NANOPOROUS POLYMERS FOR THE REMOVAL OF ORGANIC CONTAMINANTS IN WATER

BB Mamba • RW Krause • TJ Malefetse •
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Water Research Commission

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Report to the
WATER RESEARCH COMMISSION

by

BB MAMBA · RW KRAUSE · TJ MALEFETSE ·
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EXECUTIVE SUMMARY

The contamination of water by organic compounds has caused an escalation in efforts to find new solutions to help reduce the threat posed by these substances. Organic compounds can be harmful to human health and the environment, and they pose unique challenges in several industrial applications. Of the currently available technologies, activated carbon and reverse osmosis successfully remove most of the organic contaminants. However, these technologies fail to absorb the organic contaminants to desired low concentrations (ng/L levels). Even when present at very low concentrations, organic contaminants cause serious environmental and human health problems; they are liable to bioaccumulate and interact with sensitive endocrine systems, respectively. Recent studies have explored the capabilities of **nanoporous polymers**, a class of nanomaterials that show great potential to absorb organic contaminants in water.

This project was undertaken to further develop this polymer technology and assist industries and municipalities in their quest to solve the problem of water contamination by organic compounds. The study was conducted with the following specific objectives in mind:

- To synthesize cyclodextrin-based (CD) polymers using a variety of cross-linking reagents such hexamethylene diisocyanate and toluene-2,6-diisocyanate, and to characterize the polymers using IR spectroscopy, BET, SEM and thermogravimetric analysis (TGA).

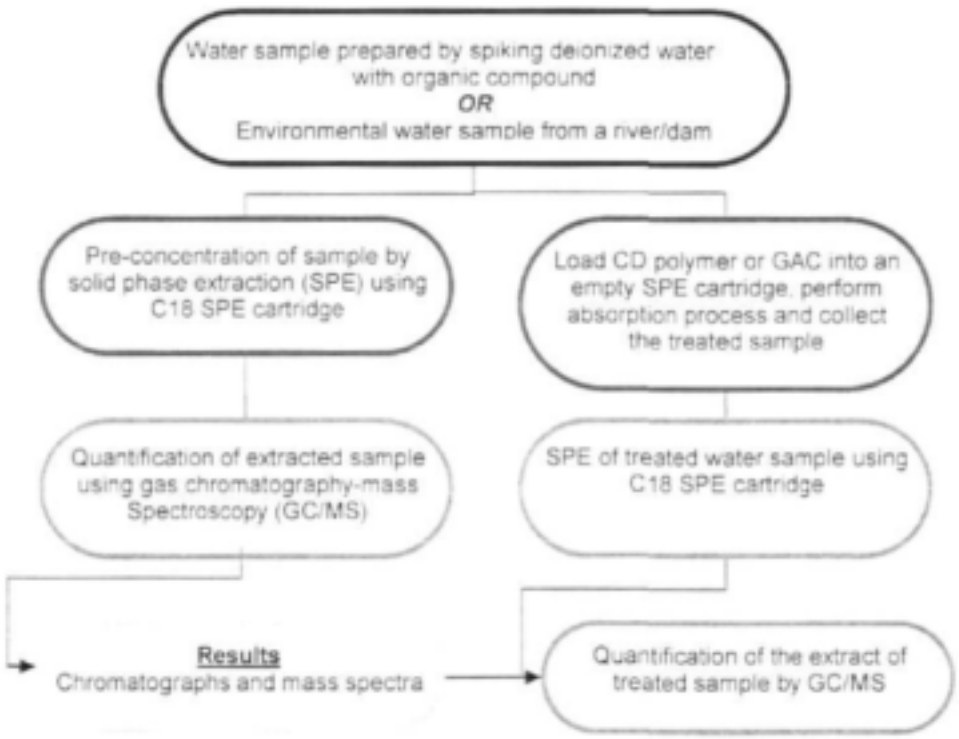
- To test the ability of the CD polymers synthesized in (i) to absorb selected high priority organic pollutants from water to µg/L and ng/L levels. This will be achieved by performing simple isotherm and kinetic studies such as jar and small scale columns tests, respectively.

- To perform a comparative study of the polymers based on the type of parent CD used, the type of linker used, and the physical properties of the polymers. Furthermore, a study of a comparison the most effective polymers and granular activated carbon (GAC) will be pursued.

- To study the effect of absorbed organic guest molecules on the CD polymers by characterizing the formed inclusion complexes using TGA and DSC.

- To investigate the recyclability efficiency of the CD polymers.

Most of the work was carried out using rapid small scale column tests (RSSCTs) that were designed in our laboratories. The general **design of the study** and pathway that was followed while conducting these experiments is shown in the flow diagram below.



The **findings** of the entire study are summarized as follows:

- Toluene-2,6-diisocyanate (TDI) and hexamethylene diisocyanate (HDI) linked α-, β- and γ-cyclodextrin polymers were successfully prepared in the laboratory giving a 100% percent yield of the product. The products were characterized mainly by infra-red spectroscopy due to the insoluble nature of the nanoporous polymers.

- Polymers with different physical properties were synthesized from the same parent cyclodextrin and a complementary linker by varying the reaction conditions. It was shown that these polymers have different affinities for organic compounds in water.

- Water samples with concentrations of contaminants as low as 10 ng/L were prepared. These were pre-concentrated by solid phase extraction (SPE) or purge/trap cycles and successfully analyzed using Gas Chromatography-Mass Spectrometry (GC/MS).

- When water samples containing a high concentration of organic pollutant (concentrations of 10 mg/L) were treated, the polymers were not as effective at removing organic contaminants as granular activated charcoal (GAC) at such high levels of concentration.

- The polymers were however extremely effective when lower concentrations (10 ng/L) of water samples spiked with known organic contaminants were treated. In contrast, the organic pollutants could still be detected after treating the same sample with GAC.

- The polymers were recycled and tested for durability. It was observed that the polymers could still be effective even after 20 cycles. The measure of such effectiveness was achieved by washing the polymers with ethanol to clean their cavities.

- While the study was performed at laboratory scale, it was observed from the regeneration studies that the polymers did not reach the breakthrough stage.

- The parameters used for the determination of the iodine number, phenol value and methylene blue number for GAC were not ideal for the assessment of the CD polymers. The concentrations of solutions treated were relatively high and these had to be reduced particularly in the determination of the phenol number.

- Analyses of samples using Total Organic Carbon (TOC) method of analysis and Ultraviolet (UV) Visible Spectroscopy were successfully accomplished. Reduction in TOC and UV absorbance was observed after treatment of the water samples with CD polymers. However, only a small amount of humic acid (HA) was removed in all experiments using a more concentrated 10 mg/L HA sample.

- Problems of consistency were encountered with TOC analysis especially at higher concentrations and measures to overcome these were implemented.

- The polymers were absolutely effective at removing 2-MIB (and geosmin) from water at the ng/L level. GAC on the other hand failed to remove it completely.

- The preparation of the polymers is inexpensive and simple. From 10g of β-CD, 10 mL of HMDI linker and 150 mL of DMF, approximately 18 g of polymer material was obtained. Although the CD polymers are more expensive to produce compared to activated carbon, they can be used in industries or applications where ultra pure water is an imperative.

- TGA and DSC analysis showed that the polymers are stable within a wide temperature range. The techniques were not suited for studying the inclusion complexes of such compounds due to the fact that host-guest ratios could not be ascertained given the low levels of contaminant. The possibility of inclusion complex formation was however confirmed through the qualitative comparison of the TGA thermograms and DSC curves obtained.

The following **recommendations** were made in compliance with the findings of research study:

- A study that would investigate the minimum contact time required for the absorption of organic contaminants by varying the flow rates at which water is passed through the polymer may be crucial.

- A mini-scale column setup that resembles a real situation where CD polymers could be applied in conjunction or as a substitute for GAC may be designed for further studies.

- Small scale commercialization of CD polymers such as the manufacturing of small filtering gadgets may be an ideal step in the utilization of these polymers.

- Pilot studies may have to be performed to investigate how these could be effectively implemented in large scale applications such as in water treatment plants.

- The polymers may be used as the last clean up step in water treatment processes after all conventional technologies have played their role.

- A much more comprehensive study should be undertaken to investigate any adverse effects that the polymers could have on humans and the environment. None have been discovered so far.

- Specific applications (such as the absorption of endocrine disrupting compounds, EDC's) of these polymers should be conducted on real-water samples to investigate the efficacy of the polymers in the presence of interfering pollutants.

- Funding of the project may enhance further work on the applications of the polymers which, with the sharing of knowledge both from local and international sources, may see the implementation of these come into effect sooner than anticipated.

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Dr. G. Offringa (Chairman)	Water Research Commission (WRC)
Mrs S.D. Freese	Umgeni Water
Dr. B.B. Mamba	Envi Sabi
Mr. R.W. Krause	Envi Sabi

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Dr. B.B. Mamba	Mr. S.D. Mhlanga
Dr. T.J. Malefetse	Mr. E.N. Nxumalo
Mr. R.W. Krause	Mr. M.F. Bambo

The authors also wish to highlight the facilitation role done by Mr Pieter Smit (WRC) during the project tenure.

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GLOSSARY OF TERMS

Å	Angstrom
AC	Activated Carbon
APCI-MS	Atmospheric Pressure Chemical Ionization-Mass Spectrometry
ASTM	American Society for Testing and Materials
AWWA	American Water Works Association
S_N2	Bimolecular Nucleophilic Substitution
BOD	Biological Oxygen Demand
C	Residual Concentration
CD(s)	Cyclodextrin(s)
α-CD	*Alpha* Cyclodextrin
β-CD	*Beta* Cyclodextrin
γ-CD	*Gamma* Cyclodextrin
Co	Initial Concentration
COD	Chemical Oxygen Demand
d	Doublet
dd	Doublet of doublet
D/NQ	Detected but not quantifiable
DBPs	Disinfection By-Products
DCM	Dichloromethane
DMF	N,N-Dimethyl formamide
DMSO	Dimethylsulfoxide
D6-DMSO	Deuterated DMSO
DOM	Dissolved Organic Matter
DSC	Differential Scanning Calorimetry
EI	Electron Ionization
ESI	Electrospray Ionization
EtOAc	Ethyl acetate
GAC	Granular Activated Carbon
GC/MS	Gas Chromatography / Mass Spectroscopy
GPC	Gel Permeation Chromatography

HAAs	Haloacetic Acids
HMDI	Hexamethylene diisocyanate
HPLC	High Pressure Liquid Chromatography
HS	Humic Substances
HTC	High Temperature Combustion
IC	Inorganic Carbon
IR	Infra red
K	Equilibrium Constant
LLE	Liquid-liquid Extraction
m/z	Mass to charge ratio
MHz	Mega Hertz
M.pt	Melting point
2-MIB	2-Methylisoborneol
mg/L	milligrams per litre
µg/L	micrograms per litre
MWCO	Molecular Weight Cut-off
m	Multiplet
ND	Not Detected
ng/L	nanograms per litre
nm	nanometer
NMR	Nuclear Magnetic Resonance
NOM	Natural Organic Matter
NPOC	Non Purgeable Organic Carbon
pH	Value taken to represent the acidity or alkalinity of an aqueous solution
PNP	*p*-Nitriphenol
PAC	Powdered Activated Carbon
KBr	Potassium Bromide
PCP	Pentachlorophenol
POC	Purgeable Organic Carbon
ppb	parts per billion
ppt	parts per trillion
RSSCTs	Rapid Small Scale Column Tests

SEM	Scanning Electron Microscopy
s	Singlet
SOCs	Synthetic Organic Compounds
SPE	Solid Phase Extraction
TBDMS	*tert*-Butyldimethyl silane
TBAF	Tetrabutyl ammonium fluoride
THF	Tetrahydrofuran
TC	Total Carbon
TDI	Toluene 2,6-diisocyanate
Ts_2O	Toluene sulfonic anhydride
TGA	Thermo gravimetric Analysis
TLC	Thin Layer Chromatography
THMs	Trihalomethanes
t	Triplet
TIC	Total ion count
TOC	Total Organic Carbon
T_R	Retention Time
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
VOC	Volatile Organic Compounds
WRC	Water Research Commission
λ	Wavelength
XRD	X-Ray Diffraction

CHAPTER 1: BACKGROUND

1.1 Introduction

Water is a finite and vulnerable resource that is essential for sustaining life, development and the environment. Water quality in South Africa, and the world as a whole, is drastically deteriorating due to contamination by organic substances. The increase in water pollution by organic pollutants is attributable to the increased contribution of chemicals towards the advancement of technology. In a nutshell, chemicals, organic compounds included, create and feed technology.

Examples of organic contaminants found in water supplies include halogenated hydrocarbons such as trihaloethylene, tetraethylene and trihalomethanes (THMs), aromatic compounds (e.g. benzene, toluene and phenolic compounds), pesticides, hormones, plasticizers, medications and many others. These compounds are obviously undesirable in water because they are often toxic to animals including humans. Besides their carcinogenic properties, many of these organic pollutants are known to affect the central nervous system, the liver, kidneys, endocrine system, and other vital systems in the human body.

The major sources of organic pollutants can be divided into three groups and these are direct human activity, indirect production, and natural sources. Each is discussed briefly and individually below.

- Domestic, industrial and commercial activities comprise the biggest source of organic pollutants. Examples include industrial solvents, household detergents and insecticides and herbicides used in the agricultural industry. The petrochemical industry, by way of leaking gas tanks and oil spillages, also contributes substantially towards chemical pollution. The use of organic explosives is also becoming widespread.

- A number of organic compounds have found widespread use in the water treatment industry. The water treatment process is itself accompanied by side reactions that lead to the generation of even more toxic disinfection by-products (DBPs) such as THMs.

- The breakdown of naturally occurring organic materials (commonly referred to as natural organic matter or NOM) by microorganisms that are resident both in the soil and water often gives rise to toxic degradation products. Very often the degradation products are more difficult to remove from water than the native NOM.

The removal of natural organic matter (NOM), a ubiquitous and main component of organic carbon in aquatic systems, is the main focus of this study. Its presence in water produces aesthetically undesirable problems such as colour, odour and bad taste.[1-4] Besides affecting many aspects of water treatment systems, NOM promotes the formation of potentially harmful disinfection by-products (DBPs) such as trihalomethanes, haloacetic acids, haloketones and other toxic chlorinated organic compounds.[1,3,5]

To date, the removal of NOM and its degradation products to parts per billion levels (ppb) (ppb = μg/L) remains a challenge to scientists, local governments and industry. These and other inert organic molecules appear to have little affinity for most chemical compounds, thus making their removal in water difficult.[6] Conventional water purification technologies such as activated carbon, reverse osmosis, zeolites, and molecular sieves have failed to remove organics to desired levels.[6,7] Also, it is not known whether these techniques are capable of facing the challenges posed by other new and emerging contaminants.[8,9]

An increasing demand for the use of ultra pure water by various industries such as the fish, pharmaceutical, electroplating, and semiconductor chip manufacturing industries, has led to researchers developing modern techniques that can solve the problem of contamination of water by organic substances. To this end, a completely new class of nanoporous cyclodextrin (CD) polymers (often referred to as "nanosponges") has recently been reported.[6] These cyclodextrin polymers are known to form inclusion complexes with a large number of molecular compounds.[10,11]

1.2 Justification of the project

Ongoing studies in our group, and elsewhere, have focussed almost exclusively on the synthetic aspects of cyclodextrin polymers. This involved the utilization of cross-linkers such as epichlorohydrin, toluene-2,6-diisocyanate (TDI) and hexamethylene diisocyanate (HMDI) in the formation of these polymers.[7] Their ability to absorb some organic molecules (e.g. nitrophenol) was also tested. To the best of our knowledge, no study has been carried out that utilizes cyclodextrin nanoporous polymers in the removal of NOM and its degradation by-products from water. Not only do CD polymers remove organic contaminants from water to parts per trillion (ppt) levels, they also offer flexibility and cost effectiveness.[6] Nanoporous CD polymers are challenged to compete with activated carbon (AC) in performance, cost and availability. Since activated carbon is not effective in ultrapure water applications, nanoporous polymers are poised to surpass activated carbon when they are commercialised.

1.3 Aims and objectives of this study

The specific objectives of this study are as follows:

(i) To synthesize CD polymers using a variety of cross-linkers (**Figure 5.1**) and characterize them using IR Spectroscopy, Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM).

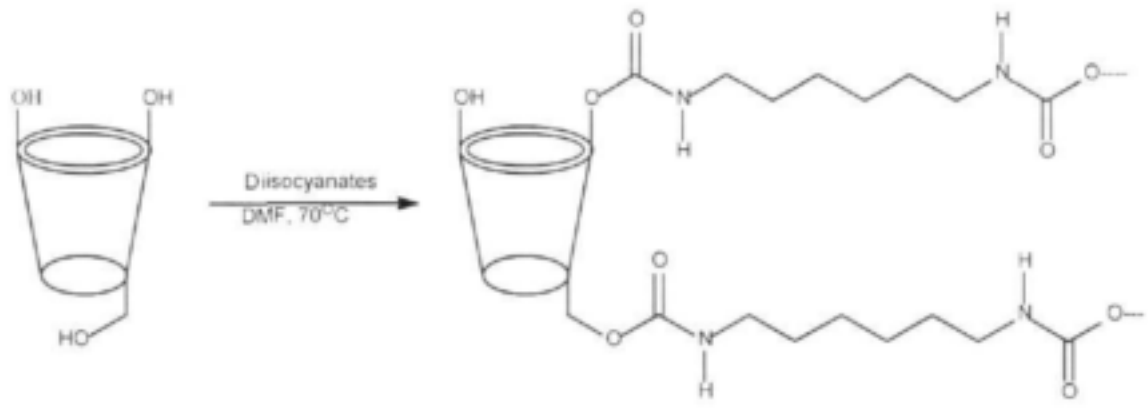


Figure 1.1: Synthetic route of cyclodextrin polymers.

(ii) To evaluate the pre-concentration of water samples using solid phase extraction (SPE) as a quantitative way of determining small amounts of pollutants by Gas Chromatography-Mass Spectrometry (GC-MS) and UV Spectroscopy.

(iii) To test the ability of the CD polymers to absorb high priority organic pollutants from water at µg/L levels by performing simple isotherm and kinetic study tests of the CD polymers using jar tests and small scale columns, respectively.

(iv) To perform a comparative study of the polymers against granular activated carbon (GAC) based on the parent CD used, the type of linker used, and the physical properties of the polymers.

(v) To study the effect of absorbed organic guest molecules on the CD polymers by characterizing the formed inclusion complexes using TGA and DSC.

(vi) To investigate the recyclability efficiency of the CD polymers.

(vii) To synthesize monosubstituted cyclodextrins (m-CDs) with a view to fine-tuning the properties of the resulting polymers. This constitutes the second section of this report and is dealt with separately in chapter 7.

(viii) To incorporate the monofunctional CDs into a nanosponge polymer and characterize the polymers using various spectroscopic techniques.

(ix) To compare the ability of the modified and unmodified polymers to absorb organic contaminants.

The understanding of NOM and CDs is critical for this study. Therefore, in the next section the chemistry of both NOM and CDs is discussed before reviewing available water treatment technologies.

2.1 What is NOM?

Natural organic matter (NOM), as the name implies, consists of a complex mixture of naturally occurring organic compounds. The organic compounds that comprise NOM include, among others, amino acids, carbohydrates, lipids, waxes, organic acids and humic substances (HS). Of all the NOM components mentioned above, HS appears to have attracted considerably more attention from water scientists than the other components. This is mainly due to their more complex macromolecular structure. In addition, HS are a major component of dissolved organic matter (DOM) found in aquatic life. Humic substances, also called humic matter, can be classified into three main categories; humic acid, fulvic acid and humin. This classification is based on the conditions under which the respective components can be extracted or isolated and are defined as follows:

- Humic acid – the fraction of humic substances that is soluble in water at pH>2.
- Fulvic acid – the fraction of humic substances that is soluble in water under all pH conditions.
- Humin – the fraction of humic substances that is not soluble in water at any pH value.

The understanding of NOM is necessary because it impacts on many processes that occur during water treatment systems.[12] Its presence in water supplies is undesirable for a number of reasons. It is known to:

- produce aesthetically undesirable problems such as colour, odour and bad taste of the water.[1,13]
- act as a precursor of toxic low- and high–molecular weight chlorine containing organic compounds that are produced during chlorination and oxidation by ozonation.[1]
- lower the efficiency of water treatment processes.[1]
- provide an undesirable biological growth substrate.[4]
- compete with polluting compounds for adsorption sites in granular activated carbon (GAC).[1]

- stabilize dispersed and colloidal particles during coagulation processes.[1]
- precipitate in the distribution system leading to deterioration of tap water quality thus increase the need for cleaning the interior of pipes.[1]
- serve as the precursor material for the formation of drinking water disinfection by-products (DBPs).[1]

The humic matter of ecosystems is mainly controlled by a net balance of formation, degradation and transfer paths. The occurrence and flow path of dissolved humic substances in the natural environment is shown in **Figure 2.1**.[14-16]

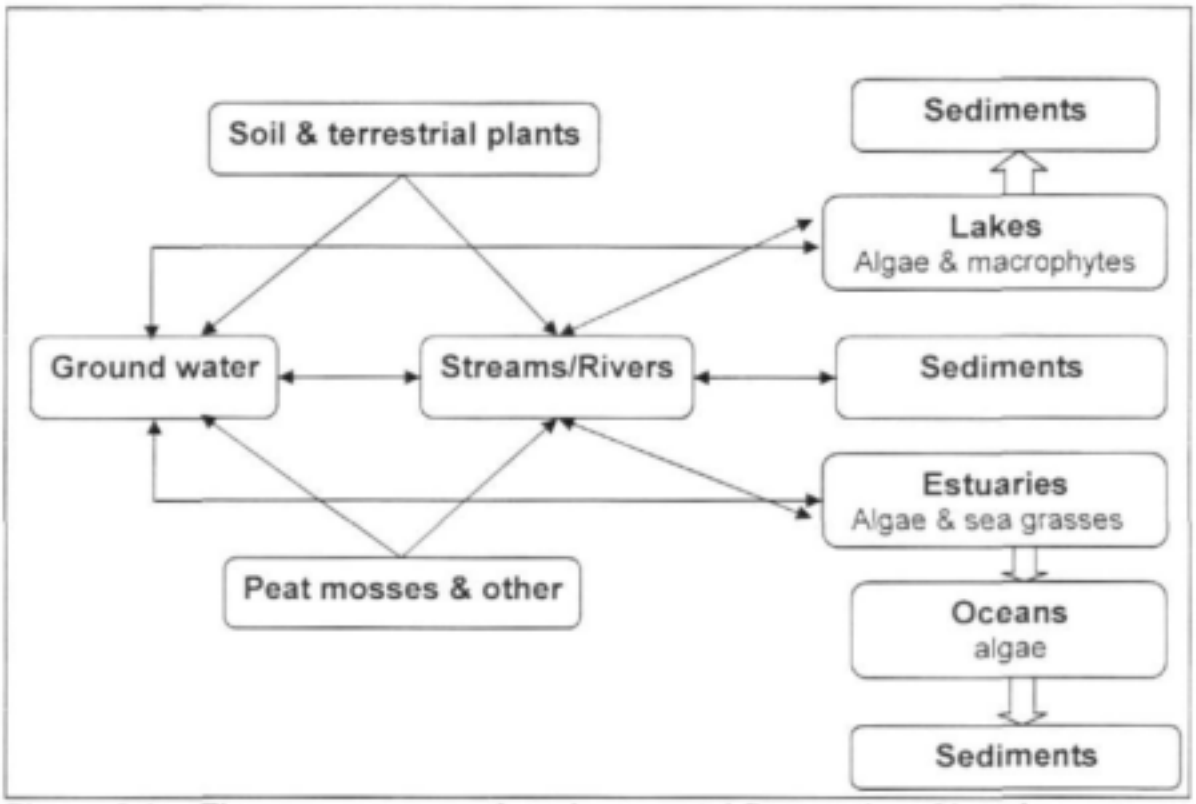


Figure 2.1: The occurrence and environmental flow paths of humic substances.

