO_3 to form Fe-doped WO_3 nanocomposite material for the photodegradation of methylparaben as model organic substance to test the efficiency of the nano-photocatalyst using advanced oxidation process [38]. WO_3 was also doped with a metal chalcogenide namely, cadmium sulphide (with a small band gap of 2.4 eV), to form CdS-WO_3 for degradation of ethylparaben (EP) under solar simulated light. The photocatalyst employed Z-scheme nanocomposite where two semiconductors are employed as they exhibit better photoactivity due to suitable bandgap matching between the semiconductors. Novel Z-scheme Co_3O_4/WO_3 nanocomposite was studied for photocatalytic degradation of ethylparaben and methylene blue under visible light irradiation. Another dopant for WO_3 investigated, was tricobalt tetroxide (Co_3O_4) to form Co_3O_4/WO_3, used as a novel Z-scheme photocatalyst Co_3O_4/WO_3, investigated for the photodegradation of organic pollutants namely, ethylparaben and methylene blue under simulated solar light.

G2. Nanotechnology Methods for Degradation of Organic Contaminants

Samples collected from the secondary treated water were subjected to filtration using nanomaterials for water treatment. These nanomaterials were fabricated in our laboratory in the Department of Applied Chemistry, University of Johannesburg. Briefly, the following experimental procedures were employed in the preparation of nanomaterials. WO_3 nanoparticles were prepared by use of microwave used by [44]. In the synthesis of Fe-doped WO_3 nanoparticles, microwave was used as per Abhudhahir and Kandasamy [44] with modifications according to [45] producing final products for WO_3 and Fe-doped WO_3 as pale yellow and brown, respectively. . Similar methods by [46] were used for syntheses of CdS-doped WO_3 to obtain orange powder as confirmation of CdS-WO_3 nanocomposite. The preparation of Z-scheme CO_3O_4/WO_3 a deep green-yellow powder indicated successful formation of CdS-WO_3 nanocomposite. The synthesized nanomaterials including pristine WO_3 materials, Fe-doped WO_3, CdS-doped WO_3, Z-scheme Co_3O_4-doped WO_3 nanocomposites were characterized using X-ray diffraction, Brunauer-Emmett-Teller (BET)-nitrogen adsorption-desorption isotherms, UV-Vis diffuse reflectance spectroscopy, Raman analysis, transmission electron microscope and high-resolution transmission electron microscopy (TEM and HRTEM), X-ray Photoelectron Spectroscopy (XPS).

G3. Summary Results on Photocatalytic Nanomaterials for Degradation of Organics

Figure G1 shows a remarkable performance of Z-scheme Co_3O_4/WO_3 heterojunction photonano catalyst owing to doping of WO_3 by Co_3O_4, and also due formation of Z-scheme between n-type WO_3 and p-type Co_3O_4 which aided in lowering the electron-hole pair recombination at the interface.

It was observed that the degradation of ethylparaben by Co_3O_4/WO_3 nanocomposite photocatalyst can be quantified by first-order equation [54] shown in Equation **G1**:

$$-\ln C_t/C_o = k_{app}t \qquad \text{Eq. } \mathbf{G1}$$

Where C_o is the concentration of pollutants before degradation, C_t is the concentration of pollutants at irradiation time *t*, and k_{app} is the apparent kinetic coefficient (min^{-1}) of the degradation reaction.

The *k* values for degradation of EP and MB over Co_3O_4/WO_3 was 0.0353 min^{-1} and 0.2558 min^{-1}, respectively. These results represented 1.756 times higher than Co_3O_4 (0.0201min^{-1}) and 1.878 times for WO_3 (0.0188 min^{-1}) in EP and 4.490 times higher than Co_3O_4 (0.0575 min^{-1}) and 3.242 times higher than bare WO_3 (0.0789 min^{-1}) in degradation of MB.

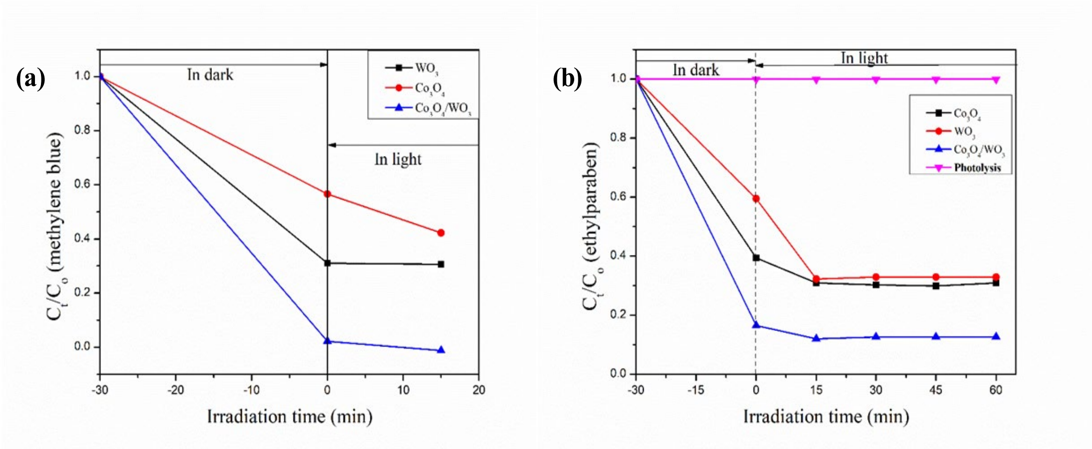


Figure G1: Adsorption and photodegradation of ethyl paraben (EP) and methyl blue (MB) Co_3O_4, WO_3, and by Z-scheme Co_3O_4/WO_3 nanocomposite