Understanding the structure of NOM could therefore assist in the design of new treatment processes for its removal from water and thereby reducing or preventing the formation of DBPs.[7] However, the elucidation of the structure of NOM is still proving to be a challenging task. Previous studies using Gel Permeation Chromatography (GPC) suggest that humic acids have molecular weights ranging from 100 to 100000 while new information provided by Electrospray Ionization (ESI) and Atmospheric Pressure Chemical Ionization-Mass Spectrometry (APCI-MS) show much lower molecular weight distributions (e.g. 300–1200 for humic

acid).[8,9] Due to uncertainties in molecular weight, the Gas Chromatography–Mass Spectrometry (GC/MS) technique cannot be used for the quantification of humic acid (HA). Studies on the complexation of humic and fulvic acids can, however, can be achieved using UV Spectrometry and Total Organic Carbon (TOC) measurements.[17]

2.2 NOM as a precursor for drinking water disinfection by-products (DBPs)

DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs) are formed when disinfectants (e.g. chlorine, hypochlorite, ozone, chlorine dioxide and chloramines) react with NOM in source water.[17] Although present at low concentrations (μg/L levels), DBPs are known to be persistent organic pollutants that (i) possess toxic characteristics; (ii) show propensity to bioaccumulate; (iii) are prone to long range deposition, and (iv) can result in adverse environmental and human health effects at locations far from their source.[5,17]

Latest human exposure studies by Richardson[8] indicate ingestion as not the only important route of exposure. Inhalation from showering and dermal absorption (from bathing and other activities) often provide equivalent or even greater exposure to some DBPs.[8] Although currently available water purification technologies such as granular and powdered activated carbon remove some organic materials from water, they fail to reduce many organic materials including NOMs to μg/L levels.[6] It is hoped that CDs will accomplish this task.

3.1 Source and nomenclature of cyclodextrins

Cyclodextrins (CDs) were first discovered in 1891 by Villiers.[10,18-20] CDs, which are sometimes called Schardinger dextrins, cycloamyloses, or cycloglucans, are polysaccharides of low molecular weight belonging to the general class called oligosaccharides. They are produced by treating starch with the amylase *Bacillus macerans*.[10,20,21]

3.2 Structure and physical properties of cyclodextrins

The three common types of cyclodextrins are α-CD, β-CD and γ-CDs, which are referred to as the first generation or parent CDs. These CDs possess six, seven and eight glucose units respectively, linked together by α-(1,4)-linkages **(Figures 3.1** and **3.2)**.

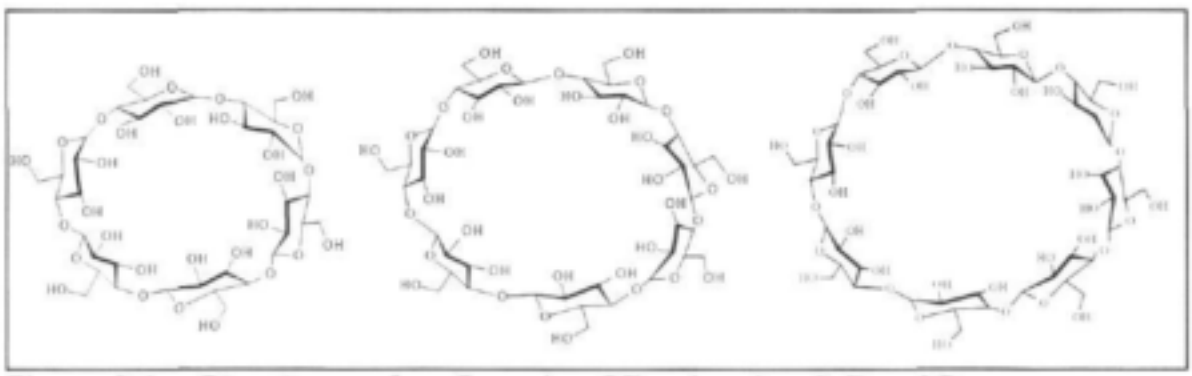


Figure 3.1: Structures of α-, β- and γ- CDs showing 6, 7 and 8 glucopyranose units respectively.

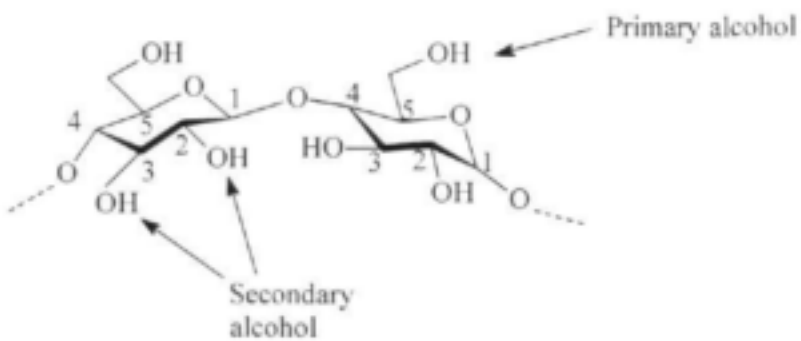


Figure 3.2: Illustration of α-(1,4)-linkages and the primary and secondary alcohol groups.

Other higher molecular weight CDs have been isolated but, because they are currently too expensive, they have not been used extensively in industry.[10,20] The β-CD is the most accessible, lowest in cost and generally the most useful, it has been used extensively in this study

A characteristic feature of CDs is that they possess a toroidal shape that form well defined cylindrical cavities of about 8Å deep and 5 –10Å in diameter.[10,18,21] The cone is formed by the carbon skeleton of the glucose units and the glycosidic oxygen atoms that are in between them. The primary hydroxyl (OH) group of the glucose is located at the narrow end of the cone (primary face) and the secondary OH groups are at the wider secondary face (see **Figure 3.3**). The main properties and dimensions of α-, β- and γ-CDs are summarised in **Table 3.1** below.[20]

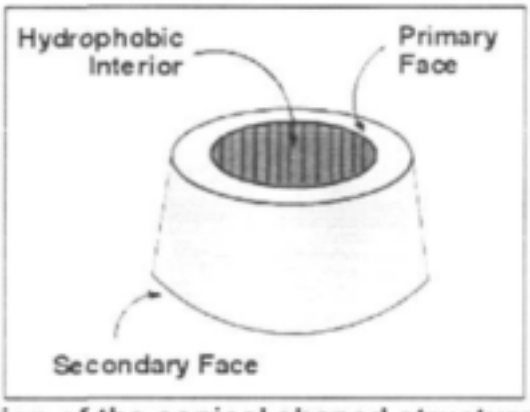


Figure 3.3: Illustration of the conical shaped structure of a cyclodextrin.[20]

Table 3.1: Properties of cyclodextrins

Property	α-cyclodextrin	β-cyclodextrin	γ-cyclodextrin
Number of glucose units	6	7	8
MW (g/mol)	972	1135	1297
Water solubility (g/100mL)	14.5 at 25°C	1.85 at 25°C	23.2 at 25°C
Internal Diameter (Å)	4.9	6.2	7.9
External diameter (Å)	14.6	15.4	17.5
Cone height (Å)	7.9	7.9	7.9
Cavity volume (Å^3)	174	262	427

The primary and secondary hydroxyl groups on the outside of the CDs make them water soluble. CDs are also insoluble in most common organic solvents. The cavity of the CD ring consists of a ring of C-H groups, a ring of glycosidic oxygen atoms followed by another ring of C-H groups. This renders the cavity of the CD rings less polar. Another important feature is that, although CDs have a hydrophilic surface, they contain hydrophobic cavities that enable the encapsulation of the hydrophobic guest molecules into these cavities.

Since parent CDs are soluble in water and some organic solvents (e.g. DMF and DMSO), they cannot be used directly in the absorption of organic pollutants from water. As a result, CD polymers that are insoluble in water but possess enhanced affinity for organic contaminants in water have been synthesized.[6,7,19] The design of these CD polymers is based primarily on the reactivity of the hydroxyl groups.[22] Treatment of the hydroxyl groups of the parent CDs with a bifunctional group led to the generation of highly cross-linked nanoporous polymers.[6] These polymers can be prepared as granular solids, powders or films by a simple variation of ratios of the reacting species and other conditions.

The reactivity of the hydroxyl groups can also be exploited by forming monosubstituted derivatives. However, the significance of this modification is only realized once the solubility and absorption capability of the resulting polymers has been established. Monosubstituted and polymeric CDs are at the core of this study and are hence reviewed in the following section.

3.3 Derivatives of Cyclodextrins

3.3.1 Reactivity patterns of the hydroxyl groups

CDs are polyfunctional;[23] they can, therefore, undergo a wide variety of reactions. These may involve cleavage of the O-H, C-O, C-H or C-C bonds. The most frequently studied reaction is the electrophilic attack of the hydroxyl groups. In fact, almost all modifications of CDs take place at one of the hydroxyl groups.

Of all the three types of OH's present in CDs (**Figure 3.4**), those at the 6-position (the primary hydroxyls) are the most basic and often most nucleophilic, those at

the 2-position are most acidic and those at the 3-position are most inaccessible.[24,25] Thus, each CD moiety has several sites of modification.[26,27]

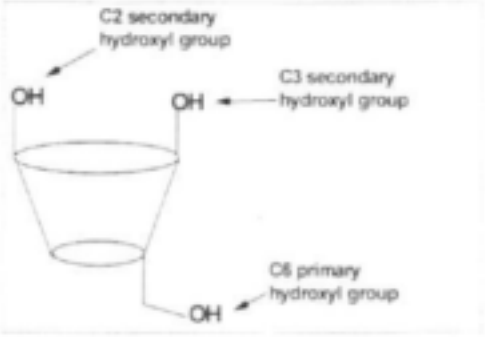


Figure 3.4: Representation of the different hydroxyl groups of a CD unit.

Under normal circumstances, an electrophilic reagent attacks at the 6-position, since this is the most nucleophilic and the least hindered. The hydroxyl groups at 2-position are the most acidic, they are the most susceptible to being deprotonated.[28] The oxyanion formed at the 2-position is much more nucleophilic than the non-deprotonated OH's at the 6-position.

Several factors need to be considered in the chemistry of CDs for their modification. The methods that have been developed for the controlled modification of CDs exploit:

i. the different reactivities of C-2, C-3 and C-6 hydroxyl groups,
ii. use of protecting groups to block reactive centres,
iii. the complexation of reagents in the CD hydrophobic cavity.

3.3.2 Mono-modification of Cyclodextrins

Chemically modified CDs are synthesized so as to vary their solubility behaviour, to modify their complexation properties (i.e. stability constant, guest selectivity) and introduce functional groups that can achieve specific functions (e.g. catalytic activity).[29]

There are generally two ways in which the CD hydroxyls groups can be functionalized:

i. Mono-functionalization - functionalizing of only one hydroxyl group.

ii. Per-functionalization – functionalizing of an entire set of hydroxyl groups.

Multiple functionalization is also possible by sequential monofunctionalization or by incomplete per-functionalization.[30] Among the several possible types of modifications, monosubstituted CDs have been particularly popular in the functionalization of these starch derivatives.[29,31] These mono-functionalizations can be achieved by a reaction of the hydroxyl groups with an electrophile. However, the large number of hydroxyl groups at the three different positions of CDs does not easily lend themselves to modification at a single desired place. Although selective monofunctionalization at a desired 2-, 3-, and 6-position is a challenging task, the differences in the chemical properties and reactivities among these sites can be exploited to yield a particular product.

Mono-substitution of a CD is achieved by using less than one equivalent of the reagent. The presence of a large excess of the electrophilic reagent must be avoided when uniform substitution of all glucose units in a CD is required.[27] Bulky reagents react preferably with the primary hydroxyl groups (C6), because they are easily accessible.[26] The secondary hydroxyl groups (C2) have the highest acidity. Under anhydrous conditions they can be selectively deprotonated and allowed to react with electrophilic reagents. The secondary hydroxyl groups (C3) are the least reactive and can react selectively only after (C2) and (C6) have been blocked. The product distribution can be greatly influenced by the reaction conditions.[32]

Required substituents may be introduced directly through alkylation, acylation and sulphonation. Alternatively, sulfonates, halides and related species may be prepared as intermediates for the subsequent introduction of substituents through nucleophilic displacement. In turn, an amino group incorporated in this manner provides a nucleophilic site for further elaboration.[26] Oxidation of hydroxyl functionality produces aldehydes and ketones while reactions with acid chlorides (benzoyl chloride, ethanoyl chloride) and acid anhydride e.g. phthalic acid anhydride, yield esters. Reactions with sulphonic acid chlorides and alkylhalides would yield the corresponding sulfonic esters, while alkyl ethers can be made by reaction with alkyl halides.[32-34]

3.3.2.1 Primary Face Mono-modification

(a) Mono-substitution at the 6-position of the CDs

The most common method for functionalizing at the 6-position of the CDs is nucleophilic attack of a reagent containing the appropriate group on displacement of the bulky toluenesulfonyl group from mono-6-tosyl CD. These mono-sulphates are prepared by reacting 1 equivalent of *p*-toluenesulfonyl chloride with CD in pyridine or DMF in the presence of a base. Mono-tosylates have also been extensively investigated. An excellent method for the synthesis of mono-tosyl CD is by the reaction of a CD moiety with tosyl anhydride in aqueous alkaline medium for a short period time to obtain the mono-6-tosylate (**Figure 3.5**) in fairly good yield.[35]

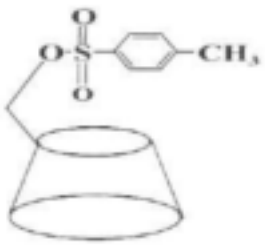


Figure 3.5: A structure representing a cyclodextrin monotosylate.

6-Tosyl CDs are important precursors to a variety of modified CDs because nucleophiles can attack the electrophilic carbon atom at the 6-position to produce a functionalized derivative. Nucleophiles such as such as iodide, azide, thioacetate, hydroxylamine, alkyl or poly-alkylamine can displace the tosyl group on the CD to afford monoiodo,[36] azido,[37,38] thio-,[39,40] alkylamino CDs, respectively.[41,42] This strategy is also used in the synthesis of artificial enzymes where only one functional group that acts as a catalyst is attached to the 6-position of CDs.[29,43] This is achieved by reacting a nucleophile containing the catalytic species with the 6-tosylated CD to give the artificial enzyme.

Bulky groups such as 4-*N*-(*tert*-butoxycarbonyl)-2-ethylimidazonyl have been linked to the CD and characterized by X-ray diffraction (XRD).[44] Mono-toluidinyl or (alkylamino) CDs can recognize the size, shape and chirality of amino acids with good enantioselectivity.[45] Essentially the same strategy has been utilized in the synthesis of the mono-hydroxylamine derivative of CD, where the mono-tosylate shows a 1900 fold increase in selectivity during trans-acylating behaviour compared to unfunctionalized CDs.[46]

Mono-thio derivatives are synthesized from mono-tosylates or mono-iodo CDs and the respective alkyl thiolate ion. A variety of mercapto CD derivatives have been obtained from mono-tosylated CDs and have been used to study immobilized films on gold surfaces.[47] The direct synthesis of mono-thio CDs with aromatic thiol and unprotected CD in DMF or pyridine is performed through a thio-Mitsunobu reaction. This reaction gives a mixture of mono-, di-, and trisubstituted products which are purified by chromatography.[48] Mono-amino derivatives of CD have made also been reported. These are conveniently obtained from mono-azides of CDs by reduction with triphenylphosphine in the presence of ammonia.[49] Mono-azides of CD are indirectly obtained by heating the mono-tosylate with sodium or lithium azide salt containing triphenylphosphine in DMF.[50] Mono-amines show greater solubility and react with isocyanates without the need to protect the primary hydroxyl groups to produce isothiocynato CDs.

Mono-aldehydic CD derivatives are also important because they provide a route for further modifications. The mono-aldehyde has been prepared by oxidation of 6-tosyl-CD in DMSO using collidine as a hindered base.[35,51,52] They can also be synthesized by reacting the CDs with Dess-Martin periodinane (DMP) in 85–100% yields.[50,53,54] Oxidation of the mono-aldehyde leads to its carboxylic acid derivative. Hydroxylamine reacts with the mono-aldehyde to produce a mono-hydrazone derivative.[52] Alkyl ethers of CDs cannot be synthesized from tosylates because nucleophiles in this case (alkoxide ions) act as strong bases which abstract protons from hydroxyl groups at the 3-position and produce the 3,6-anhydro compound by ring conversion.[55]

β-CD alkyl ethers are obtained by a longer method in which the primary side is first protected by TBDMS. This is followed by per-methylation of the secondary face, desilylation of the primary side and then mono-tosylation of the primary side. The reaction of the alkoxide ion with this protected tosylate gives the desired alkyl ether on the primary side without the formation of the 3,6-anhydro derivative.[55] The main problem with this approach is that the methyl groups in the secondary site cannot be easily removed. This limitation can be overcome by using acetyl groups to protect the secondary side which can not be subsequently hydrolyzed.

The direct approach for alkylation has been demonstrated.[56-58] This reaction involves the treatment of the CDs with alkyl halides in an alkaline solution to afford a mixture of products which are separated by chromatographic methods. An example of this random reaction is hydroxypropylation, which results in a mixture of 2-*O*, 3-*O*, and 6-*O* derivatives. Such a substitution reaction can be controlled by the concentration of base used during the reaction.[59] Another example of direct alkylation is the synthesis of mono-(dicyanoanthracene) derivative.[60] The pyrolysis of solid complexes of aromatic diazo CD compounds is another good example of a direct approach for monoalkylation. This reaction proceeds via the insertion of carbine into hydroxyl groups. The mixture of 2-, 3-, and 6-*O*-isomers produced are in turn separated by HPLC to give the desired mono-alkyl CD derivative.[61]

3.3.2.2 Secondary Face Mono-modification

(a) Mono-substitution at the 2-position of the Cyclodextrin

Mono-2-tosyl β-CD has been synthesized using several strategies.[62] *m*-Nitrophenyl tosylate reacts with CD in a DMF/aqueous buffer at pH 10 in a low yield. This reaction proceeds *via* complex formation to transfer the tosyl group to the 2-position.[62] The tosyl group gets transferred preferentially to the 2-position due to the orientation of the reagent with the host molecule. This procedure is referred to as the group transfer strategy. Several workers have prepared mono-2-tosylate derivatives of CDs as a mixture with other isomers by using an aqueous alkaline medium or DMF and p-toluene sulfonyl chloride. These have been well characterized after chromatographic purification of the mixture.[63-66] Dibutyltin oxide has been used to facilitate this reaction in DMF.[60] The mono-2-mesylate of the beta CD with a methanesulfonyl (mesyl) group at the 6-position has also been reported.[66] Other examples of mono-2-sulfonates such as nitrobenzenesulfonyl or naphthalenesulfonyl groups, also obtained as mixtures and later purified, are mentioned in the literature.[56,67-69]

As noted earlier, the hydroxyl groups at the 2-position are more acidic than those at the 6-position. This feature has been exploited by using NaH or LiH as strong bases under anhydrous conditions for selective tosylation at the 2-position. Yields in all these cases are compromised by the elimination of the sulfonate group due to its good leaving behavior.[62] The elimination of the tosyl group at the 2-position

by the hydroxyl groups affords the manno-2,3-epoxy CD. Although symmetrical alkyl ethers with substitutions at all three positions have been synthesized, very few examples of mono derivatives at the 2-position are known. Mono-2-methyl, ethyl and allyl, derivatives are prepared directly from CDs and the respective dialkyl sulfates in aqueous solution, giving a low yield after purification.[28] Mono-2-propyl derivatives are obtained upon hydrogenation of the mono-2-allyl CDs. Monoalkyl ethers with terminal aromatic esters appended through amide linkage show intramolecular inclusion complex formation.[70] Mono-(isoalloxazinomethyl) CD is another example of a mono-2-ether which is obtained by exploiting the acidity of the 3-hydroxyl group by reacting with a strong base and subsequent conversion of the product to a flavin moiety after several steps.[71-73]

Mono-2,3-epoxy CDs are synthesized from the classic mono-tosylate in a basic medium.[74,75] Two types of epoxides are produced during the reaction depending on the position of the sulfonate group on the pyranose residue. The per-6-silylated manno-mono-2,3-epoxy derivative is synthesized from the per-6-sily-mono-2-tosyl derivatives. Mono-2-amino CDs have been synthesized from per-acetylated CDs of all the three types of these starch derivatives (α-, β- and α-CDs) by the cleavage of the CD ring in an acidic medium. This is subsequently followed by coupling with D-glucosamine derivatives which gives the final products after several steps of cyclization and deprotonation.[45] Another method for the synthesis of this compound (mono-2-amino CD) involves the use of per-benzoylated β-CD. This reaction also involves numerous steps including de-benzoylation reaction at one of the C2 hydroxyls, followed by oxidation and oxime formation, and finally reduction of the oxime.

(b) Mono-substitution at the 3-position of the CDs

Mono-substitution at the 3-position is complicated by the fact that the hydroxyl groups at this position are most inaccessible and thus less reactive compared to the highly accessible ones at the 2- and 6-positions. Most modifications at the 3-position are proceeds *via* the synthesis of manno-mono-2, 3-epoxy CD. *p*-Toluene sulfonyl chloride has been reacted with the CD to give the mono-3-tosylates,[63,75-77] at very low yields. However, higher yields have been obtained when 2-naphthalene sulfonyl and 3-nitrobenzene sulfonyl chloride reacted with the

CD.[68,78,79] Thio derivatives[80] of CDs are produced by reacting the mono-3-sulfonates with alkali thiolates in DMF. This is an S_N2 type of reaction. Under basic conditions these intermediary sulfonates can be converted to allo-mono-2,3-epoxy CDs.[68,79,81]

Generally epoxy CDs reacts with certain nucleophiles to give a substitution at the 3-position. Mono-3-amino CDs are synthesized by this method; by treating manno-2,3-epoxyCDs with ammonia solution at room temperature.[65,82-84] Subsequently, hydroxylamine reacts with this epoxide to give 3-hydroxylamino CD.[85] Various nucleophiles have been utilized in the opening of the epoxy ring of per-6-silyl-mono-2,3-epoxy CD to produce exclusively 3-substituted derivatives.[84] These include among other nucleophiles ethylenediamine, lithium azide or anhydrous ammonia. Homo and hetero-dimers that have been protected are formed by coupling amino-6-α- and β-CDs with the phenyl ester of dicarboxylic acid to produce a protected homo or hetero-dimer. The products obtained are then desilylated with tetrabutylammonium fluoride (TBAF) by refluxing with THF to give the matching CD derivatives.[84-88] To obtain mono-3-alkyl CDs, the primary hydroxyl groups are first protected with TBDMS and then reacted with a specific alkyl halide ([N-methyl-4-(chloromethyl)-2-nitroaniline)] in lutidine at high temperatures.[88] The protected CD is believed to complex with this reagent to direct its reactive site towards the OH at the 3-position to give the product. However, CD chemistry continues to offer various possibilities to synthesize derivatives with different functionalities.

3.3.3 Cyclodextrin Polymers

A considerable amount of work has been done using cyclodextrins to synthesize polyester, polyurethane and various other types of polymeric materials.[6,7,88] When two or more cyclodextrins are covalently linked they are known as polymers. The cyclodextrins fixed into polymeric structures behave differently from their monomeric derivatives, often showing greater binding constants, higher solubility, and improved stability. Cyclodextrin polymers can be classified as soluble in water and water insoluble. By varying the reaction conditions, either water soluble or insoluble polymers can usually be obtained.

Girek *et al* [89] gave two ways in which cyclodextrin can be polymerized, one where the CD is a pendent group on other polymer chains, and the other where the CD forms part of the polymer chain. This study will focus on the later method where CDs are reacted with bifunctional agents. One of the first linking agents used to make these polymers is epichlorohydrin, but since then other linking agents such as dihalogenated hydrocarbons and dicarboxylic derivatives have been used. These nucleophilic substitution reactions with bifunctional agents usually occur in strong alkaline conditions in order to deprotonate the hydroxyl groups of cyclodextrin.

Water soluble polymers have been a subject of several previous investigations. They have a wide variety of potential applications such as to control the release of a soluble substance across a membrane and partitioning of organic compounds in aqueous two-phase systems. The usefulness of these polymers lies mainly in their ability to form an inclusion complex with lipophilic guests. The polymeric form can increase the stability constant of the complexes.[90]

Short reaction times and low concentrations of cyclodextrins generally result in water soluble polymers that often have higher solubility in aqueous solutions than their parent cyclodextrins. The main applications of these polymers are related to chromatographic techniques (TLC and LCC).[91] Insoluble CD polymers with a high water sorption capability have been made by either crosslinking the CDs or using hydrophobic linkers in the linear chain. Alternatively longer reaction times and high concentration conditions are also successfully employed.

Polymers of cyclodextrin are finding very diverse applications, including pharmaceuticals, food technology, cosmetics, analytical chemistry, chemical synthesis, and catalysis.[20,88] A recent report on the properties of chemically modified epichlorohydrin-β-CD polymer as chiral support demonstrates how the polymer can be used in liquid chromatography.[92] The enatioselective properties of supports based on silica coated with a β-CD polymer have also been investigated.[93]

In food the CD polymers have played a major role in the reduction of the bitterness components in grape fruit and navel orange juices,[94] while Jiang *et al*

prepared a β-cyclodextrin epichlorohydrin polymer then functionalized it with 1-(2-pyridylazo)-2-naphthol for use in the determination of cobalt in foods.[95]

A porous tubular ceramic membrane impregnated with a β-cyclodextrin polymer was used to obtain a chiral-selective membrane, which have been evaluated for the ability to separate the enantiomers of the racemic pharmaceutical chlorthalidone (CT).[96]

Finally, Gao and Zhao used a β-cyclodextrin polymer to prepare electrorheological (ER) materials of an inclusive complex, named β-cyclodextrin-PAN. This material was synthesized by the supramolecular reaction of β-cyclodextrin polymers with 1-(2-pyridlazo)-2-naphthol.[97]

Various studies demonstrate that any toxicity previously attributed to CDs originate from complexed impurities, an inadequate form of administration, or extreme dosing. This implies that there is no inherent toxicity associated with CDs that can inhibit their widespread utilization.[23]

Since CDs are non-toxic, they are suitable for the removal of high-priority and highly toxic organic contaminants that are critical in current water treatment and environmental research. The problems associated with the native CDs can be overcome by polymerizing them with suitable co-monomers. The CD polymers can be applied in water treatment processes where ultrapure water is required such as in semiconductor chip fabrication and manufacturing. Because of the different dimensions associated with the α-, β- and γ-CDs, polymeric CD nanosponges are capable of quenching a range of organic contaminants of varying sizes from aqueous solutions. As an added advantage, the CD polymers can be fine-tuned by selective modification of their remaining hydroxyl groups, thus allowing a specific organic contaminant to be targeted. Therefore, it means that CD polymers could be tailor-made for a specific industry, something that is difficult to achieve with current separation technologies.[6] It is anticipated that these polymers will also remove colour, flavour, and odour causing compounds such as geosmin and 2-methylisoborneol (2-MIB) from drinking water.

A major advantage of any new technology for water treatment is its regeneration or recycleability. This property is crucial when evaluating the application of the

technique since its cost-effectiveness can be estimated. Although GAC can be regenerated, it has been reported to reach breakthrough after a few number of cycles.[98] The regeneration of cyclodextrin polymers can be achieved by treatment or washing of the polymer with ethanol. This serves to remove the absorbed organic molecules within the cavities of the CD polymers.

While cyclodextrin polymers may be more costly than current technologies, this aspect is offset by the fact that they can be regenerated and that they can find application where current technologies break down. Ongoing breakthrough studies of these polymers will allow us to determine the number of cycles they can undergo and hence determine the cost-dilution. These studies are reported in the latter section of this report.

3.4 The cyclodextrin inclusion process

3.4.1 Formation of cyclodextrin inclusion complexes

Inclusion complexation refers to a molecular phenomenon where one molecule of guest (organic contaminant) and one molecule of the host (CD) come into contact with one another to associate and form a complex (**Figures 3.6** and **3.7**).[11,88,99-106] Generally, the parent CDs can undergo *molecular inclusion* with a variety of low molecular weight compounds ranging from aliphatic non polar molecules to polar acids and amines. These non-covalent interactions are highly solvent dependent and typically have formation constants of the order 10^3 or higher.[107] Formation constants formed by CD-based polymers during *polymer inclusion* are several orders of magnitude greater than solution phase inclusion.[7]

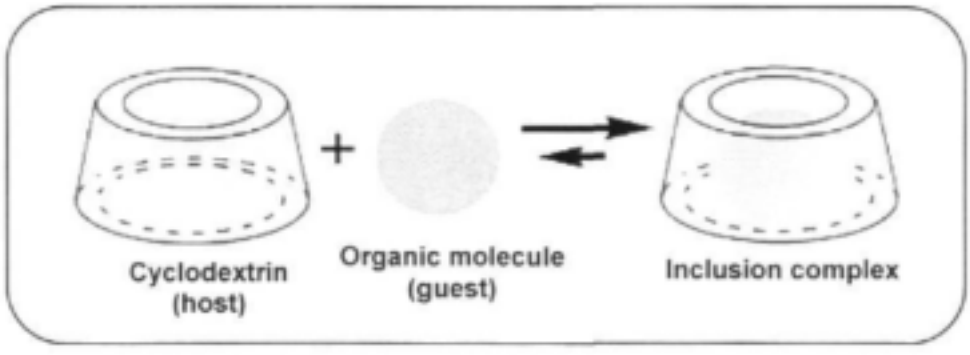


Figure 3.6: Formation of an inclusion complex with an organic guest molecule.

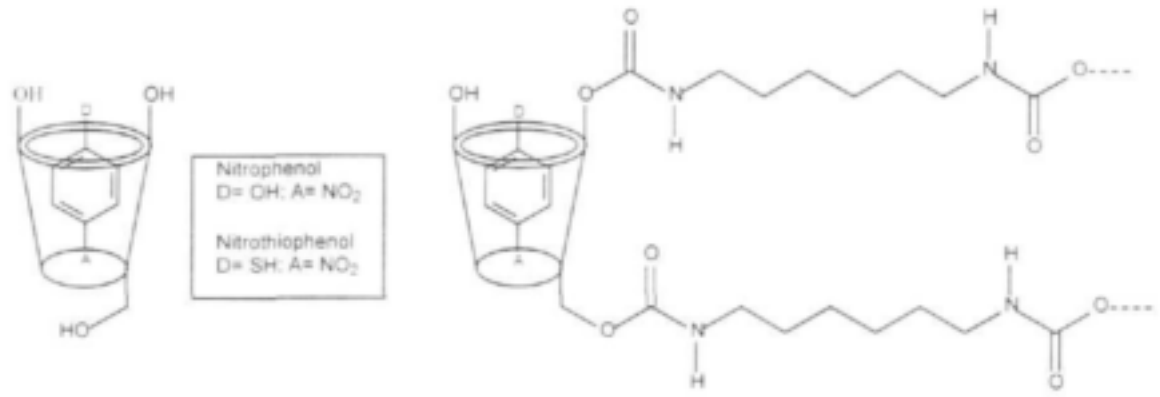


Figure 3.7: Depiction of an inclusion complex of a parent CD and a polymerised CD with an organic guest molecule.

The relatively apolar cavity in comparison to the polar exterior enable CDs to form inclusion compounds with hydrophobic guest molecules in aqueous media. The formation of inclusion complexes involves hydrophobic interactions; no covalent bonds are broken or formed.[20,108] The main driving force behind formation of the inclusion complex is the displacement of enthalpy–rich water molecules from the CD cavity by the more hydrophobic guest molecule in the solution to acquire an apolar-apolar association and a decrease of the CD ring strain thus resulting in a more stable lower energy state.[11] It should, however, be noted that the possibility to form hydrophobic interactions represents only one of the requirements. Another important requirement is that the guest molecule must be able to fit into the cavity of the CD (geometric compatibility).[19,23,109]

In general, many factors play a role during the inclusion complex formation process. These include geometric compatibility, polarity of the guest molecule, the medium and molecular weight. There are four energetically favourable interactions that help the equilibrium to form the inclusion complex, namely:[20]

- the displacement of polar water molecules from the apolar CD cavity.
- the increased number of hydrogen bonds formed as the displaced water returns to the larger pool.
- a reduction of the repulsive interactions between the hydrophobic guest and the aqueous environment.
- an increase in the hydrophobic interaction as the guest enters the apolar cyclodextrin cavity.

The type of complex can be of 1:1 ratio where one CD molecule includes one organic guest molecule.[11,13,41] The general equation is as follows:

$$S + CD \rightleftharpoons S{\cdot}CD$$

Where S = organic pollutant (guest)
CD = cyclodextrin polymer (host)
S·CD = inclusion complex

It is also possible to form complexes where the guest molecules are significantly larger than the CD cavity. This is done in such a way that only certain groups or side chains penetrate into the CD cavity. A 2:1 complex of CD and guest molecule may be formed when the guest is too large or long to find complete accommodation in one cavity and having its other end also susceptible to complex formation.[11,110] However, no universal method exists for the formation of CD inclusion complexes.

3.4.2 Characterization of CD inclusion complexes

It is evident from the literature that most inclusion complexes that have been studied are derived from β- and γ- CDs. As a result, a vast number of methods such as NMR spectrum, UV circular dichroism, fluorescence, HPLC and mass spectrometry have been used for the characterization of these complexes. However, due to the insoluble nature of the polymers synthesized, thermoanalytical methods such as thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were chosen to fulfil this requirement.[112] From a TGA spectrum, the ratio of the host and guest can be ascertained by measuring changes in weight (mass) of a sample as function of temperature and/or time. DSC, on the other hand, is useful in ascertaining the thermal stability of the polymers and the complexes.[112-115] Other techniques such as X-ray diffractometry (XRD) and scanning electron microscopy (SEM) can be used for further characterization of CD inclusion complexes.[116] Different polymers exhibit different thermal transitions that are unique to the polymer. For instance, the DSC of a pure β-CD-HMDI polymer would differ from that of an inclusion compound formed by the same polymer.

3.5 Comparison of the performance of CD polymers with currently available technologies

The solubility of parent CDs in water renders them ineffective in the direct removal of organic pollutants from water. The challenge, therefore, is to synthesize nanoporous CD polymers that are insoluble in water with an enhanced affinity for organic contaminants in water, but that also release the same contaminants in other solutions.[6,7] Not only do the CD polymers remove organic contaminants from water to ppb or μg/L levels, they also offer flexibility, cost effectiveness and ease of use. CD nanoporous polymers are poised to compete with activated carbon (AC) in performance, cost and availability, especially if combined with the beneficial environmental aspects of recycleability. Since activated carbon is not effective in ultrapure water applications, nanoporous polymers may fulfil this need when the polymers are commercialised. The quantitative performance of the CD nanoporous polymers are listed in a table (**Table 3.2**) along with the test results for activated carbon and molecular sieves.[6,7]

Table 3.2: Comparison of the characteristics and performance of nanoporous polymers with different activated carbons and molecular sieves at room temperature.

	CD Polymer	Activated Carbon		Molecular Sieves	
Material	**B-CD-HDI**	**Charcoal 1**	**Charcoal 2**	**Hydro-philic**	**Hydro-phobic**
Pore diameter (Å)	**7 - 9**	20 - 1000	av. 28	9 - 10	7.6
Surface area (m^2/g)	**1.7 – 1.9**	750	650	n/a	601
Concentration at equilibrium	**3.6 ng/L**	1.3 mg/L	53 μg/L	n/a	n/a
Formation constant K (M^{-1})	**5.0×10^9**	1.4×10^4	3.4×10^5	≈ 0.0	≈ 0.0
Maximum loading(mg/cm^3)	**40**	29	26	≈ 0.0	≈ 0.0
Leaching organics	**No**	Yes	Yes	Yes	Yes

The absorption of common organic contaminants (e.g. trichloroethylene and toluene) by CD polymers from water has been investigated.[6] The affinity of CDs for common organic molecules at low loadings, measured by the formation constants (K), was also studied. As indicated by high K values shown in **Table 3.3**, nanoporous polymers (α-, β- and γ-CDs) were found to possess a very strong affinity for the various organic contaminants studied.

Table 3.3: Inclusion of various common organic molecules by CD polymers at low organic guest loading[6]

Cyclodextrin Polymer	Organic guest molecule	Formation constant K, M^{-1}	Loading level mg/cm^3 (%)	Free energy ΔG Kcal/mol
β-CD-HDI	4-Nitrophenol	5×10^5	40 (86)	- 13.2
β-CD-OCH_3-HDI	Toluene	1×10^5	17 (56)	- 10.9
β-CD-OCH_3-HDI	Trichloroethylene	2.2×10^5	35 (79)	-12.7

The K values shown in **Table 3.3** were found to be amongst the largest ever to be obtained for non-covalent inclusion phenomenon. A comparative study with existing adsorbent technologies such as activated carbon (AC) and molecular sieves was also conducted.[6]

Recent years have experienced a steady growth in the need for water purification. A broad range of applications and requirements for water quality has stimulated researchers to improve existing methods and to investigate and develop new water purification technologies. The baseline study by Li and Ma[6,7,11] has certainly triggered further research regarding the use of CD nanoporous polymers for water treatment purposes. As a result, our research has focussed extensively on developing this technology by synthesizing polymers of various kinds and quantitatively evaluating their ability to remove new and emerging priority pollutants from water. Before considering our group's strategies towards the improvement of water quality, it is important at this point to evaluate currently available water treatment technologies.

CHAPTER 4: TECHNIQUES FOR THE REMOVAL OF NOM AND OTHER ORGANIC COMPOUNDS

4.1 Introduction

Water treatment processes used for the removal of organic contaminants from water are similar.[117] When water quality authorities decide on which technology to use, factors such as the characteristics of the water, the cost of the treatment process and the types of water quality problems likely to be presented need to be considered. As a result, the most widely applied water treatment technology tends to be a combination of some or all of the processes.

Various techniques for the removal of NOM and other organic contaminants are being utilized in water treatment plants world-wide. These are granular activated carbon (GAC) adsorption, membrane filtration and coagulation. Other technologies such as ozonation, zeolites, molecular sieves and synthetic resins have also been explored.

The most widely used technique for the separation of NOMs is coagulation.[118] However, the prevalence of various types of organic contaminants in South African waters has seen the application of GAC gradually coming into utility. Nonetheless, the use of GAC in Southern Africa is limited.[119]

4.2 Activated Carbon

Activated carbon (AC) has been considered to be the most effective single treatment step for taste and odour problems.[120,121] Although AC is generally non-selective and has an affinity for most organic contaminants in water, it does not remove many organic contaminants to the desired µg/L levels. This is a serious problem because even when present in small concentrations, organic compounds can bioaccumulate and result in death. AC is also known to absorb moisture from air and subsequently loses its absorptive effectiveness in water.[6,7]

Two forms of AC are available for use in water treatment; namely Granular Activated Carbon (GAC) and Powdered Activated Carbon (PAC). The adsorption of NOM in water was studied by McGuire *et al.*[117] The study revealed that PAC or GAC is capable of removing 90% of all taste- and odour-causing organic

compounds from water. GAC was found not able to totally remove all organic carbon; some non-adsorbable TOC still led to DBP formation.[25,117]

Both PAC and GAC are used in water treatment plants for the removal of taste- , odour- and colour-causing compounds, synthetic organic chemicals (SOC), pesticides, herbicides and precursors of trihalomethanes (THMs). While PAC is used mostly in liquid applications, GAC is favoured for gas-phase applications.[121] GAC is capable of removing a broader spectrum of compounds. Unlike PAC, GAC is not associated with sludge disposal problems. For these reasons, the use of GAC in water treatment is much more prevalent.[122] GAC has also been successfully used in the place of granular media in filter absorbers, however, is less successful in the removal of less strongly adsorbed species (i.e. THMs, volatile organic compounds (VOCs) and some fractions of TOC).[25,123] According to Huber *et al*,[124] GAC is preferred to PAC when high concentrations of VOCs are present in water. However, PAC is more efficient when the water is lower in background NOM and contains strongly adsorbing compounds such pesticides.[125]

4.2.1 Performance of GAC on the Removal of Various Determinants from Water

Collective results obtained from studies carried on GAC performance without ozone pre-treatment at three southern African Water Treatment Plants (Windhoek, Wiggins and Rietvlei) were reviewed by Haarhoff and co-workers.[126] The data obtained is shown in **Table 4.1** as a summary of average residual concentration divided by the initial concentration (C/Co) values at five sampling points.[126]

Table 4.1: Average C/Co values for selected sampling points during GAC performance studies.

Determinant	Windhoek		Wiggins		Rietvlei
	Wood-based	Coal-based	Wood-based	Coal-based	Coal-based
Physical					
Colour	0.65	0.36	n/e	0.79	0.61
Conductivity	n/e	n/e	n/m	n/m	n/m
pH	n/e	n/e	n/e	n/e	n/e
Turbidity	0.61	0.55	0.57	0.50	0.63
Micro-Determinants					
Aluminium	n/m	n/e	n/e	n/e	n/m
Boron	n/m	n/e	n/m	n/m	n/m
Bromide	n/e	n/e	n/m	n/m	n/m
Cadmium	n/m	n/e	n/m	n/m	n/m
Chromium	n/m	n/e	n/m	n/m	n/m
Copper	n/m	n/e	n/m	n/m	n/m
Gold	n/m	n/e	n/m	n/m	n/m
Iron	n/m	n/e	n/m	n/m	n/m
Lead	n/m	n/e	n/m	n/m	n/m
Manganese	n/m	n/e	n/m	n/m	n/m
Mercury	n/m	n/e	n/m	n/m	n/m
Nickel	n/m	n/e	0.50	0.19	n/m
Pesticides	n/m	n/e	n/m	n/m	n/m
Selenium	n/m	n/e	n/m	n/m	n/m
Silver					
Organic					
2-MIB	n/m	n/m	0.85	0.83	n/m
$CHBr_3$ FP	n/e	n/e	1.18	1.46	n/m
$CHCl_3$ FP	0.85	0.53	0.74	0.50	n/m
$CHCl_2Br$ FP	n/e	0.74	0.91	0.80	n/m
$CHClBr_2$ FP	n/e	n/e	n/e	1.06	n/m
COD	0.86	0.65	n/m	n/m	n/m
DOC	0.94	0.87	n/e	0.90	0.55
Geosmin	n/m	n/m	n/e	n/e	n/m
Phenol	n/e	n/e	n/m	n/m	n/m
TTHM FP	0.87	0.64	0.88	0.78	n/m
UV	0.80	0.50	0.87	0.67	0.44
n/e = no effect; n/m = no measurement					

The following conclusions were drawn from this study:

- Physical determinants were reduced.
- Inorganic micro-determinants were not affected at all.
- Macro-determinants were also not affected.

- Most importantly, GAC has an effect on the removal of organic determinants. However, only the phenols and geosmin were not significantly removed at any of the sampling points.

It is evident from these results that the removal of organic contaminants cannot be achieved by the sole use of GAC. Therefore, it was anticipated at the beginning of this project that the GAC could be used along with CD polymers or be completely replaced by the polymers for this application.

4.3 Membrane filtration

The use of membrane filtration technology in the removal of NOM and its DBPs as well as other organic compounds is common.[118] The most commonly used membrane filtration techniques are pressure-driven and are based on the following factors:

- pore size of the membrane
- geometry and membrane material
- molecular weight cut-off (MWCO)
- materials to be removed
- type of water quality to be treated
- application of the treated water

The various pressure-driven membrane processes are shown in **Figure 4.1** together with the size ranges of various materials that are found in water.[118]

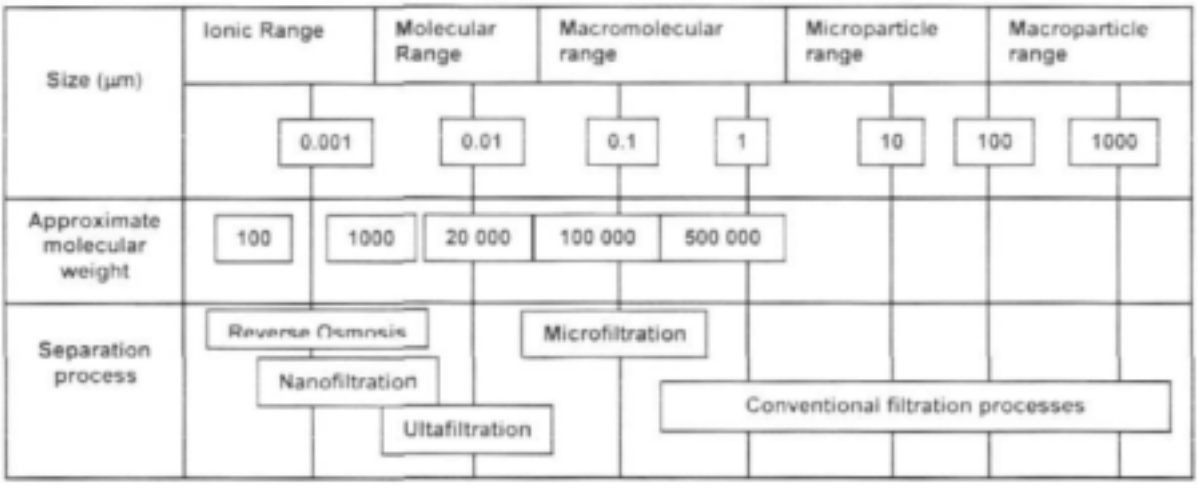


Figure 4.1: Various pressure-driven membrane filtration processes

Reverse osmosis (RO) appears to be the most common type of membrane filtration technology and is best known for its use in desalination of sea water (i.e. turning seawater into drinking water). It is also becoming a common home treatment method for contaminated drinking water; it can reduce the amount of both organics and inorganic compounds, bacteria and particulates that can be found in contaminated drinking water.

Just as with most water treatment technologies, reverse osmosis does not solve all water purification problems. First and foremost, RO requires high pressure to overcome hydrophobic resistance produced by the dense membrane. The process consumes a lot of energy in achieving separation efficiency. About 75% of the water entering the system is recovered and it does not remove small organic molecules from water. A low concentration of small molecules normally leaks into the permeate side because the membrane is not perfectly semipermeable.[6] Therefore, the cost and inefficiency associated with this technology makes it an ineffective decontamination technique.

4.4 Coagulation

Before the 1970's, research into the presence of natural organic matter (NOM) in drinking water and into methods for its removal was primarily driven by the desire to remove colour from public water supplies.[118] However, due to regulations enforced by the United States on THM control, an increased interest in NOM removal, especially by coagulation, became prevalent.[126-130]

According to Jacangelo *et al.*,[118] coagulation is broadly defined as a process that includes addition of chemicals, rapid mixing and flocculation. Although coagulation is the most widely used technology in the water treatment, it is not capable of removing small concentrations of NOM to enable the control of DBPs. This obviously mitigates the exploration of other forms of water treatment technologies.

4.5 Ozonation

Powerful oxidants like ozone (O_3) are continuously used in municipal water treatment and disinfection of water supplies. Other advanced oxidation

technologies have emerged as some of the main environmentally friendly technologies in the remediation of wastewater and for the general treatment of water.[131] The combined use of UV, ozone and hydrogen peroxide to facilitate the complete degradation of contaminants is also receiving increasing interests.