G4. Conclusions

Degradation of parabens and methyl blue in the wastewater using photocatalyst nanomaterials was investigated using tungsten trioxide (WO_3) modified with various dopants. The photodegradation by-products were analysed with LC-MS/MS to identify and quantify these products. The novel Z-scheme Co_3O_4/WO_3 nanocomposite proved to be an excellent candidate for the photocatalytic degradation of organic pollutants. Pollutant removal efficiency of 99% was achieved when secondary treated water was subjected to in-house fabricated nanosorbents as filters.

G5. References

[1] Che H, Liu C, Hu W, Hu H, Li J, Dou J, Shi W, Li C, Dong H (2018) NGQD active sites as effective collectors of charge carriers for improving the photocatalytic performance of Z-scheme g-C3N4/Bi_2WO_6 heterojunctions. Catalysis Science & Technology 8 (2):622-631. doi:10.1039/C7CY01709J

[2] Ye L, Su Y, Jin X, Xie H, Zhang C (2014) Recent advances in BiOX (X= Cl, Br and I) photocatalysts: synthesis, modification, facet effects and mechanisms. Environmental Science: Nano 1 (2):90-112

[3] Dong S, Feng J, Fan M, Pi Y, Hu L, Han X, Liu M, Sun J, Sun J (2015) Recent developments in heterogeneous photocatalytic water treatment using visible light-responsive photocatalysts: a review. RSC Advances 5 (19):14610-14630. doi:10.1039/C4RA13734E

[4] Wen Z, Wu W, Liu Z, Zhang H, Li J, Chen J (2013) Ultrahigh-efficiency photocatalysts based on mesoporous Pt-WO_3 nanohybrids. Physical Chemistry Chemical Physics 15 (18):6773-6778. doi:10.1039/C3CP50647A
[5] Che H, Che G, Dong H, Hu W, Hu H, Liu C, Li C (2018) Fabrication of Z-scheme Bi_3O_4Cl/g-C_3N_4 2D/2D heterojunctions with enhanced interfacial charge separation and photocatalytic degradation various organic pollutants activity. Applied Surface Science 455:705-716. doi:https://doi.org/10.1016/j.apsusc.2018.06.038
[6] Adhikari S, Sarkar D (2014) Hydrothermal synthesis and electrochromism of WO_3 nanocuboids. RSC Advances 4 (39):20145-20153. doi:10.1039/C4RA00023D
[7] Qian J, Zhao Z, Shen Z, Zhang G, Peng Z, Fu X (2016) Oxide vacancies enhanced visible active photocatalytic $W_{19}O_{55}$ NMRs *via* strong adsorption. RSC Advances 6 (10):8061-8069. doi:10.1039/C5RA23655J
[8] Ahmed Y, Yaakob Z, Akhtar P (2016) Correction: Degradation and mineralization of methylene blue using a heterogeneous photo-Fenton catalyst under visible and solar light irradiation. Catalysis Science & Technology 6 (4):1233-1233. doi:10.1039/C6CY90011A
[9] Sayed Abhudhahir MH, Kandasamy J (2015) Synthesis and characterization of Manganese doped Tungsten oxide by Microwave irradiation method. Materials Science in Semiconductor Processing 40:695-700. doi:http://dx.doi.org/10.1016/j.mssp.2015.07.031
[10] Ngigi EM, Nomngongo PN, Ngila JC (2019) Synthesis and Application of Fe-Doped WO 3 Nanoparticles for Photocatalytic Degradation of Methylparaben Using Visible-Light Radiation and H 2 O 2. Catalysis Letters 149 (1):49-60
[11] Ngigi EM, Kiarii EM, Nomngongo PN, Ngila CJ (2018) Application of Z-Scheme CdS WO_3 Nanocomposite for Photodegradation of Ethylparaben under Irradiation with Visible Light: A Combined Experimental and Theoretical Study. ChemistrySelect 3 (34):9845-9856
[12] Li K, Liang Y, Yang J, Zhang H, Yang G, Lei W (2018) BiOCl/Fe_2O_3 heterojunction nanoplates with enhanced visible-light-driven photocatalytic performance for degrading organic pollutants and reducing Cr(VI). Journal of Photochemistry and Photobiology A: Chemistry 364:240-249. doi:https://doi.org/10.1016/j.jphotochem.2018.06.001