Although ozonation is effective in the rapid decomposition of phenolic compounds in aqueous media, decomposition of halogenated organic compounds is more rapid in organic solvents.[132,133] Ozonation is an effective process for the reduction of by-products of chlorobiphenyls (CBP's).

Ozonation is less versatile than AC and can produce by-products that are less desirable; some of the by-products are biodegradable and can be removed by biological processes. A major limitation of the ozonation process is the relatively high cost of ozone generation process coupled with very short half-life period of ozone.[134]

4.6 Zeolites and molecular sieves

Molecular sieves contain a network of uniform pores and empty cavities. They are non-toxic and insoluble in water and most organic solvents. They are often used as selective absorbents for both organic and inorganic materials.[135]

One type of molecular sieves i.e., carbon molecular sieves (CMSs), has been known to be effective in the purification of fluid mixtures. CMSs can be manufactured by depositing very fine carbon particles on the pores mouth of activated carbon to narrow them.[136]

Another type of adsorbent material is zeolites. Zeolites have a high surface area and well defined porosity but show little affinity for organic compounds. Like activated carbon and molecular sieves, zeolites tend to absorb moisture and thus lose their effectiveness in removing organic compounds to low levels.

4.7 Synthetic resins

Many types of synthetic resins have been used for the removal of organic compounds.[137] The principles of the removal of the contaminant by this technique are similar to the adsorption techniques employed using activated carbon; there seems to be some similarities in the large pore size distribution and available surface area. However, adsorbent resins (e.g. styrene divinylbenzene resin and the phenol-formaldehyde resin) possess functional groups that make it possible for substances to be taken up by ion exchange or by specific interaction with the functional group. In addition, the cross linking between the polymers that constitute the matrix can be varied thus allowing the preparation of resins with different pore size distribution.

Resins are more selective than activated carbon. Therefore, resins are not capable of removing a broader spectrum of organic compounds from water and are, as a result, not useful as a general adsorbent for drinking water treatment. They may be applicable in specific situations that require only a particular type of contaminant to be removed.

5.1 Introduction

This section explains the analytical methods and experimental procedures that were carried out in order to achieve the objectives of the study. It explains the processes used to carry out laboratory assessment experiments of CD polymers. The preparation of samples, pre-concentration and quantification procedures are also outlined. The techniques used were selected on their merits to fulfil the requirements of this study.

5.2 Synthetic procedure of standard CD polymers

Insoluble nanoporous CD polymers were prepared according to a modified literature method.[6] The preparation of these polymers was based on the use of parent cyclodextrins as starting material. Cyclodextrins (CDs) were purchased from WACKER – Germany. These CDs have been reported to have hierarchical structures consisting of multiple cyclic glucopyranose units; as a result they behave differently from single cyclic glucopyranose molecules.[6]

Nanoporous CD polymers were synthesized in the form of powder and granular solids by treating the hydroxyl (OH) groups of the CDs with bifunctional isocyanate compounds in a 1:8 molar ratio using dimethylformamide (DMF) as a solvent. The diisocyanate compounds used were hexamethylene diisocyanate (HDI) and toluene 2,4-diisocyanate (TDI). Purified CDs were weighed into a clean reaction flask and dissolved with DMF. TDI or HDI was then added dropwise, while stirring using a mechanical stirrer to form a homogenous clear solution of CD and diisocyanate. The clear solution was then heated at about 70°C for 16 – 24 hours under inert conditions. The reaction was then removed and washed with acetone and dried to produce white nanoporous polymers. The resultant polymer material was characterized by infrared spectroscopy and thermal analysis.

5.3 Pre-concentration of water samples

It is crucial to pre-concentrate trace compounds or elements before analysis is done due to low concentration levels in water samples.[138] In addition, analytes are

usually engulfed with high levels of non-toxic components and, as a result, a cleaning up step is usually required.

Liquid-liquid extraction (LLE) is a classical method for pre-concentrating metal ions and organic compounds, as well as matrix removal. Solid phase extraction (SPE), however, has proven to outclass this and other conventional pre-concentration techniques in that it provides a number of important advantages. These include reduction in solvent usage and exposure, disposal costs and extraction time for sample preparation. This technique was selected taking into consideration that the water samples of interest are of very low concentrations (ng/L levels). Water samples were pre-concentrated to achieve concentrations that are within the detection limit of the analytical instrument.

The SPE method consists of four successive steps as shown by **Figure 5.1**. First, the solid sorbent is conditioned using an appropriate solvent, followed by the solvent that is most similar to the sample solvent. This step is important, as it enables the wetting of the packing material and the solvation of the functional groups. Possible impurities initially contained in the sorbent as well as the air present in the column are removed in this step. The nature of the solvent used for conditioning depends on the nature of the solid sorbent. For reversed phase sorbent, methanol is frequently used, followed by water or aqueous buffer whose pH and ionic strength are similar to that of the sample. Care must be taken not to allow the solid sorbent to dry between the conditioning and the sample treatment steps, otherwise the analytes would not be efficiently retained and there could be poor recoveries.

The second step is the penetration of the sample through the solid sorbent. Volumes can range from 1 ml to 1L depending on the system used. The sample may be infiltrated through the column by gravity, pumping, aspirated by vacuum or by an automated system. The sample flow rate should be low enough to allow efficient retention of the analytes, and high enough to avoid excessive duration. During this step the analytes are concentrated on the sorbent. The solid sorbent may also retain matrix components though some of them may pass through allowing some purification (matrix separation) of the sample.

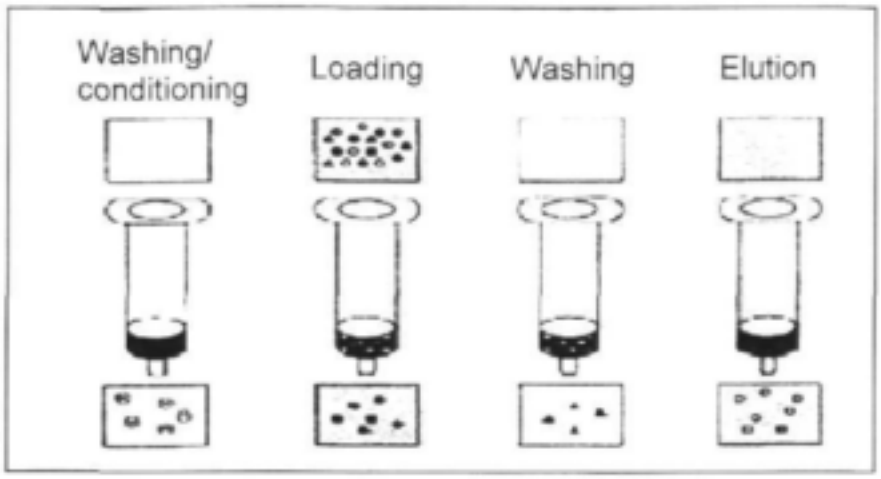


Figure 5.1: SPE operation steps

The third step, which is optional, is the washing of the solid sorbent with an appropriate solvent, having low elution strength, to eliminate matrix components that have been retained by the solid sorbent, without displacing the analytes. Usually a drying step is necessary for aqueous matrices, to remove traces of water from the solid sorbent. This eliminates the presence of water in the final extract, which in some cases, may hinder the subsequent concentration of the extract and/or the analysis.

The fourth and final step is the elution of the desired analytes by an appropriate solvent. This should be done without removing the retained matrix components and the solvent volume should be adjusted so that quantitative recovery of the analytes is attained with subsequent low dilution. Also, the flow rate should be adjusted to ensure efficient elution. Most often, it is recommended that the solvent volume be fractionated into two aliquots, and before the elution to let the solvent soak the solid sorbent.[138]

The quantities and types of solvents used during isolation and concentration are almost certainly determined by the nature of compounds to be isolated. As a result, an approved Environmental Protection Agency (EPA) method "525.2" was adopted to fulfil this requirement. The specific parameters involved are described in the next section.

5.3.1 The Environmental Protection Agency (EPA) Method 525.2

The method 525.2 is a drinking water method for the determination of a wide variety of semi-volatile organic compounds including polycyclic aromatic hydrocarbons (PAHs), pesticides and polychlorinated biphenyls (PCBs). It uses solid phase extraction for isolation and concentration and Gas Chromatography-Mass Spectroscopy (GC/MS) for determination and quantification.[139]

The method is generally performed by loading a one litre sample of water onto a conditioned C-18 or C-8 SPE cartridge. The cartridge is then dried and eluted with a combination of ethyl acetate (EtOAc) and dichloromethane (DCM). The extract (10 mL) is dried by passing 5g of anhydrous sodium or magnesium sulphate and concentrated under nitrogen to 1 mL. The instrument used for this purpose was an Autotrace Extractor by Zymark Corporation. The extraction procedures are summarized in **Table 5.1**.

Table 5.1: A summary of Zymark Autotrace Extraction Procedures

Loading Procedure:	***Flow Rate:***
Step 1: Process x samples using the following procedure*	Cond. Flow: 40 mL/min
Step 2: Wash syringe with 2 mL of MeOH	Load Flow: 20 mL/min
Step 3: Rinse column with 5 mL of EtOAc into solvent waste	Rinse Flow: 40 mL/min
Step 4: Rinse column with 5 mL of DCM into solvent waste	Elute Flow: 5 mL/min
Step 5: Condition column with 10 mL of MeOH into solvent waste	Cond. air push: 15 mL/min
Step 6: Condition column with 10 mL of water into aqueous waste	Rinse air push: 20 mL/min
Step 7: Load 1000 mL of sample onto column	Elute air push: 5 mL/min
Step 8: Dry column with gas for 10 minutes	
Step 9 : End	
Eluting Procedure:	***Flow Rate:***
Step 1:Process x samples using the following procedure*	Cond Flow: 40 mL/min
Step 2 : Manually rinse sample container with 7 mL to collect	Load Flow: 5 mL/min
Step 3: Manually rinse sample container with 10 mL to collect	Rinse Flow: 40 mL/min
Step 4: Soak and collect 3 mL fraction using EtOAc	Elute Flow: 5 mL/min
Step 5: Collect 2mL fraction into sample tube using EtOAc	Cond air push: 15 mL/min
Step 6: Soak and collect 3mL fraction using DCM	Rinse air push: 20 mL/min
Step 7: Collect 2mL fraction into sample tube using DCM	Elute air push: 5 mL/min
Step 8: END	
*x = 1 to 6 samples	

The instrument gave extraction efficiencies of between 30-50% with both C-18 and C-8 SPE Cartridges. Although the recoveries were not as good as expected, they were high enough to achieve the goals of the study.

5.3.2 Manual SPE method

The manual SPE method was designed as a result of the malfunctioning of Autotrace SPE Workstation. The setup was devised by connecting a separatory funnel, an SPE cartridge, and a collection flask that was connected to a water tap to create a constant pressure for the water sample to pass through cartridge. The setup is shown by **Figure 5.2**.

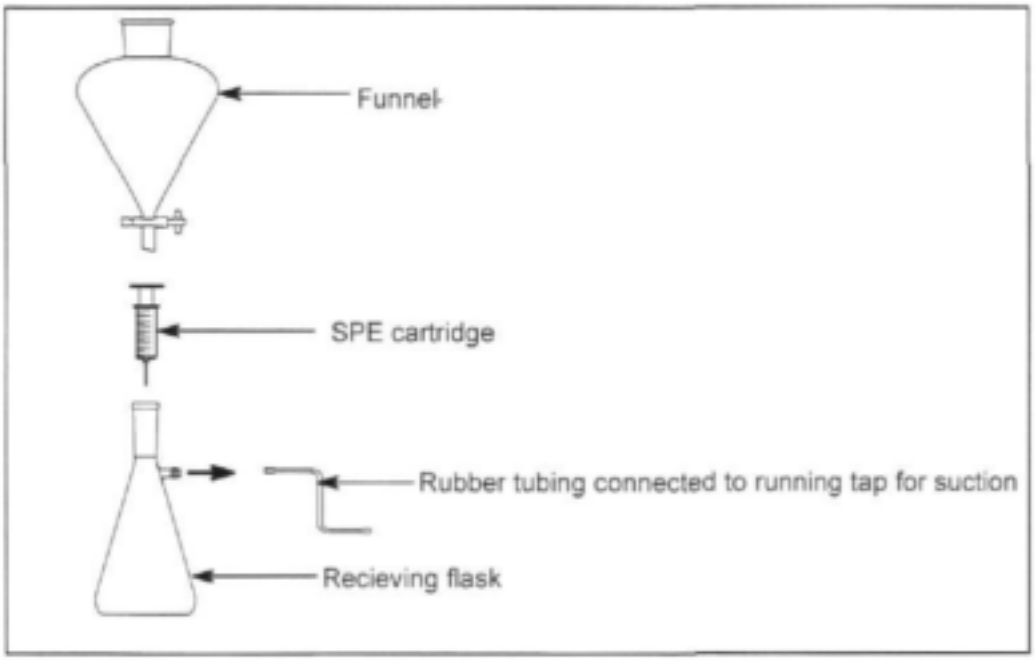


Figure 5.2: Manual SPE experimental setup used in this study

The utilization of the manual SPE method led to the modification of the extraction procedure used with the Autotrace extractor. **Table 5.2** shows the changes that were made. To be noted is that 500 mL instead of 1000 mL of sample was pre-concentrated to a 10 mL extract (step7). This method seemed to be time consuming and only allowed for one experiment to be run at a time due to working conditions in the laboratory. As a result a maximum flow rate of 10 mL/min could be achieved with the manual SPE method hence the amount of sample was

reduced to optimize the extraction time. However, the extraction efficiency was high enough to fulfil the purposes of the study.

Table 5.2: Modified extraction procedure

Loading procedure	Flow rates
Step 1: Process one sample using the following procedure	Condition Flow: 10 mL/min
Step 2: Wash syringe with 2 mL of MeOH	Load Flow: 10 mL/min
Step 3: Rinse column with 5 mL of EtOAc into solvent waste	Rinse flow: 10 mL/min
Step 4: Rinse column with 5 mL of DCM into solvent waste	Elute Flow: 5 mL/min
Step 5: Condition column with 10 mL of MeOH into solvent waste	Condition air push : 10 mL/min
Step 6: Condition column with 10 mL of deionized water into aqueous waste	
Step 7: Load 500 mL of sample onto column	
Step 8: Dry column with gas for 15 minutes	
Eluting Procedure:	
Step 1: Soak and collect 3 mL fraction using EtOAc	
Step 2: Collect 2 mL fraction into sample tube using EtOAc	
Step 3: Soak and collect 3 mL fraction using DCM	
Step 4: Collect 2 mL fraction into sample tube using DCM	
Step 5 END	

For extraction of water samples carried out at Rand Water Analytical Laboratories, a method similar to the manual SPE method was used. This method was slightly different in that it utilized a vacuum manifold SPE manufactured by Agilent Technologies.

5.4 Absorption by SPE method

The method used to perform the kinetic studies of the CD polymers on a laboratory scale was based on the utilization of empty used SPE cartridges to form columns. Kinetic study in this case is referring to studies whereby the sample was caused to flow through the polymers as opposed to isotherm or jar tests whereby the sample is mixed with the polymer in a closed container and stirred. The empty cartridges were packed with the CD polymers and water samples were loaded onto the column by means of an SPE method at controlled rates. The sample that had been flushed through the column was collected in a clean

container and re-extracted through a C18 SPE cartridge and quantified by GC/MS. **Figure 5.3** summarizes the absorption and quantification routes taken.

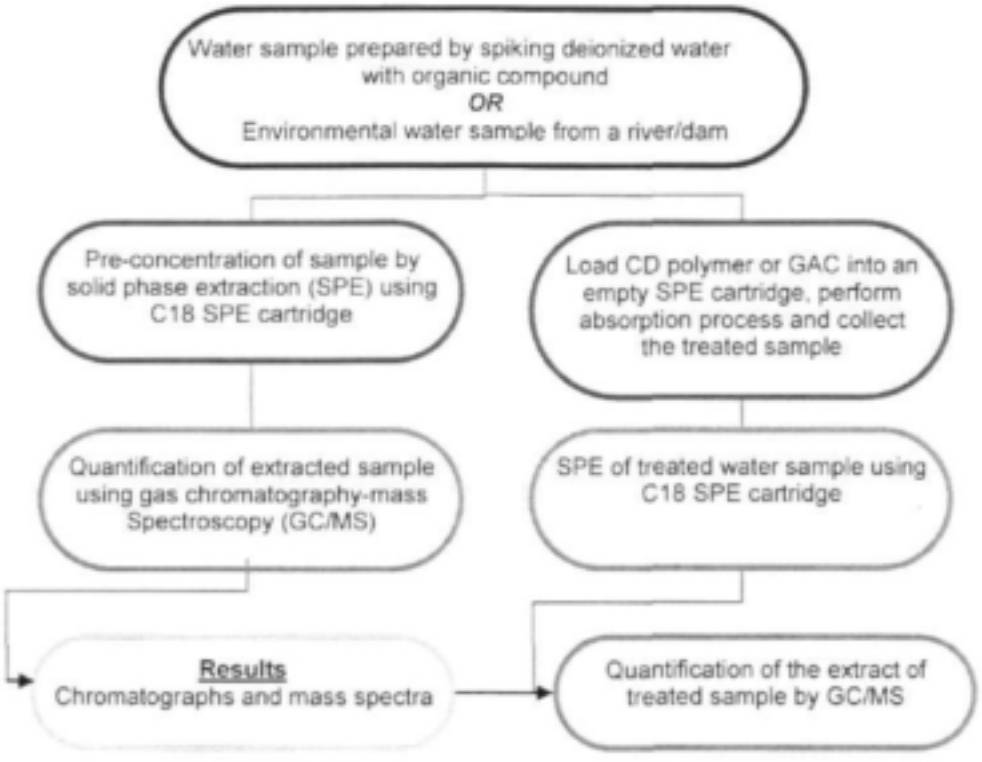


Figure 5.3: A flow diagram of the treatment and quantification of water samples.

The absorption procedure by SPE method did not involve the conditioning of the column. The loaded polymers were ground to fine particles before packing into the SPE cartridges. The absorption procedure by SPE is shown by **Table 5.3**.

Table 5.3: Absorption procedure by SPE method

Loading and Elution steps:	Flow rate
1. Process x samples using the following procedure 2. Load 500 mL of sample onto cartridge loaded with CD polymers or GAC 3. Dry column with gas for 15 minutes Soak and collect 10 mL fraction into sample tube using 5mL of EtOAc and 5 mL of DCM 4. END	Load Flow: 10mL/min Elute Flow: 10mL/min

5.5 Gas Chromatography-Mass Spectroscopy quantification procedures

5.5.1 Why use GC/MS

The combination of Gas Chromatography (GC) for separation and mass spectrometry (MS) for detection and identification of a mixture of compounds is rapidly becoming the definitive analytical tool in the laboratory. The GC/MS systems come in many varieties depending on the work they are designed to accomplish.[140]

Several reasons mitigated the selection of this technique for quantification purposes in this study ahead of other techniques such as Ultra-violet Visible Spectroscopy and High Performance Liquid Chromatography (HPLC). Gas chromatograph (GC) and mass spectroscopy (MS) make an extra effective combination for chemical analysis.[140] GC is a popular, powerful, reasonably inexpensive, and easy-to-use analytical tool. Mixtures or samples to be analyzed are injected into an inert gas stream and swept into a tube with a solid support created with a resolving liquid phase. Absorptive interaction between the components in the gas stream and the coating leads to a differential separation of the components of the mixture or sample, which are then swept through a detector flow cell. The mass spectrometer takes the injected material, ionizes it in a high vacuum and channels these ions and their fragmentation products through a magnetic mass analyzer, and then collects and measures the amounts of each selected ions in a detector.[140]

The combination of the two components into a single GC/MS system forms an instrument capable of separating mixtures into their individual components and identifies them. The system then provides quantitative and qualitative information on the amounts and chemical structure of each compound.[140] GC/MS is a suitable technique for the quantification of volatile and semivolatile organic compounds and also provides very low detection limits of as low as 0.01µg/L for such compounds. The amount of time that a compound is retained in the GC column is known as the *retention time* (T_R). The retention time can be useful in differentiating between some compounds although it is not a reliable factor to determine the identity of the compound.[141]

Ion trap mass spectrometers similar to the one used in this study, are gradually being utilized by GC/MS laboratories. Laboratories that use them claim they are 10–100 times more sensitive than a quadrupole. They can easily be switched between *chemical ionization* (CI) and *electron ionization* (EI) modes; require less maintenance, and can easily be upgraded and made fit for MS/MS studies.[140,142-144]

5.5.2. EPA Method 8270 for semivolatile organic compounds

Gas chromatographic analyses in this study were carried out using a Varian 3800 capillary gas chromatograph coupled with a Saturn 2000 mass spectrometer. An EPA Method 8270 for semivolatile organics was used for the GC/MS analysis.[145] This method uses similar conditions to method 525.2 except that it is most suitable for determination of phenol and substituted phenols which were selected as target compounds in the study. Method 525.5 is developed for mainly the determination of pesticides. The method 8270 GC/MS conditions in each experiment are as shown in **Table 5.4**.

Table 5.4: EPA Method 8270 for determination of semivolatile organic compounds.

Column Type	Capillary Chrompack CP Sil 8 CB, 30m 0.25mm ID, 0.25μm
Injector	1μl splitless (hold 0.4 min.)
Injector temperature	300°C
Carrier gas	Helium, constant flow
Flow rate	1mL/min
Oven temperature	35°C (hold 2 min.) to 260°C@20°C/min, to 330°C @6°C/min (hold 1 min.)
Detector	Mass Spectrometer (Ion trap)
Transfer line temp.	280°C
Scan Range	35-550 amu
Ionization	Electron ionization (EI)
Mode	Full scan

The sample to be analyzed was first introduced to the GC instruments through an *injector port* (a septum port on top of the GC) using a graduated capillary syringe. The Gas Chromatograph is a temperature controlled oven designed to hold and heat the GC column. Helium, which served as a carrier gas, was used to sweep

the injected sample onto and down the column where the separation occurs and then out into the mass spectrometer interface.[140]

5.5.3 GC/MS Data Analysis

An advantage of the GC/MS output is that it can provide qualitative and quantitative results. The simplest data output from the mass spectrometer analyzer is a measurement of the total ion chromatogram (TIC). GC evidence may raise concern if the spectral peaks are broad, overlapping or evenly formed.[141]

Quantification of the spectral peaks was performed using the MS data handling method of the mass spectrometer. A compound table was selected and built with characteristic mass fragments and their relative signal strengths for each compound to be analyzed. The main identifier mass fragment for a compound is called the target ion. Other identifier mass fragments for the same compound are called qualifiers. When these mass fragments appear in the spectra of a compound with the correct retention time in the injected sample chromatogram, the identity of the targeted compound is confirmed. A library of printed and computerized databases was used to compare both masses of fragments and their intensities with those obtained from the analysis. Once a match was found, it was confirmed by comparing the relative retention time and mass spectra. Specific ion chromatographs (peaks) obtained from the total ion current (TIC) were integrated and peaks from standards that were compiled in a compound table were used to give the results in µg/L. The absolute amount of analyte was determined by comparing the peak area from a run in which the amount was unknown to that of a calibration standard.

5.5.4 Analysis of geosmin and 2-MIB

Geosmin and 2-methylsoborneol (2-MIB) were analysed using the method shown in **Table 5.5**. The method is used by Umgeni Water for the analysis of these compounds. SPE was used to pre-concentrate the water samples spiked with these compounds prior to GC/MS analysis. Several other methods such as those used by Rand Water and the City of Cape Town could be used. These were

eliminated due to the type of column used and thus the method which gave best results was used.

Table 5.5: GC/MS method used for the analysis of geosmin and 2-MIB.

GC Column	Capillary Chrompack CP Sil 8 CB, 30m 0.25mm ID, 0.25μm
Injection mode	1μl splitless
Injector temperature	250°C
Carrier gas	Utra Pure Helium, constant flow
Flow rate	1mL/min (35 cm/sec)
Column program	70°C for 2 min, ramp 20°C/min to 270°C
Detector	Mass Spectrometer (Ion trap)
Transfer line temp.	280°C
Scan Range	35-550 amu
Ionization	Electron ionization (EI)
Mode	Full scan

5.6 Laboratory scale column tests

5.6.1 Effect of cyclodextrin polymers on the removal of selected high priority organic contaminants

Preliminary studies, which involved the investigation of the SPE efficiency were carried out using pentachlorophenol, 2-chlorophenol, 2,4,6-trichlorophenol and 2,4-dimethylphenol as contaminants. These were the available drinking water disinfection products in the lab at the early stages of the study. The amount of contaminants investigated was later increased to test the effectiveness of these polymers on a wide variety of organic contaminants.

5.6.1.1. Sample preparation

Standard water samples were prepared by spiking deionized water with a known amount of organic contaminant. Samples were prepared at 10 mg/L and 10μg/L. The standard samples were prepared at these concentrations in order to study how the loading capacity of the CD polymers is affected by concentration of pollutant. Insoluble compounds were first dissolved in 1 mL of methanol before addition of deionized water. The homogeneity of the samples was enhanced by shaking using ultrasound for about 3 minutes.

Calibration standards of each of the organic pollutants were prepared in dichloromethane (DCM) and stored in GC vials before injection. All the compounds readily dissolved in DCM which was used for both extraction and GC/MS analysis. A volume of 1 µL of each standard was injected into the GC. Calibration curves were obtained by plotting peak areas of each the standards against the concentration of that standard.

The **detection limit** of the GC/MS was determined by injecting a series of the standard samples under dilution. The GC/MS could detect samples up to 0.01 µg/L (0.01 ppb).This was a positive result for the study since the aim was to investigate whether the CD polymers could remove the organic contaminants at µg/L and ng/L levels as they naturally occur in real water samples.

5.6.1.2. Absorption process using simple setup

Preliminary studies for the absorption of the organic pollutants were carried out using a simple column setup that was designed in the laboratory (**Figure 5.4**). Samples used along with this method were extracted by means of a Zymark Autotrace Extractor and quantified by GC/MS as described earlier.

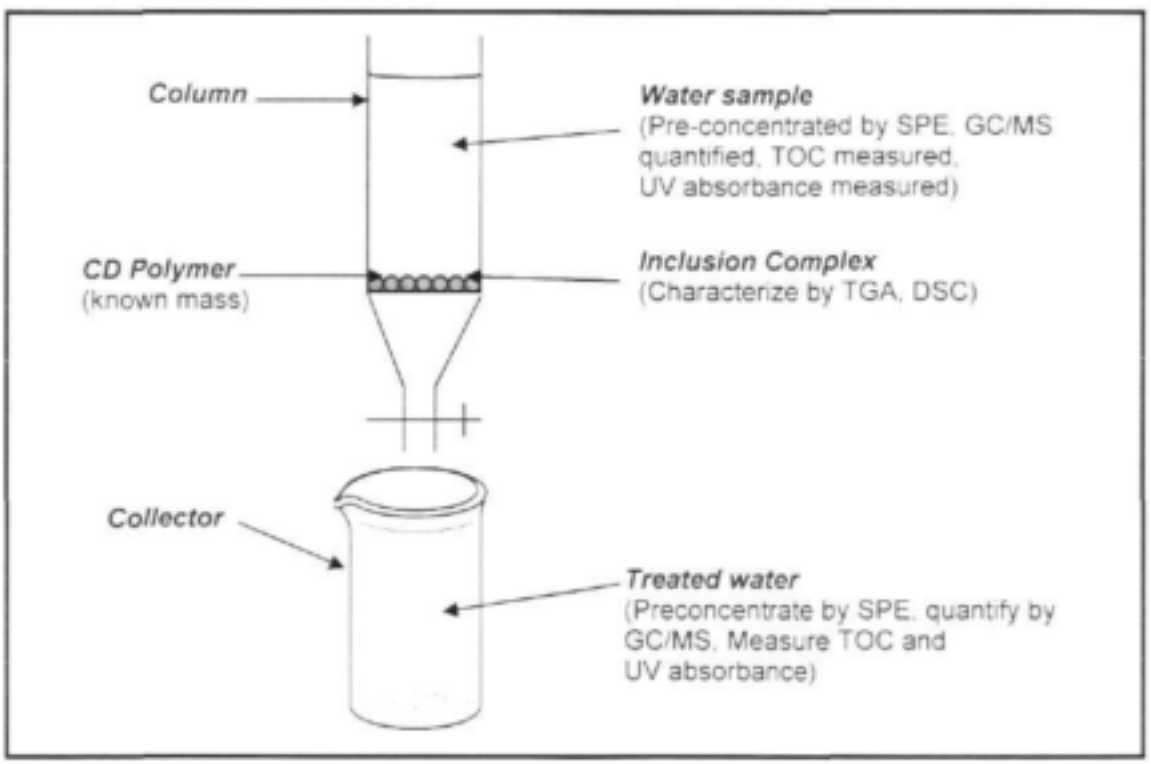


Figure 5.4: Setup of the absorption process initially used in the study.

The setup proved to be more time consuming and was not ideal for replicate experiments. As a result, the manual SPE setup (**Figure 5.1**) was designed to fulfil the role of the former.

5.7 Iodine number, phenol value and iodine number determination

It was necessary to assess the absorption capability of cyclodextrin nanoporous polymers by performing laboratory testing methods similar to those done for activated carbon. The tests that were performed in this study are the iodine number, phenol value and methylene blue number. Similar procedures to those conducted for activated carbon assessment by Umgeni Water were adopted and applied. Slight modifications were done on these tests in order to suit the working conditions and/ or apparatus available in the laboratory. The experimental procedures and apparatus that were used in each case to with examples of calculations are outlined in **appendix B**. It may be noted that in all experiments where a certain volume of activated carbon is used, equivalent amounts of CD polymers were used instead.

5.8 TOC analysis

5.8.1 Introduction

The term Total Organic Carbon (TOC) has mostly been encountered in recent studies. A relationship between biological oxygen demand (BOD), chemical oxygen demand (COD) and TOC was established in the late 1970s. Prior to that, most laboratories were equipped with COD and BOD determining apparatus. However TOC analyzers have become the main analytical tool in many water treatment and quality control laboratories.[17,146]

According to data obtained from an article by Furlong and Wallace,[146] the typical applications and levels of TOC in various water streams are as shown in **Table 5.6**.

Table 5.6: Typical applications and levels of TOC in various water streams.

Type of Water	TOC level (mg/L)
High Purity Water	< 0.01
Water for injection	< 0.50
Ground water	< 1
Sea Water	< 1
Drinking Water	< 4
Surface Water	< 10
Waste Water	> 10

Various TOC Analyzers have been introduced by manufacturers over the years. These use different oxidation technologies and the two major oxidation technologies that dominate the TOC market are combustion and UV persulfate, in that order. Both technologies have advantages and disadvantages.

5.8.2 Why measure TOC?

Measuring the amount of NOM in sources of surface waters has been a crucial requirement for municipal and drinking water treatment and waste water facilities. As mentioned earlier, when raw water containing NOM is chlorinated during the disinfection process DBPs are formed. In order to reduce NOM before disinfection, a direct correlation between TOC and NOM was established as per Standard Methods 5310 and the USEPA's disinfectants/disinfection by-products rule. Therefore for measuring NOM, TOC analysis was chosen.

TOC analysis was chosen in this study in order to determine the effectiveness of the CD polymers in the removal of NOM. Hence, humic acid (HA) which is a component of NOM was chosen. Humic acid has been suggested as a standard for simulating NOM in the laboratory. Studies by Wallace[17] indicate that modern TOC analyzers such as the one available in our laboratory have shown good

recoveries of (90–95%) of HA. It was also observed that since HA is partially insoluble at pH ≤ 2, the particulate TOC fraction has been more accurately measured using High Temperature Combustion (HTC) oxidation technologies rather than UV persulfate.

5.8.3 Operation principles

The major oxidation technologies used for TOC analysis are described in Standard Method 5310. These are the HTC and low UV persulfate oxidation.[147] Either oxidation techniques either remove or measure inorganic carbon (IC), defined as dissolved carbon dioxide, carbonate and bicarbonate. A common technique that was used is one that measures non-purgeable organic carbon (NPOC) by introducing the sample and a small amount of inorganic acid to an inorganic removal chamber. Through the acidification of the sample, the IC is converted into carbonic acid (H_2CO_3) also known as dissolved organic carbon (DOC). The sample is usually sparged (gas stripped) with the carrier gas to drive off the dissolved CO_2. Loss of purgeable organic carbon (POC), in the form of volatile organic substances can occur during the sparging of the sample. However the amount of POC is usually negligible and can be ignored. In such cases NPOC is equivalent to TOC.[148] TOC can also be measured by subtracting IC from total carbon TC (TOC = TC – IC). This is known as TOC by difference. The NPOC method was however the preferred way for analyzing TOC in drinking and surface waters due to its more precise measurements.

An Apollo 9000 TOC Analyzer by TEKMAR DOHRMANN was used for all TOC measurements. The instrument uses the High Temperature Combustion (HTC) – Infrared Method – 5310B that is more accurate than the UV-Persulfate method. The instrument was calibrated using a series of Potassium Hydrogen Phthalate (KHP) standard samples. The calibration curve was used to calculate the TOC values of unknown samples. The operation of the instrument was performed according the manufacturer's operating manual.

Particulate-free standard humic acid samples were prepared by accurately dissolving a known amount of standard humic acid with a small volume of 0.1M NaOH solution in a volumetric flask. Dilution to the mark was done using

deionized water and the samples were homogenized by means of a sonicator. The same deionized water was injected as a blank sample. Samples were transfered onto clean sample vials. Aliquots of each sample were introduced into the instrument by an auto sampler syringe. All samples were analysed in triplicate. The TOC for each sample was measured before and after the absorption (complexation) process was carried. The process was done in a similar way as described in section **5.6.1.2**.

5.9 UV Absorbance

The UV absorbance of samples was measured using a CARY 50 UV Spectrophotometer before and after treatment of standard solutions with the CD polymers. A 10mm quartz cuvet cell was used. The instrument was calibrated and used to quantify results. The general procedure used is as described in method 5910B of the Standard Methods for the Examination of Water and Waste Water, 1989.

5.10 Thermogravimetric Analysis (TGA)

This is a thermal analysis technique used to measure changes in the weight (mass) of a sample as a function of temperature and/or time. TGA is commonly used to determine polymers degradation temperatures, residual solvent levels, absorbed moisture content, and the amount of inorganic (non-combustible) filler in polymer or composite material compositions.[112-115,149]

5.11 Differential Scanning Calorimetry (DSC)

DSC is a technique used to study the heating profile of polymers as the temperature increases. It is basically used to study the *thermal transitions* in a polymer. Thermal transitions are changes that take place in a polymer as it heats up. The melting temperature of a crystalline polymer can be determined using this technique. The *glass transition* is also a thermal transition.[112-115,149]

6.1 Introduction

The aim of this chapter is primarily to present the results obtained after investigating the efficiency of the standard cyclodextrin polymers in the removal of selected high priority persistent organic pollutants (POPs) from water. The pollutants were selected by one or more of the following factors: (a) the pollutant was readily available in the laboratory at the beginning of the study; (b) the pollutant was detected in a local river or sewage sludge; (c) the compound is a current issue of concern for the local water bodies. **Table 6.1** and **Figure 6.1** show respectively, the properties and structures of organic pollutants that were investigated in this study.

Table 6.1: Properties of selected organic contaminants.

Organic pollutant	*b.pt (°C)*	*m.pt (°C)*	*Ion fragments (m/z)*
4-chloroaniline[a]	232	67-71	127
2-chlorophenol[a]	175	8-10	129
1,3-dichlorobenzene[a]	60-62	-24	147
2,4-dichlorophenol[a]	209-210	41-44	163
2,4-dimethylphenol[a]	209-213	22-24	122
geosmin[a]	270	-163	95
humic acid[b]	-	> 300	-
2-methylisoborneol (2-MIB)[a]	210	-113	112
naphthalene[a]	218	79.5-81	128
4-nitrophenol[a]	279	113-114	139
pentachlorophenol (PCP)[a]	310	187-189	266
phenol[a]	181	39-40	94
2,4,5-trichlorophenol[a]	253	67	198
2,4,6-trichlorophenol[a]	246	65-68	198

[a]Analyzed by GC/MS. [b]Analyzed by UV Spectroscopy and TOC

The study focussed specifically on water samples that were prepared by spiking deionized water with the selected organic contaminants. The concentration of the water samples was varied from mg/L and µg/L to ng/L levels. This was done in order to observe how the polymers performed within a wide concentration range of water samples. Several environmental water samples obtained from the Rietvlei dam were used for comparison purposes. A comparative study of the absorption capacity of the CD polymers with granular activated carbon (GAC) was carried out.

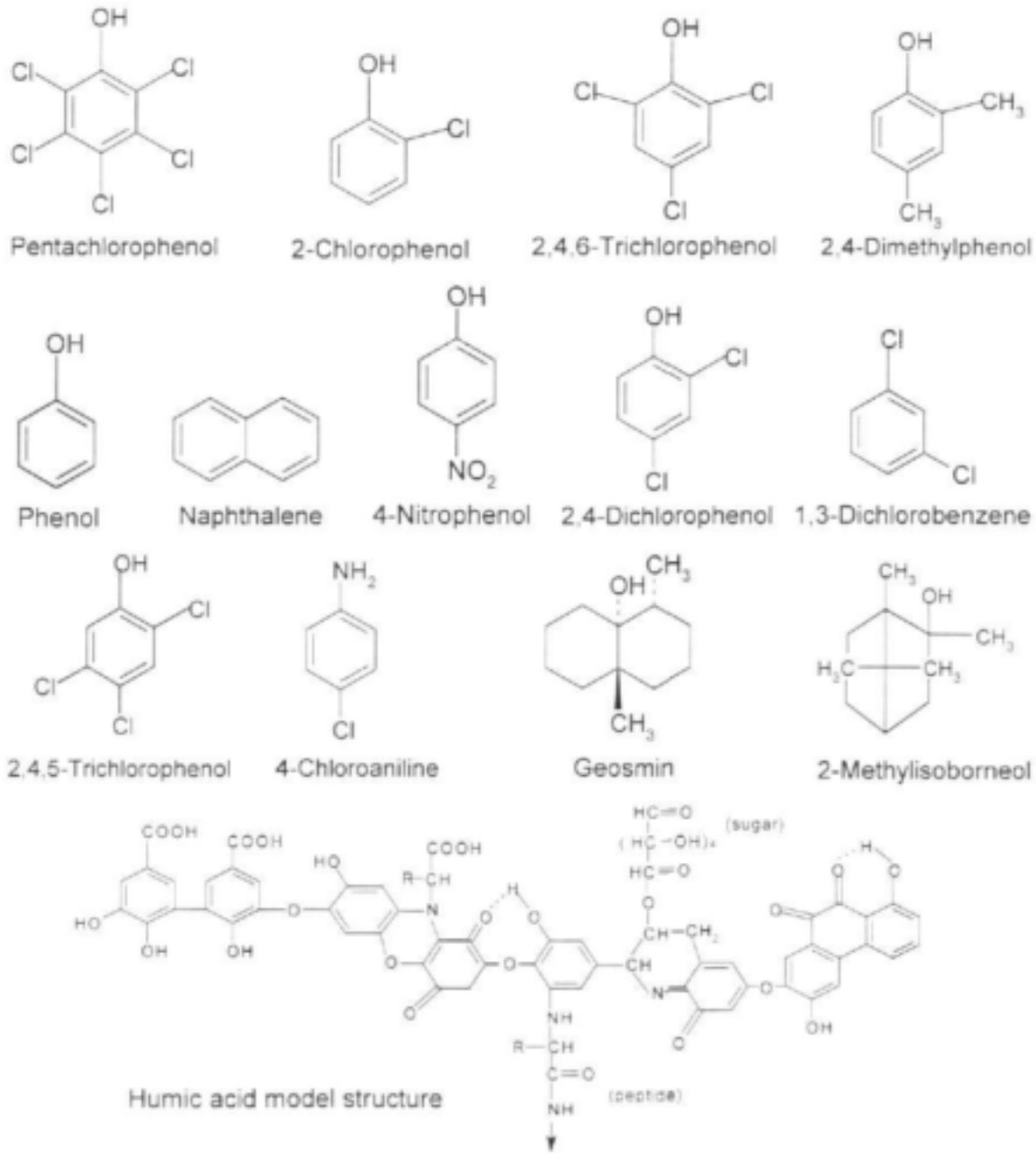


Figure 6.1: Molecular structures of the organic pollutants used in this study.

6.2 Synthesis of CD polymers and their monitoring by IR

The α-, β- and γ-CD polymers were accessed by reacting a DMF solution of a CD with the relevant linker (HDI or TDI) (**Figure 6.2**). The polymers were obtained in a quantitative yield by washing off the residual DMF with acetone before drying the sample under vacuum.

A typical reaction that yielded a *soft powdery polymer* (Polymer A) is as follows: β-CD (1.00g, 0.00088 mol) was dissolved in 15 mL of DMF while stirring to form a homogeneous solution. HDI linker (1.15 mL) was then added dropwise while stirring. The reaction was left in an oil bath at 70°C for 21h to form a gel like solution. For similar amounts of β-CD and DMF, TDI (1.02 mL) was added to produce a similar type of polymer in a quantitative yield.

A second type of the polymer that was classified as *hard pellet polymer* (Polymer B) was synthesized. This type of polymer was obtained with the use of 10 mL or smaller volumes of DMF for 1g of β-CD and HDI (1.15 mL) or TDI (1.02 mL).

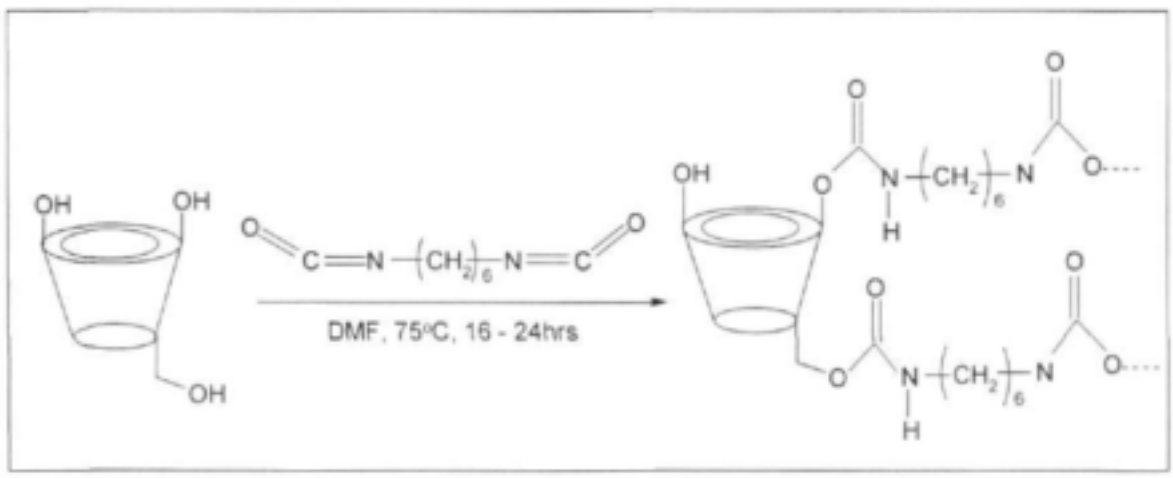


Figure 6.2: Reaction pathway for the formation of CD polymers.

As evidenced by the disappearance of the isocyanate peak at $\tilde{\nu}$ = 2273, the reaction was complete within 21 hours (**Figure 6.3: A-D**). Similarly, successful incorporation of the linker was supported by the appearance of peaks corresponding to C=O at $\tilde{\nu}$ = 1600.

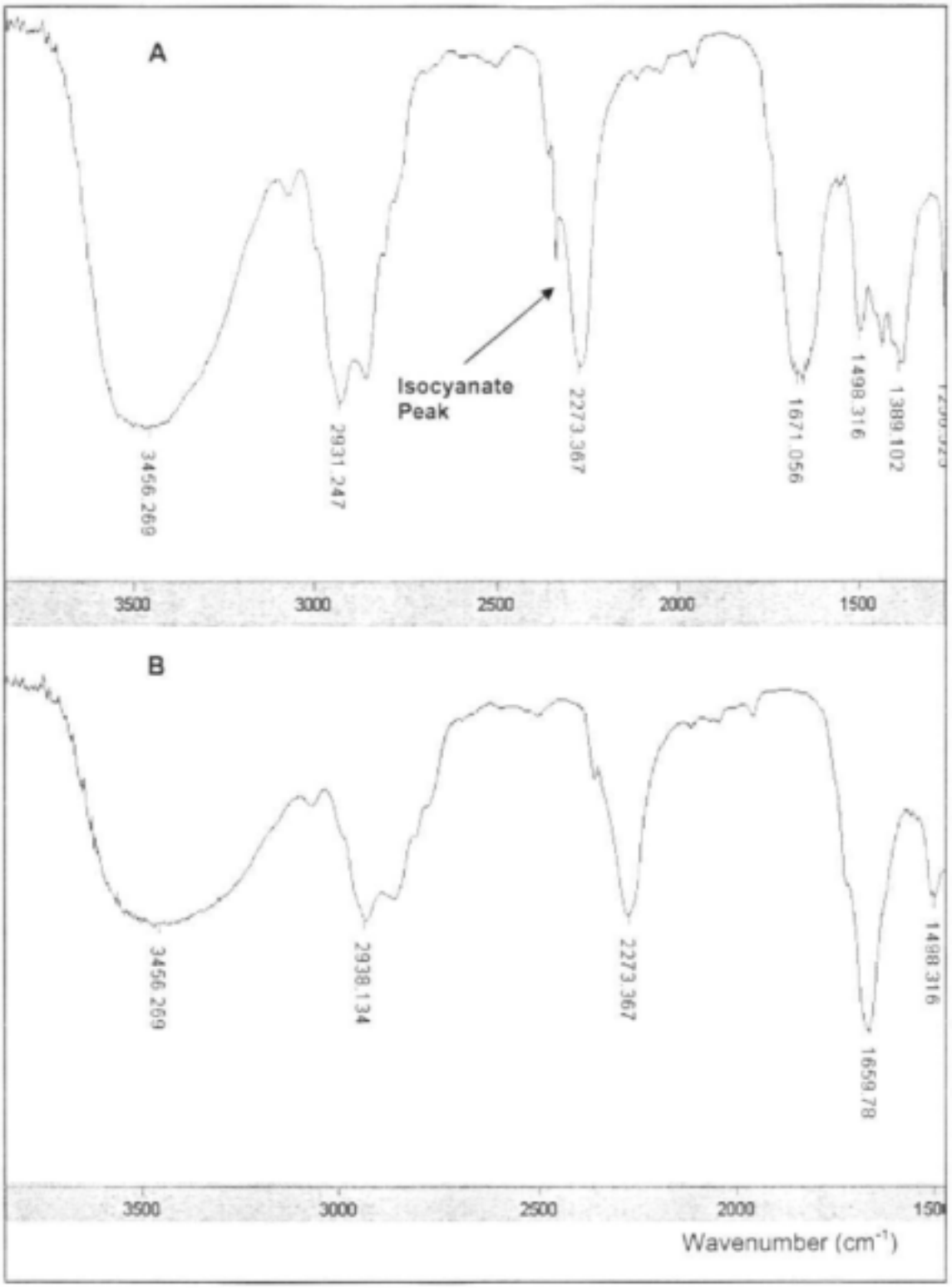


Figure 6.3:A – IR Spectrum of reaction mixture at 0 minutes; B – IR Spectrum after 1 hour of reaction time

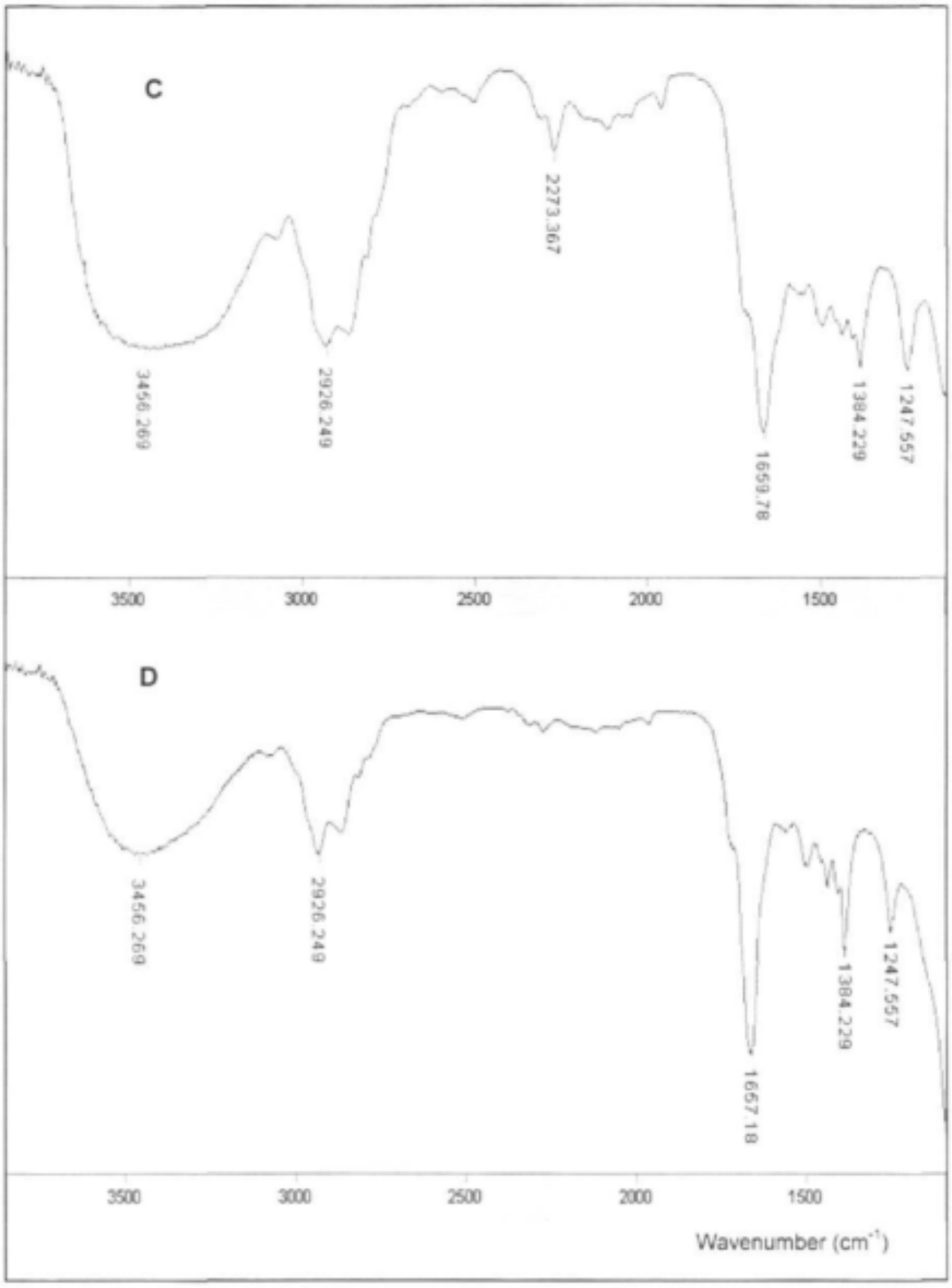


Figure 6.3:C – IR Spectrum of reaction after 19 hours; D – IR spectrum of reaction after 21 hours

6.3 Comparative study of the absorption efficiency of the different polymers that were synthesized

The investigation of the absorption efficiency of the soft powdery (Polymer A) and hard pellet (Polymer B) types of HDI- and TDI-linked β-CD polymers (β-CDHDI) was carried out by mixing known amounts of spiked water sample with the polymer. A comparison of the performance of the powdery polymers versus the hard pellet polymers (**Figure 6.4**) shows a clear advantage of using the powdery polymers. On average, polymer A showed considerably better absorption efficiency of 62% from two batches of the same type of polymer. This observation, which signifies a good absorption efficiency, was attributed to the suspected larger surface area of absorption this type of polymer. With polymer B, an average absorption of 1% was obtained

The absorption experiments were carried out using the Zymark SPE instrument for pre-concentration of samples and the manual SPE method for absorption of the contaminants. 500 mg of the β-CDTDI polymers, 1000 mL of sample, and pentachlorophenol (PCP) was used as a pollutant.

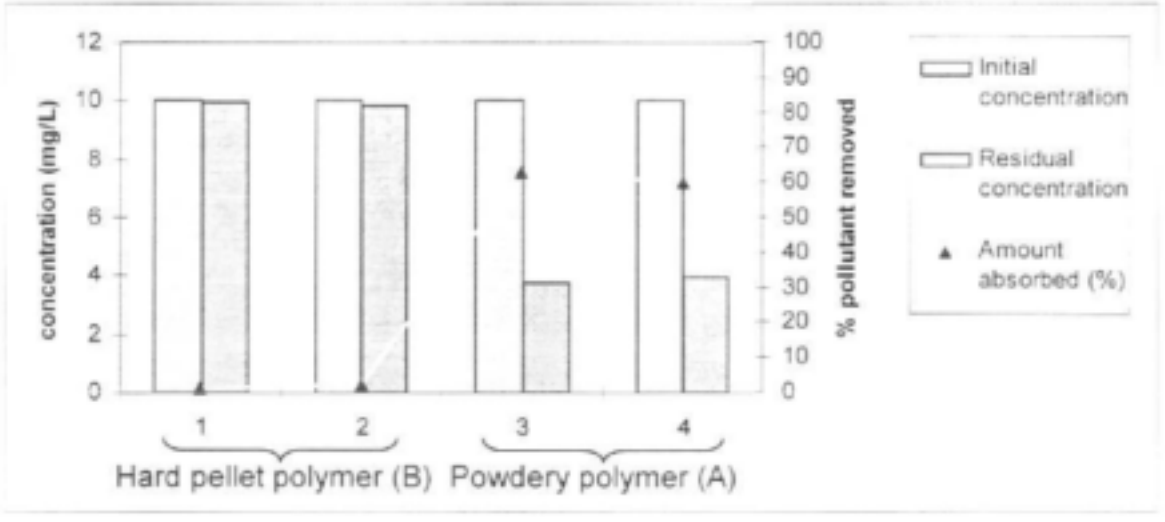


Figure 6.4: The amount of PCP removed using different types of polymers and the Zymark Autotrace SPE.

The experiment was repeated using the manual SPE method for pre-concentration and absorption by the polymers. With this experiment, 500mg of β-CDHDI polymer and 500 mL of a pentachlorophenol spiked water sample was used as pollutant. The results obtained for the HDI-linked polymer are similar to those of the TDI linker (**Figure 6.5)**.

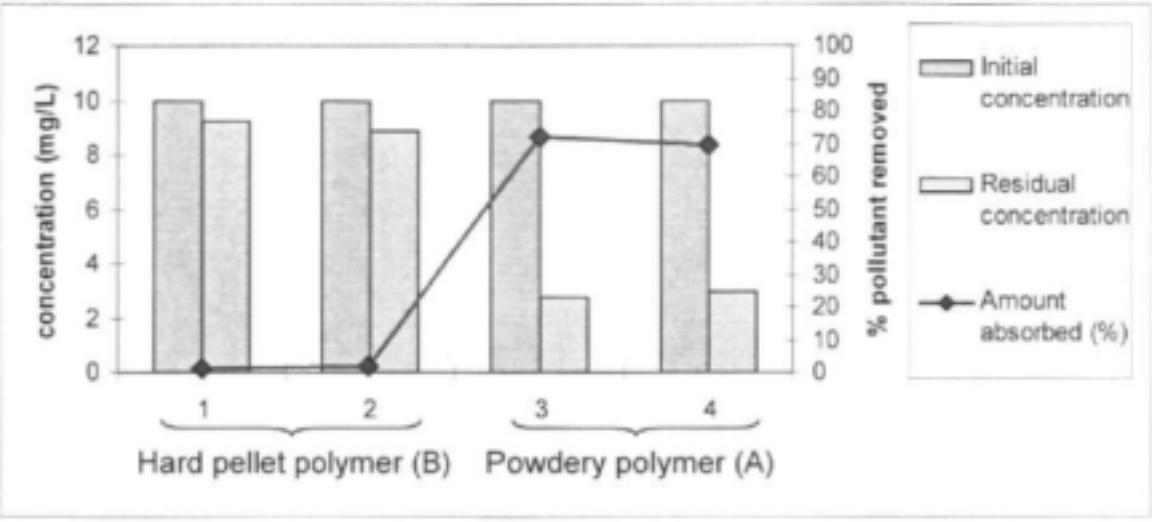


Figure 6.5: The amount of PCP removed using different types of polymers and the manual SPE method.

Polymer A proved to be more effective at absorbing the organic pollutants (70%) than polymer B (5%). As a result of these findings only the powdery polymers were used throughout the remainder of project. It was possible to synthesize both HDI- and TDI-linked CD polymers as powdery polymers.

6.4. Absorption studies - results and discussions

Hexamethylene diisocyanate (HDI) linked CD polymers were used for preliminary investigations. **Table 6.2** shows the results obtained after treating the CD polymers using the setup in **Figure 5.3** and extraction by the Zymark Autotrace Extractor. A summary of the parameters for each of the experiments performed is also shown in **Table 6.2.** The concentration before, in each of the experiments is the concentration after pre-concentration of the initial feed concentration (Co). In each experiment, samples were prepared in 2000 mL or 5000 mL volumetric flasks so that there were enough samples for both pre-concentration and performing the absorption process without having to prepare a new sample.

Table 6.2: Results obtained after HDI linked β-CD treating of standard water samples together with the summary of parameters.

Compound	(m/z)	T_R (min)	Conc. Before (Co) / mg/L	Conc. After (C) mg/L	C/Co
Pentachlorophenol	266	11.995	10	4	0.4
			10	4	0.4
2,4,6-trichlorophenol	198	10.388	10	6	0.6
			10	5	0.5
2-chlorophenol[a]	128	7.792	10	9	0.9
			10	9	0.9

[a]The volume of sample used in the experiments with 2-chlorophenol was 500 mL

Mass of polymer = 500 mg, Feed volume = 1000 mL, Initial feed concentration (Co) = 10 mg/L, SPE cartridge – C18, Flow rate (SPE extraction) = 20 $mLmin^{-1}$

The values of the concentration after treatment divided by the initial feed concentration (C/Co) indicate the efficiency of the polymers in each experiment. The closer the value of C/Co is to 0, the higher the absorption and values close to 1 signify poor absorption efficiency. The C/Co value multiplied by 100% gives the absorption capacity and the results were calculated based on this equation and reported in percentage. The highest absorption efficiency was 63%, obtained with pentachlorophenol and the lowest was obtained with 2-Chlorophenol at 10%. The difference in the absorption of the compounds was asserted to their different polarities, a property that certainly affects the degree of absorption during inclusion complexation.

This result showed that the polymers have good absorption efficiency. However our aim was focussed on the application of these polymers at very low concentrations where other conventional technologies become ineffective. The feed concentration that was used, for instance, was much higher than would be found for these pollutants (see appendix D for maximum level guides). As a result, water samples were spiked with contaminants at µg/L levels and the absorption studies were repeated.

The results obtained after treating water samples contaminated with the same organic contaminants, but this time prepared at 10 µg/L, are shown in **Table 6.3** together with the parameters used for the experiments.

Table 6.3: Results obtained after treating of standard water samples at low concentration together with the summary of parameters.

Compound	(*m/z*)	T_R (min)	Conc. Before (Co) µg/L	Conc. After (C)	C/Co
Pentachlorophenol	266	11.995	10	ND	-
			10	ND	-
2,4,6-Trichlorophenol	198	10.388	10	ND	-
			10	ND	-
2-Chlorophenol[a]	128	7.792	10	ND	-
			10	ND	-

[a]The volume of sample used in the experiments with 2-chlorophenol was 500 mL

ND = not detected, Initial feed concentration (Co) = 10 µg/L, Flow rate = 20 $mLmin^{-1}$

Both the results in **Table 6.2** and **Table 6.3** were obtained using the Autotrace SPE for pre-concentration and using the simple column setup for performing the absorption experiments. After pre-concentration of the treated water samples and quantification by GC/MS the organic contaminants were not detected in each of the experiments. As a result, the C/Co values could not be calculated, signifying 100% absorption of the organic contaminants.

This simple manual process of percolating the solution through a simple column gave positive results but the process was time consuming since no pressure connection was used to enhance the flow rate. This setup was therefore replaced by a method where the contents of an SPE cartridge were replaced by the CD polymer under investigation and the solution was sucked through the polymer using a normal laboratory filter. 500 mL of feed solution had to be used because of the extra time taken to filter through the column.

The initial and final concentrations standard water samples (**Table 6.4**) were compared using the manual SPE method. The amount of polymer used was 500 mg. A feed volume of 500 mL with an initial feed concentration of 10 mg/L was percolated through the polymer packed column at a flow rate of 10 $mLmin^{-1}$.

Table 6.4: Results obtained after treating standard water samples using manual SPE method.

Compound	(*m/z*)	T_R (min)	Conc. Before (Co) mg/L	Conc. After (C) mg/L	C/Co
Pentachlorophenol	266	11.995	10	2	0.2
			10	2	0.2
2,4,6-Trichlorophenol	198	10.388	10	5	0.5
			10	6	0.6
2-Chlorophenol	128	7.792	10	5	0.5
			10	6	0.6
2,4-Dimethylphenol	122	8.900	10	8	0.8
			10	8	0.8

The highest absorption of pollutant was observed with pentachlorophenol. About 80% of this compound was absorbed. An absorption of about 50% was observed for both 2,4,6-trichlorophenol and 2-chlorophenol. There seemed to be a huge improvement in the absorption of 2-chlorophenol from 10% to 50%. This may be explained by the fact that a different method was used and may have affected the absorption of this compound. 2,4-dimethylphenol was the least absorbed at about 20% as indicated by the C/Co values. This compound was also selected from a list of priority organic pollutants and was available in our laboratories.

The experiments were repeated using a different feed concentration (10 μg/L). Other parameters were kept as in the previous experiments. Not only were the initial and final concentrations determined, but the CD cavities were also cleaned by eluting the polymers with DCM and EtOAc (**Table 6.5**).

Table 6.5: Results obtained after treating standard water samples using manual SPE method and Co = 10 µg/L.

Compound	(*m/z*)	Conc. Before (Co) µg/L	Conc. After (C)	Elution with DCM + EtOAc
Pentachlorophenol	266	10	ND	9
		10	ND	10
2-Chlorophenol	129	10	ND	7
		10	ND	9
2,4,6-Trichlorophenol	198	10	ND	6
		10	ND	9
2,4-Dimethylphenol	122	10	ND	5
		10	ND	10
ND – not detected				

100% absorption was again observed in these experiments. All the organic compounds could not be detected and therefore could not be quantified after treatment of the water samples. To find out whether the organic contaminants were absorbed by the polymers, these were washed (eluted) with 5 mL of EtOAc and DCM and analyzed by GC/MS. The results clearly indicate that the pollutants were indeed being absorbed (**Table 6.5).** However the amount eluted did not equal the amount of the initial feed concentration before absorption. This observation was attributed to the reason that the eluting solvents may not be ideal, in terms of eluting strength.

6.5 Comparative study of the CD polymers and granular activated carbon (GAC) to remove organic contaminants

The efficiency of the hexamethylene diisocyanate (HDI) and toluene diisocyanate (TDI) linked α-, β- and γ-CD standard polymers as well as that of granular activated charcoal (GAC) were studied. Standard water samples were prepared at concentration levels that are normally be found in natural water systems. The preparation of samples is as described in **section 5.6.1.1**. The results obtained after treating of water samples with both technologies using the same processes were used make conclusions on their performance at µg/L and ng/L levels.

6.5.1 Preparation of standard water samples

The instrument used for preparation of water samples was an SPE manufactured by Agilent Technologies. C18 cartridges from ENVI were used with 500mg of solid sorbent packing for extraction. Standard water samples (5 litres) were prepared by spiking deionized water with a standard mixture (8270 MegaMix – from Restek) which contained 76 semivolatile organic compounds in methylene chloride (methanol free). **Figure 6.3** shows the chromatograph of a 1000µg/L standard.

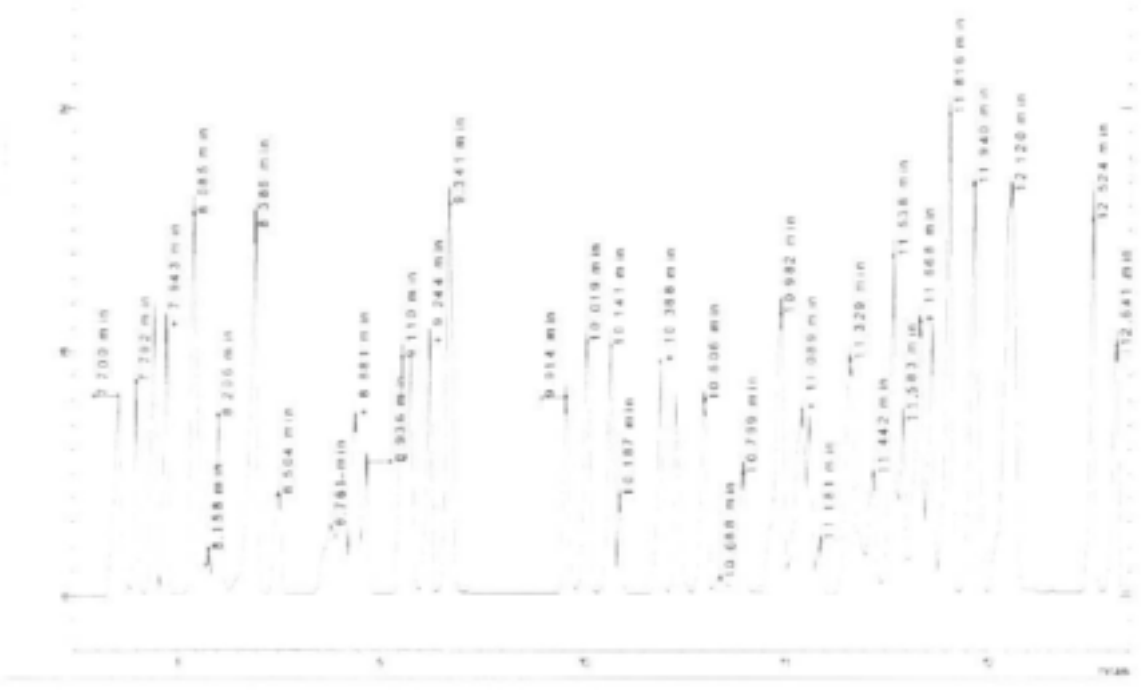


Figure 6.6: Chromatograph showing the peak intensities and retention times of some of the compounds in the standard mixture.

Selected organic compounds present in the standard mixture are listed in **Table 6.6** together with their respective molecular ions (*m/z*) and retention times. Each of these compounds was monitored by GC/MS before and after flushing the spiked water samples through the polymers and GAC.

Table 6.6: Selected organic compounds molecular ions and retention times.

Compound	m/z	Retention time, T_R (min)
Phenol	94	7.747
2-Chlorophenol	129	7.792
1,3-Dichlorobenzene	147	7.868
2-Nitrophenol	139	8.822
2,4-Dimethylphenol	122	8.881
Naphthalene	128	9.244
4-Chloroaniline	127	9.341
2,4,6-Trichlorophenol	198	10.388
2,4,5-Trichlorophenol	198	10.469
2,4-Dichlorophenol	163	10.982
Pentachlorophenol	266	12.915

Each of the compounds in Table 7.6 was confirmed using the mass ratio ions from the mass spectra together with a library match of the entire spectrum. **Table 6.7** below summarizes some of the key parameters pertaining to the small scale column tests (SPE cartridges) that were used to carry out the absorption studies of the polymers.

Table 6.7: Summary of column parameters for each of the experiments performed.

Column Description	Empty SPE cartridge
Column size	6 mL syringe body
Packing length	2 cm
Polymer type	Powdery
Mass of Polymer	500 mg
Feed volume	500 mL
Feed concentration	20 µg/L
Flow rate	10 $mLmin^{-1}$

The parameters were kept fixed in all the experiments. This was done in order to check the best polymers for absorption of the organic compounds under the same

conditions as well as for comparative purposes with activated carbon. The reported data was carried over a span of 5 days. The extraction of samples was carried out at Rand Water Analytical laboratories.

6.5.2 Real water samples

Real water samples were obtained from the Rietvlei Dam at the Rietvlei Nature Reserve using Schott glass sampling bottles. Samples were transported in a cooler box to the lab where they were stored in a refrigerator at 4°C until they were used. No pre-treatment of the samples was done. Analysis was performed using the raw water samples.

6.5.3 Results and discussions

Quantification of all results obtained was done using method 8270 for semivolatile organic compounds in water. A series of six data points was obtained by preparing standard solutions in a concentration range of 50 – 300 µg/L. A significantly linear regression of the calibration curve was obtained for the analyte concentration range to be tested. Each of the results was carried out under the same GC/MS conditions.

Table 6.8 shows the results obtained after treating a 20 µg/L standard solution with hexamethylene diisocyanate (HDI) linked α-, β-, and γ-CD polymers and granular activated charcoal (GAC) together with the conditions summarized in **Table 6.7**.

Table 6.8: Results obtained after treating 20 µg/L standard solution with HDI linked CD polymers and GAC.

Compound	Ret. Time (min)	α-CDHDI	β- CDHDI	γ-CDHDI	GAC
Phenol	7.747	ND	ND	ND	D/NQ
2-Chlorophenol	7.792	ND	ND	ND	D/NQ
1,3-Dichlorobenzene	7.868	ND	ND	**D/NQ**	D/NQ
2-Nitrophenol	8.822	ND	ND	ND	D/NQ
2,4-Dimethylphenol	8.881	ND	ND	ND	D/NQ
Naphthalene	9.244	**D/NQ**	ND	ND	D/NQ
4-Chloroaniline	9.341	ND	ND	ND	D/NQ
2,4,6-Trichlorophenol	10.388	ND	ND	ND	D/NQ
2,4,5-Trichlorophenol	10.469	ND	ND	ND	D/NQ
2,4-Dichlorophenol	10.982	ND	ND	ND	D/NQ
Pentachlorophenol	12.915	ND	ND	ND	D/NQ

ND = not detected; D/NQ = detected but not quantifiable

The results signify absolute absorption (100%) of the organic contaminants with all α- , β-, and γ-CDHDI polymers. However detailed analysis of the results indicate that naphthalene (T_R = 9.244 min) was detected with α-CDHDI polymer. 1,3-dichlorobenzene (T_R = 7.868) was detected with γ-CDHDI polymers. The pollutants could not be quantified. This observation could not be accounted since the results prove to be an outlier in comparison to the overall performance of the polymers in this study. The observation with the α-CDHDI is suspected to be caused by the fact that naphthalene is a larger molecule and this could have hindered its absorption into the host molecule. The results obtained are very different from those obtained with GAC in a sense that all the pollutants were detected after treatment of the same water sample with GAC.

None of the pollutants were detected after treating the water samples with TDI linked α-, β-, and γ-CD polymers. Naphthalene was detected with α-CDTDI. The pollutants were yet again detected with GAC. Nonetheless 2-nitrophenol, 2,4,5-trichlorophenol and 2,4,6,-trichlophenol were not detected. This unforeseen observation however, does not overrule the performance of GAC as observed in this study.

The absorption experiments were repeated to study the performance of TDI linked CD polymers. A 20 µg/L standard solution was treated with toluene diisocyanate (TDI) linked α-, β-, and γ-CD polymers and GAC respectively (**Table 6.9**).

Table 6.9: Results obtained after treating a 20µg/L standard solution with TDI linked CD polymers and GAC.

Compound	Ret. Time (min)	α-CDTDI	β-CDTDI	γ-CDTDI	GAC
Phenol	7.747	ND	ND	ND	D/NQ
2-Chlorophenol	7.792	ND	ND	ND	D/NQ
1,3-Dichlorobenzene	7.868	ND	ND	ND	D/NQ
2-Nitrophenol	8.822	ND	ND	ND	**ND**
2,4-Dimethylphenol	8.881	ND	ND	ND	D/NQ
Naphthalene	9.244	**D/NQ**	ND	ND	D/NQ
4-Chloroaniline	9.341	ND	ND	ND	D/NQ
2,4,6-Trichlorophenol	10.388	ND	ND	ND	**ND**
2,4,5-Trichlorophenol	10.469	ND	ND	ND	**ND**
2,4-Dichlorophenol	10.982	ND	ND	ND	D/NQ
Pentachlorophenol	12.915	ND	ND	ND	D/NQ

ND = not detected; D/NQ = detected but not quantifiable

The results in **Tables 6.8** and **Table 6.9** indicate that both the HDI and TDI linked α-, β-, and γ-CD polymers were all effective at removing the organic contaminants at µg/L levels. However, after treating the same water sample with granular activated charcoal (GAC), the compounds could still be detected but could not be quantified. This indicates that the compounds were still present but at concentrations lower than the detection limit of the GC/MS instrument.

Chromatographs obtained from the extracted samples after treating with GAC gave rise to additional peaks which were previously not observed. This could be caused by the quality of activated carbon that was used in this study. The activated carbon used had characteristic ash which is suspected to have washed into the treated sample during the treatment process.

Table 6.10 shows the organic pollutants detected after extraction of real water samples obtained from the Rietvlei River. The water samples were extracted using ENVI C18-octadecyl SPE cartridges that contained 500mg of sorbent. The cartridges were conditioned using methanol and deionized water. Care was taken

to keep them wet while conditioning and loading the samples. 500mL of the real water samples was extracted using 2mL of DCM followed by 2mL of EtOAc.

Table 6.10: Organic pollutants detected from the Rietvlei River water samples.

Organic Pollutant	Rietvlei 1	Rietvlei 2
Phenol **(94m/z)**	ND	ND
2-Chlorophenol **(128m/z)**	ND	ND
1,3-Dichlorobenzene **(147m/z)**	ND	ND
2-Nitrophenol **(139m/z)**	ND	ND
2,4-Dimethylphenol **(122m/z)**	ND	ND
Naphthalene **(128m/z)**	**D/NQ**	**D/NQ**
4-Chloroaniline **(127m/z)**	ND	ND
2,4,6-Trichlorophenol **(198m/z)**	ND	ND
2,4,5-Trichlorophenol **(198m/z)**	ND	ND
2,4-Dichlorophenol **(163m/z)**	ND	**D/NQ**
Pentachlorophenol **(266m/z)**	**D/NQ**	**D/NQ**

ND = not detected; D/NQ = detected but not quantifiable

The compounds detected from the Rietvlei samples were naphthalene, 2,4-dichlorophenol and pentachlorophenol. These were not quantifiable since they were present at very low concentrations that were below the detection limit of the GC/MS. Albeit most of the contaminants were not detected, the treatment process was carried out for these water samples. Each of the samples was treated using HDI and TDI β- and γ-CD polymers. The effects of these are given in **Table 6.11**.

Table 6.11: Results obtained after treatment of Rietvlei samples with HDI and TDI linked CD polymers.

Organic Pollutant	Rietvlei 1	Rietvlei 2
Phenol **(94m/z)**	ND	ND
2-Chlorophenol **(128m/z)**	ND	ND
1,3-Dichlorobenzene **(147m/z)**	ND	ND
2-Nitrophenol **(139m/z)**	ND	ND
2,4-Dimethylphenol **(122m/z)**	ND	ND
Naphthalene **(128m/z)**	ND	ND
4-Chloroaniline **(127m/z)**	ND	ND
2,4,6-Trichlorophenol **(198m/z)**	ND	ND
2,4,5-Trichlorophenol **(198m/z)**	ND	ND
2,4-Dichlorophenol **(163m/z)**	ND	ND
Pentachlorophenol **(266m/z)**	ND	ND

The results obtained as shown by **Table 6.11** indicate that the compounds that were detected in the water samples: naphthalene (T_R = 9.244; 128m/z) 2,4-Dichlorophenol (T_R = 10.982; 163m/z) and pentachlorophenol (T_R = 12.915; 266m/z) could not be detected after treatment of the water samples. This, in association with the results obtained with the prepared water samples shown in **Tables 6.8** and **6.9**, proves that the β and γ-CD polymers are more effective than the α-CD polymer.

6.6 Regenerability studies of CD polymers

Studies on the regenerability of the CD polymers were performed using mini columns similar to those used for extraction. Studies were performed using β-CDHDI polymers. The goal was to observe how effective the polymers would be in removing the organic contaminants after a number of cycles of use. Repetitive absorption experiments were carried out using the same polymer. Studies were initially performed by flushing 500mL from a 5 litre of 10mg/L of standard pentachlorophenol water sample through a column packed with 0.5g of polymer. The recyclability was also investigated under much lower concentrations using a 10µg/L standard water sample that was prepared in a 5 litre volumetric flask. This was done to observe the ability of the polymers to remove the organic

contaminants at parts per billion levels after recycling. Experiments were performed to the twentieth cycle. **Figure 6.7** shows a graphical representation if the results obtained.

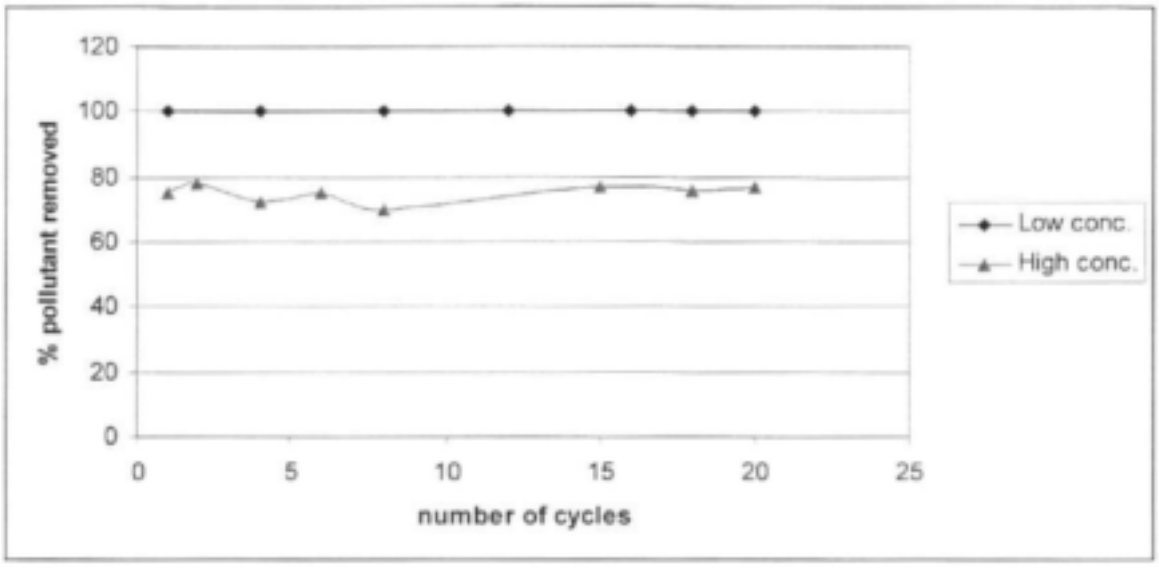


Figure 6.7: The amount of organic pollutant removed after treating 10 mg/L and 10μg/L sample with β-CDHDI polymer.

The polymer was recycled 20 times and relatively consistent absorption efficiency was observed up to the twentieth cycle. The polymer was washed with 10 mL of ethanol to remove the absorbed organic contaminants from the CD cavities. It was then dried before running the next experiment. In the first run, 75% of the 10 mg/L sample was absorbed. Better absorption of 78% was observed in the second experiment and 70% was absorbed in the eighth run. The fifteenth, eighteenth and twentieth runs showed absorption capacities of 77%, 76% and 77% respectively.

Absolute absorption of organic contaminant was obtained after treatment of the 10 μg/L contaminated water sample with the recycled polymer. The experiment was done similarly to the first study and as anticipated, a 100% absorption capacity was observed for each run that was quantified.

6.7 Breakthrough studies of CD polymers

Several tests can be performed to study the breakthrough of a particular technology. However not all tests can be ideal for different technologies. In this

study a simple process that best befits the technology under investigation was implemented. The results obtained during regenerability studies were used to study the breakthrough. No breakthrough of the polymers was achieved even though the polymer had been used twenty times. This was observed for different feed concentrations that were flushed through the polymers.

6.8 Iodine, phenol and methylene blue numbers of CD polymers

The procedures used for the determination of the iodine number, phenol number and methylene blue number of the CD polymers are as described in **Section 5.7**. The procedures were generally designed for the assessment of activated carbon. The CD polymers used in each of these tests was first ground to a fine powder and applied as it was.

The absorption capacity of CD polymers for iodine number was determined and the results are displayed in **Table 6.12**. The evaluation of the CD polymers compared to granular activated charcoal (GAC) was successfully done.

Table 6.12: Iodine numbers for CD polymers and GAC

Sample	Iodine Number
β-CDHDI	541
β-CDTDI	501
GAC	608

The iodine numbers obtained for HDI and TDI linked β-CD polymers were lower than that obtained from GAC. This result only compares the absorption capacity for iodine at high concentrations. As mentioned earlier, these were only trial tests and obviously comply with our assumption that the polymers may not be highly effective at removing high concentration of pollutant. They however outclass other technologies when very low concentrations of pollutant are to be removed from water.

A similar scenario, as mentioned in the paragraph above, was encountered during the determination of the methylene blue number and phenol value. The initial concentrations were relatively high. Nonetheless comparative studies were

performed to observe how these practically compared at such concentrations. The residual methylene blue concentrations obtained after treating a standard 1200mg/L methylene blue solution with different polymers is shown in **Table 6.13.** 100mg of CD polymer was used in each experiment.

Table 6.13: Residual filtrate concentration obtained after treating 1200 mg/L Methylene blue solution.

Sample	Residual Methylene blue concentration (mg/L)
α-CDHDI	35
β-CDHDI	32
γ-CDHDI	36
α-CDHDI	39
β-CDHDI	33
γ-CDHDI	38

A considerable reduction of the initial methylene blue concentration was observed in all the experiments. The lowest residual methylene blue concentration obtained was 32 mg/L with β-CDHDI polymer and highest was 38 mg/L obtained with α-CDHDI. It was observed that the absorption of all the polymers for methylene blue is generally equivalent. The table shows the residual concentrations only. This data was reported due to the striking effect of the polymers at reducing the methylene blue concentration: 97% absorption capacity.

As described in the experimental section, the phenol test was conducted with 200 mg/L of phenol solution on β-CDHDI and β-CDTDI polymers. The percentage amount of absorbed phenol (%X) was calculated using the % residual filtrate concentration. The remaining concentrations after each experiment are shown in **Table 6.14** and **Table 6.15**.

Table 6.14: Results showing amount of polymer absorbed by 0.4 g, 0.5 g, 0.6 g, and 0.7 g of β-CDHDI polymers.

Absorbance @ 270nm	Residual Phenol mg/L	% X	Phenol Number
2.7490	173.4	13.3	48.2
2.7232	171.9	14.0	
2.7215	171.7	14.1	
2.7114	171.0	14.5	

The calculated phenol number is 48.2 as shown in the table. The absorbed phenol was relatively low as depicted by the 14% absorption. This was observed in another set of experiments as shown in **Figure 7.15**.

Table 6.15: Results showing amount of polymer absorbed by 0.4g, 0.5g, 0.6g, and 0.7g of β-CDHDI polymers.

Absorbance @ 270nm	Residual Phenol mg/L	% X	Phenol Number
2.7601	174.1	12.9	59.2
2.6808	172.5	13.7	
2.7345	172.0	14.0	
2.7350	169.1	15.4	

The results obtained show that the amount absorbed by each of the different polymer weights was between 13% and 15%. The calculated phenol value from the obtained data was **59.2.** This clearly indicates a low absorption capacity of these polymers at high phenol concentrations. As a result, concentration of the phenol test solution was reduced to 1 mg/L and the process was repeated using the same procedure. In this experiment; 0.3 g, 0.4 g, 0.5 g, and 0.6 g of β-CDHDI polymers were used to treat a phenol test solution of 1 mg/L.

The residual phenol concentrations were calculated from a phenol calibration curve. The results obtained indicate 100% absorption of the phenol. As a result a plot of the amount of pollutant absorbed (%X) against polymer dosage (M) could not be attained as required for the determination of the phenol number at X = 90%. The result could only testify the absolute effectiveness of the CD polymers when removing much lower concentrations of organic contaminants from water.

6.9. TOC and UV analysis of humic acids

Preliminary investigations on the absorption of HA were carried out using the column setup as described in the experimental section. As mentioned before, the TOC parameter was used as a measure of DBP precursor as proposed by the United States Environmental Protection Agency (USEPA).

The recovery ability of the instrument was generally found to be good and that high standard deviations were obtained if TOC values were outside the selected range of TOC measurements. Standard KHP and HA samples were used to study the percentage recovery (% R) of these compounds. **Table 6.16** shows the results obtained for each of the standard samples. Samples were run in triplicate and the average result was taken.

Table 6.16: Relative % recoveries of the HTC TOC Analyzer

Compound	1mg/L	RSD	% R	5mg/L	RSD	% R	10mg/L	RSD	%R
KHP	0.9987	0.02	99.9	4.9989	0.05	99.9	10.001	0.03	100
HA	0.8797	9.98	88	4.2292	5.98	84.6	8.4778	3.70	84.7

The TOC results obtained after treatment of the samples were unexpected. In almost all the experiments, The TOC result after the absorption process seemed to increase drastically instead of the anticipated decrease of TOC in each sample. Several factors were assumed to be causing these inverse results:

- The finest particles of the polymers were leaching into the treated water sample,
- Small traces of the solvents used the preparation of the polymer such as DMF and acetone were washing into the treated water sample.

To resolve this problem, the absorption experiment was performed on a blank sample (deionized water) in a similar way that the HA samples were treated during the absorption process. The contribution of the polymers was displayed by the high TOC value of the blank sample. This value was then subtracted from the resultant TOC results of each of the HA samples after the absorption process. The resulting TOC results before and after the process were compared and based on these we were partly able to conclude on the absorption of the HA acid samples.

The results on the TOC analysis were inconsistent; however a majority of the experiments gave positive results.

Confirmation of the results obtained from the TOC analyses was achieved by UV absorbance measurements. The UV absorbance of the prepared HA samples were taken at 254 nm. α-CDHDI, β-CDHDI and γ-CDHDI polymers (0.3 g of each) were weighed and placed in three different 250 mL Erlenmeyer flasks. To each flask 200 mL of 10 mg/L standard HA samples were carefully added and closed using a stopper. The contents of each flask were shaken using a mechanical shaker and a magnetic stirrer at a same rate of 300 rpm. Each isotherm was left to run for 30 minutes after which they were filtered using Whatman number 5 ashless filter papers. The UV absorbance of the filtrate was measured using a CARY 50 UV Spectrophotometer and the residual filtrate concentration of each sample was calculated from the calibration curve. The results obtained in each experiment are given in **Table 6.17.**

Table 6.17: UV absorbances and residual filtrate concentrations obtained after treating a 10 mg/L standard solution with different polymers.

Experiment	Polymer	Residual Filtrate Concentration (mg/L)
Experiment 1 (Co = 10 mg/L)	α-CDHDI β-CDHDI γ-CDHDI	8.9 8.9 7.8
Experiment 2 (Co = 10 mg/L)	α-CDHDI β-CDHDI γ-CDHDI	7.5 7.6 7.2

The UV results show a lesser absorption capacity for humic acids. The maximum absorption obtained was 25% with 0.3 g of polymer and 200 mL of sample. Attempts to study the absorption of the humic acid samples at lower concentrations were futile due to limitations of the detection limit of the UV

Spectrometer. Previous work within the group encountered a similar problem. As a result the work done at higher concentrations were reported.

6.10 Removal of Geosmin and 2-MIB by CD polymers

A 200 µg/L standard sample that contained geosmin and 2-MIB in DCM was obtained from Rand Water Laboratories. From this standard a 20 ng/L was prepared in a 2 L volumetric flask and used as the contaminated water sample. 500 mL of the sample was pre-concentrated to extract the geosmin and 2-MIB using a manual SPE method.

The sample was loaded onto an ENVI C-18 SPE cartridge at a flow rate of 5 mL/min. Once the entire sample had passed through the cartridge, it was allowed to dry for 30 minutes. The column was then eluted with 2 mL of DCM into GC vials. The extract was quantified using GC/MS with the GC and MS conditions described in the experimental section. The geosmin (112m/z) and 2-MIB (95m/z) peaks obtained for the 200 µg/L standard and 20 ng/L water sample are shown in **Figure 6.9** and **Figure 6.10**. Comparison of all chromatographs is reported with the same scale of the total ion count.

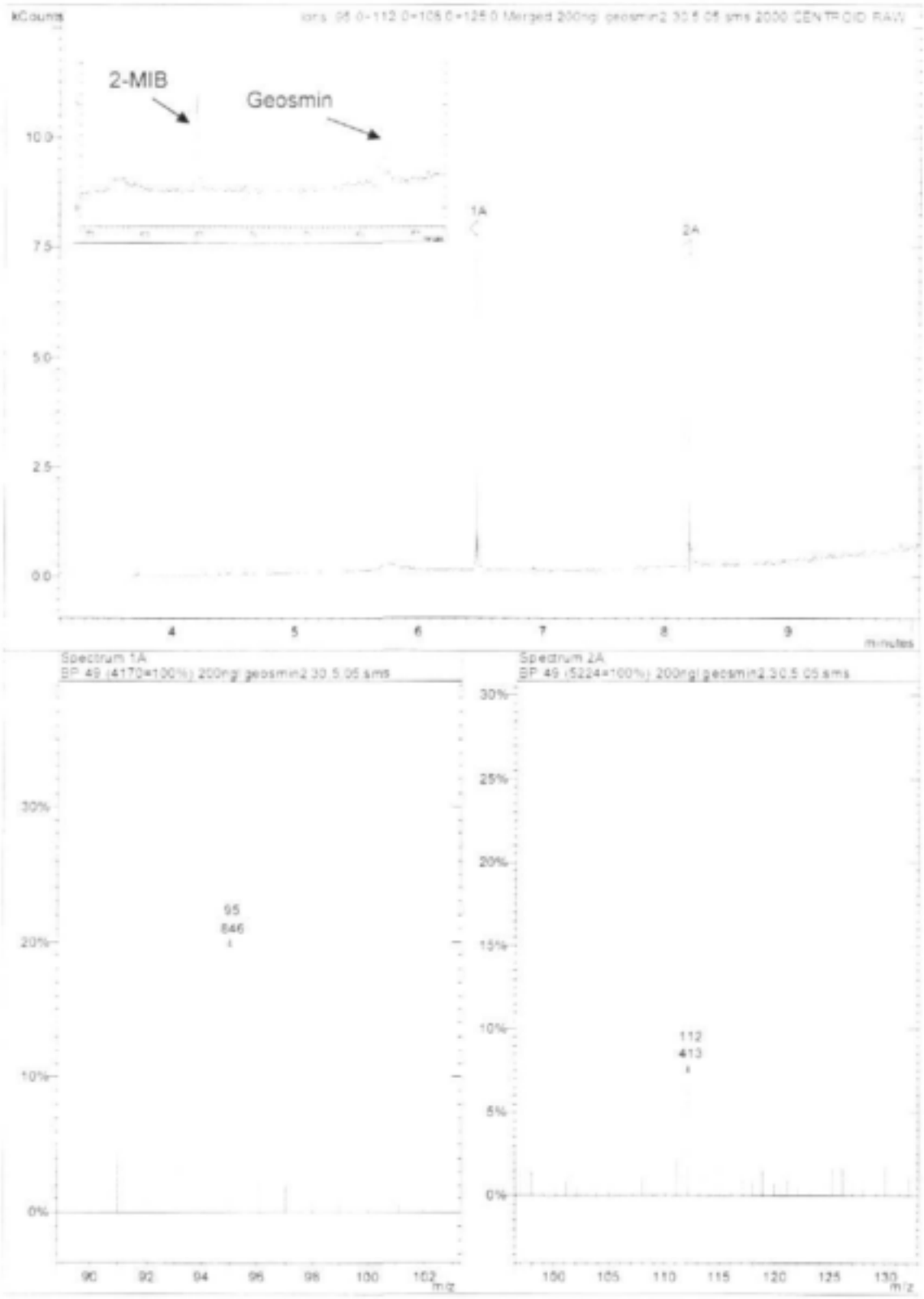


Figure 6.9: GC/MS chromatograph of 200µg/L geosmin/2-MIB standard

GC/MS chromatograph of a 200 µg/L geosmin / 2-MIB standard.

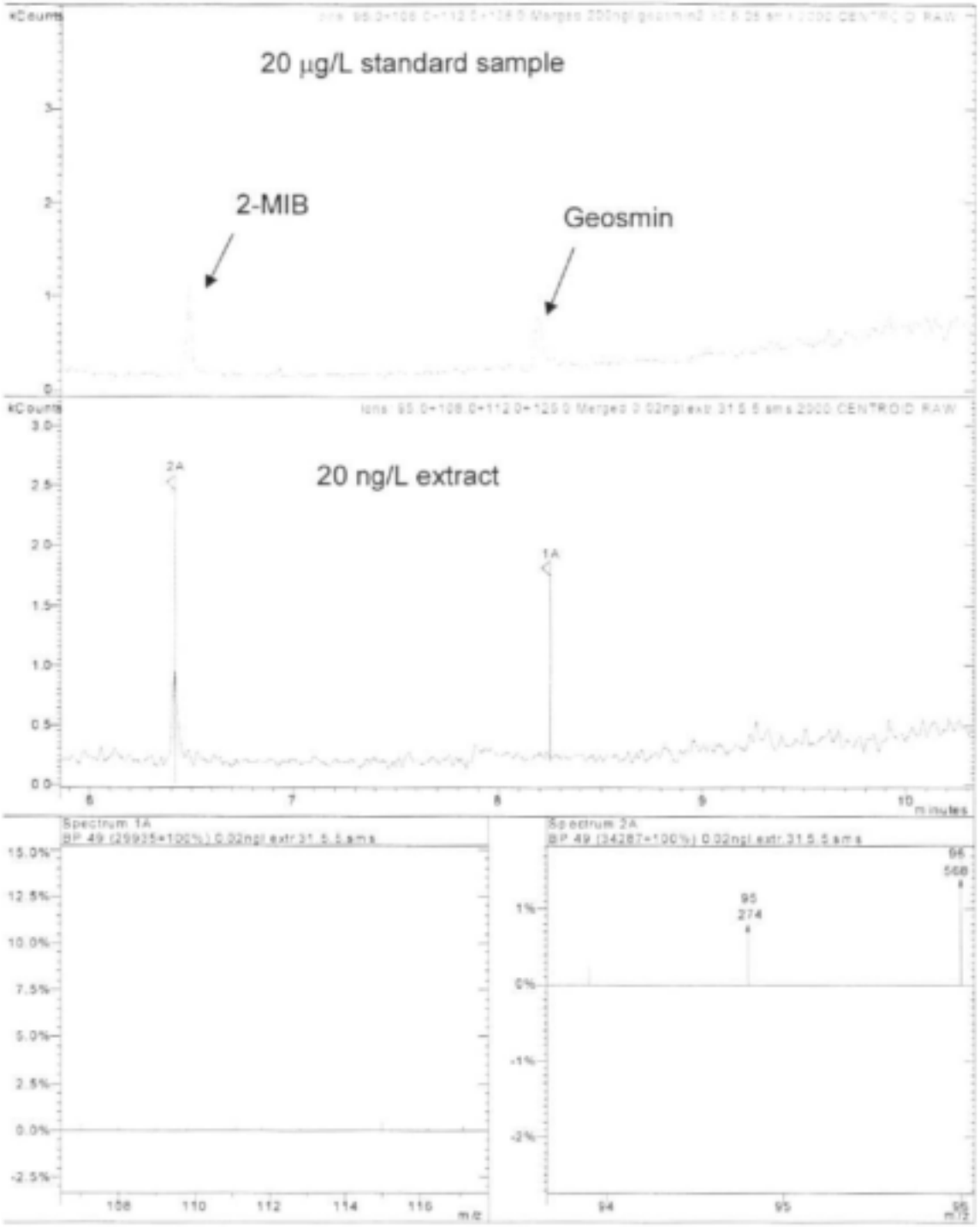


Figure 6.10: Chromatograph and spectra plots of 200 µg/l standard and 20 ng/L extracted sample.

The chromatograph in **Figure 6.10** shows that geosmin could not be detected after pre-concentration of the 20 ng/L water sample. 2-MIB could still be detected and the experiment was performed with this result. **Figure 6.11** shows the chromatograph of the treated water sample. 500mL of sample was used together with 500 mg of β-CDHDI polymer for the absorption process.

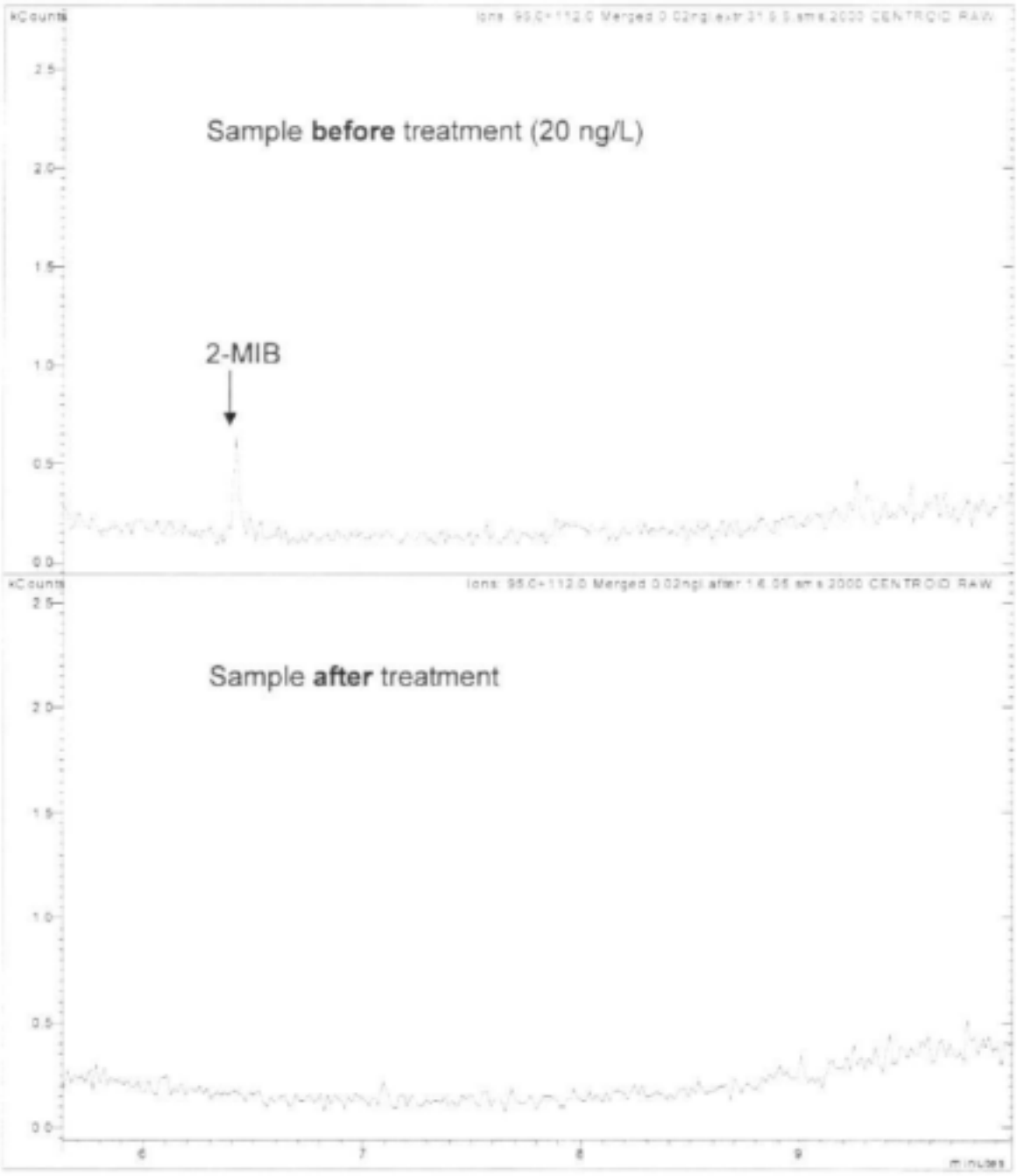


Figure 6.11: Chromatograph showing geosmin / 2-MIB results before and after absorption with β-CDHDI polymer.

The same sample was used to investigate the absorption using granular activated charcoal (GAC). The 2-MIB peak could still be detected (**Figure 6.12**). However, the compounds were not detected with the polymers.

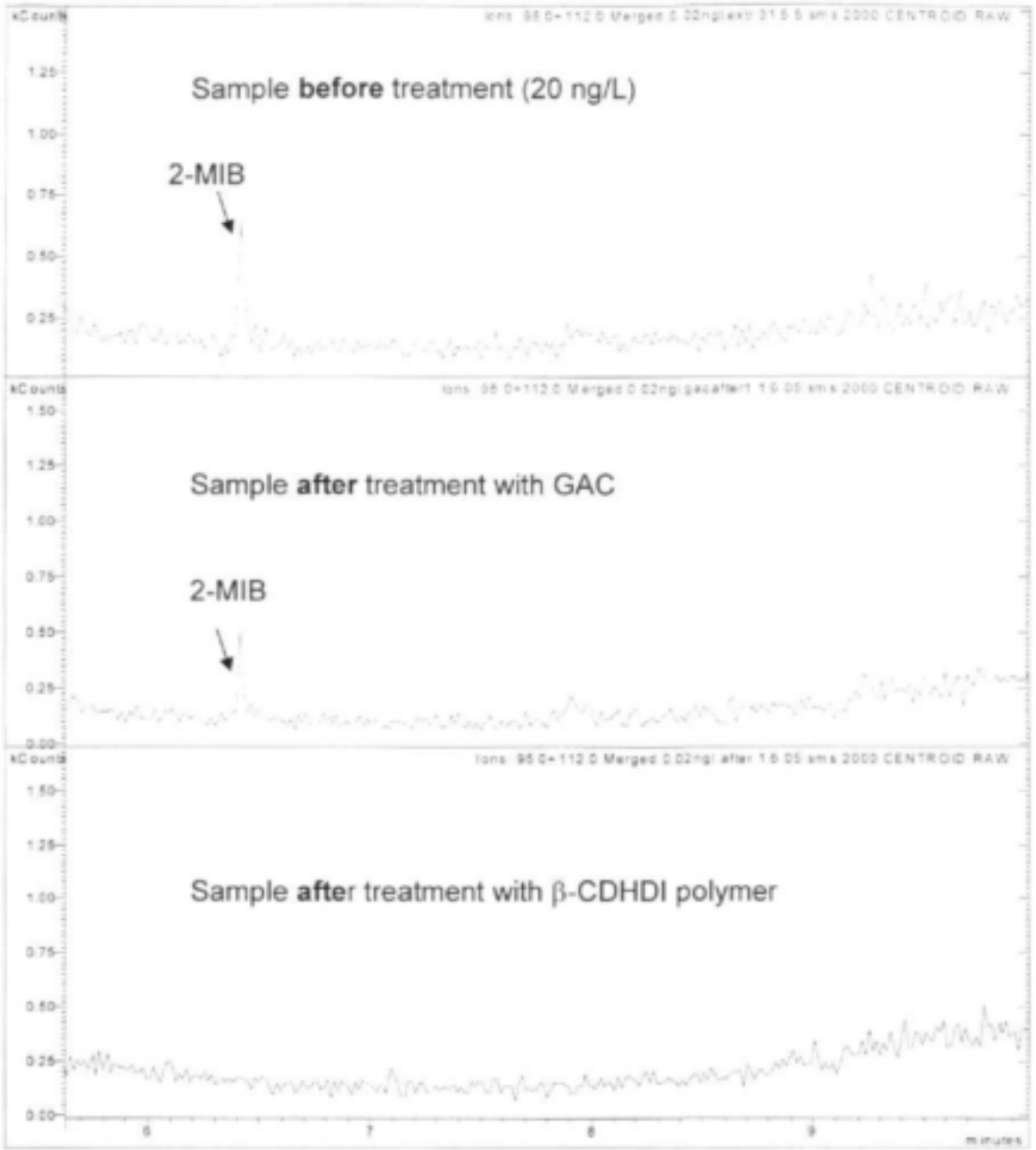


Figure 6.12: Chromatographs showing the treatment of a 20 ng/L sample (top) with GAC and β-CDHDI polymer.

Several other experiments were carried out using the same polymer which had been used in the previous experiments. After use, the polymer was washed with 10 mL of ethanol, rinsed with deionized water and dried with air. The results obtained evidently dictated that the CD polymers are more effective compared to granular activated carbon in removing 2-MIB (and geosmin) at ng/L level. All extracts were injected in triplicate or duplicate and the average of these was used. **Figure 6.13** chromatographically presents the peaks obtained in another

experiment where the polymer had been recycled together with those of fresh GAC.

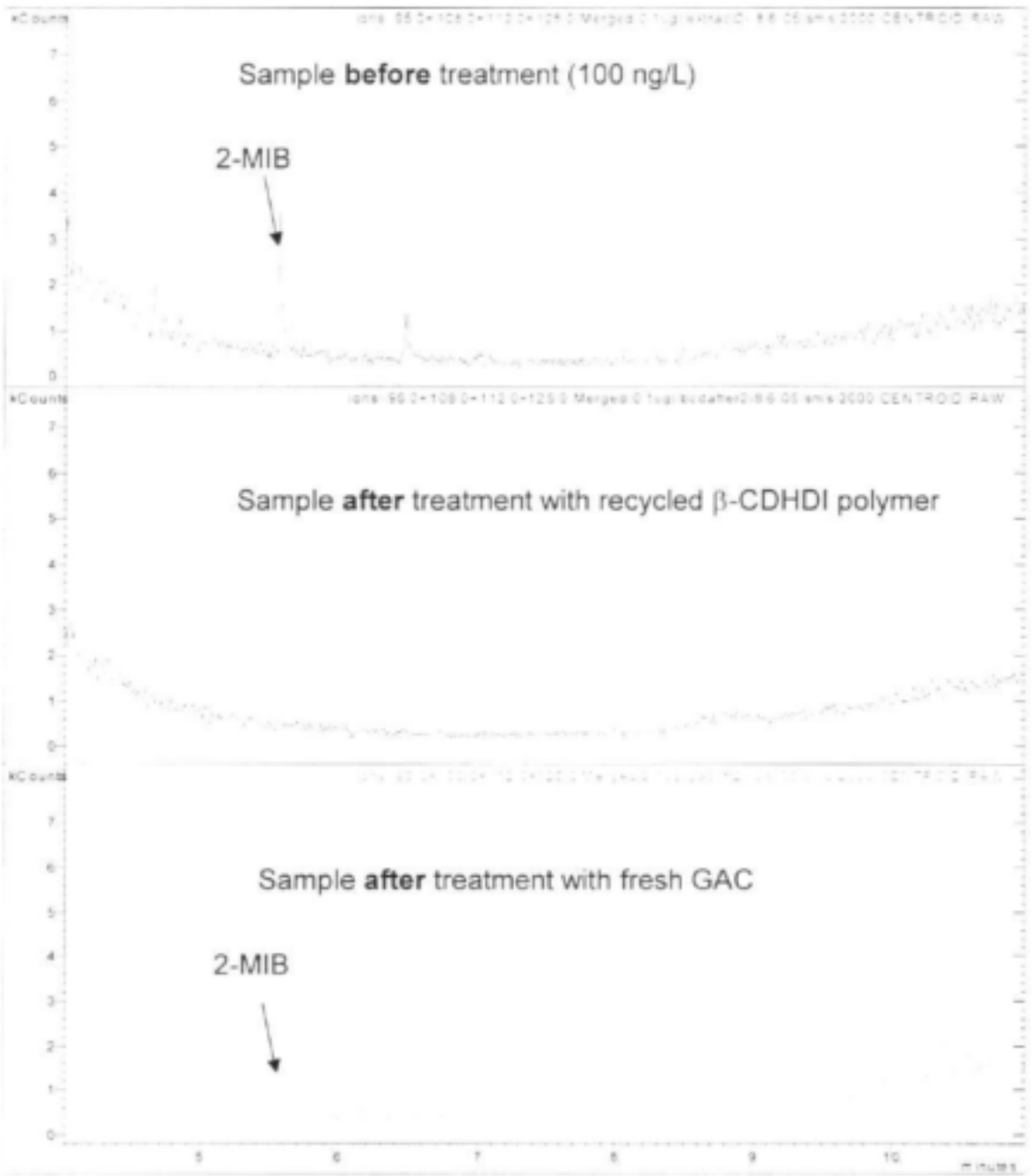


Figure 6.13: Chromatographs showing treatment of a 100 ng/L sample (top) with a recycled β-CDHDI polymer and GAC.

Besides the GC/MS analysis of the geosmin and 2-MIB samples, the absorption of these compounds was obvious from the absence of the smell in the treated samples. This was generally a simple way to confirm the results that were obtained using GC/MS. The musty odour imparted by these compounds was also detected on the used polymers. This criterion however does not tell exactly

whether the odour causing compounds were completely removed but it is reliable way of showing that the technology was effective. According to the GC/MS results, an absolute absorption of 100% was obtained after treatment of the samples with β-CDHDI polymer. However, after treatment with GAC, the compounds were detected but were not quantifiable, though peaks corresponding to 2-MIB could be observed.

6.11 Thermal stability of CD polymers

6.11.1 TGA analyses

In an attempt to study the inclusion complexes formed between the polymers and organic contaminants as well as the thermal stability of the polymers, TGA analysis was carried out. The analyses were carried out at Sasol Polymers and the University of the Witwatersrand.

Five samples were submitted to the TA laboratory at Sasol for analysis. Complexes formed with HDI linked β-CD polymers were studied. The TGA thermograms of these complexes were used to compare their thermal stability to that of the standard blank polymer. The following compounds were studied as identified on the thermograms:

1. Blank (β-CDHDI polymer)
2. 2,4,6-trichlorophenol
3. 2-chlorophenol
4. 2,4-dimethylphenol

Table 6.18 summarizes the observed % weight loss for each of the samples as well as the % residues at 500°C.

Table 6.18: 1st, 2nd, 3rd and 4th % weight loss (decomposition) steps and % residue at 500°C.

Sample	1st Weight loss step (%m/m)	2nd Weight loss step (%m/m)	3rd Weight loss step (%m/m)	4th Weight loss step (%m/m)	Residue at 500°C (%m/m)
Blank	22.58	32.66	24.06	9.659	11.04
2	42.60	3.364	28.77	16.14	9.124
3	42.78	5.971	28.17	15.32	7.768
4	27.58	37.14	23.38	-	11.91
5	5.39	49.33	28.79	-	16.50

The organic compounds appeared to have evaporated below the experimental starting temperature (50°C). As a consequence, the anticipated percentage weight loss due to evaporation of the organic compounds was very small. No concrete conclusions could be made of the formation of the complexes. However conclusions could be made on thermal stabilities of the unused and used CD polymers. **Figure 6.14** shows the TGA profiles of the samples analysed at Sasol Polymers.

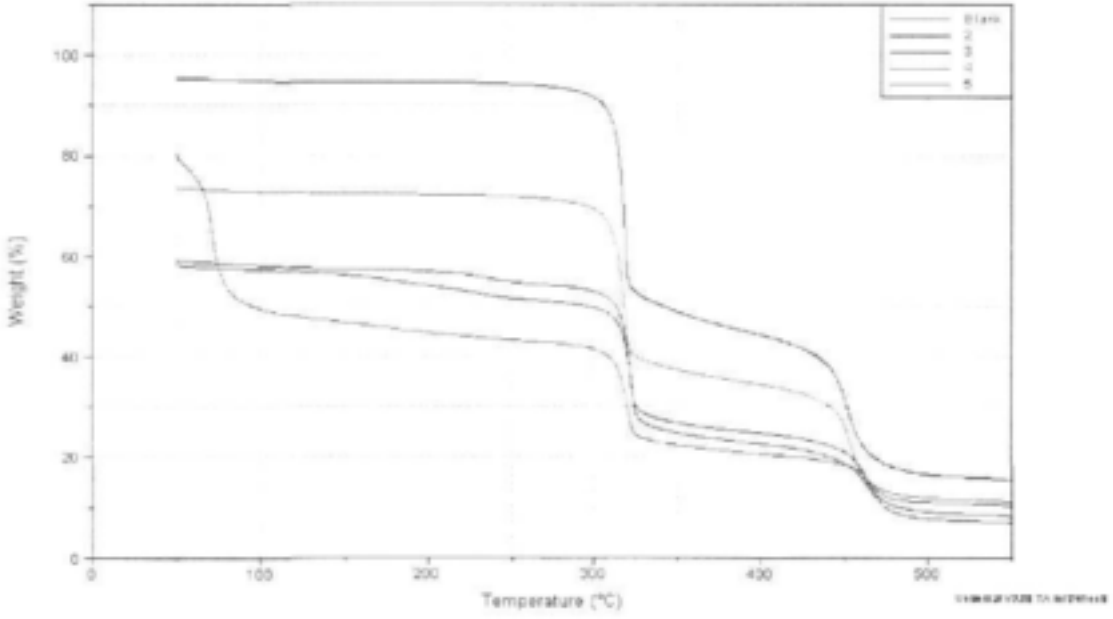


Figure 6.14: Overlay of TGA curves of a bank sample and used polymers.

Similar TGA curves were obtained with the analysis carried out at Wits and these are shown in **Figure 6.15**.

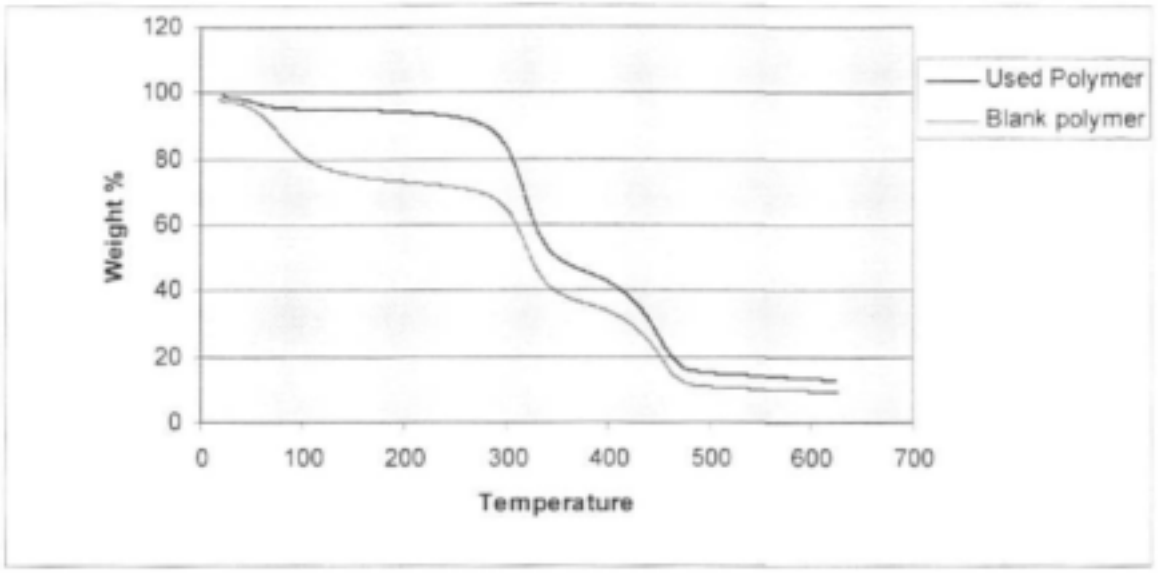


Figure 6.15: Overlay of TGA curves of a blank polymer and a used polymer.

The decomposition of the polymers occurred in a series of discrete steps. The intermediate weight % losses were stable over a limited temperature range. The polymers seemed to loose a high percentage of the weight in the 1st and 2nd steps. This was suspected to be due the moisture content as well as volatile compounds that were within the CD cavities of the samples. The third step occurring at 310°C corresponds to the melting point of the CD polymers. Overlay of selected individual thermograms with the blank are given in Appendix A2.

6.11.2 DSC analyses

DSC analysis of the CD polymers was carried out using a Mettler Toledo DSC Analyzer. The heat flows and temperatures associated with chemical transitions of the polymers were measured. It was anticipated that with knowledge of the boiling points of the specific organic compounds used to form inclusion complexes, the DSC curves should show characteristic endotherms at these particular temperatures. The polymers were heated at a constant rate of 10°C/min. Selected DSC curves are shown in the appendices. It could be inferred from the DSC curves that inclusion complexes were formed. However, the information needs to be confirmed by characterizing the complexes with other techniques to come up with concrete conclusions.

7.1 Introduction

A series of monosubstituted cyclodextrin nanoporous polymers have been synthesized and characterized. The process entails functionalizing the primary hydroxyls of the parent CD compound followed by cross linking with a suitable bifunctional linker to give the desired nanoporous polymer. This polymer is then tested for absorption of organic compounds from drinking water. The degree of absorption is quantified and measured using UV-Visible Spectroscopy and GC-MS analysis.

7.2 Experimental Methodology

7.2.1 General procedure

TLC was performed on aluminium sheets precoated with 0.25mm layer thickness silica F_{254}. TLC eluants for cyclodextrin derivatives are as follows, unless otherwise mentioned: A = 5:4:3 butanol/ethanol(95%)water, B = 7:7:5 ethyl acetate/*n*-propanol/water and C = 4:1 acetonitrile/water. TLC spots were visualized under an ultraviolet lamp (254nm and/or 365nm) or dipped in 5% H_2SO_4 in ethanol followed by heating to 350 °C on a hot plate.

Unless specified otherwise, all NMR spectra were recorded at 300 MHz on a Varian Gemini 2000 spectrometer. Proton and Carbon chemical shifts are reported in parts per million (ppm) using the residual signal DMSO (δ = 2.49 ppm for ^{1}H and 39.50 ppm for ^{13}C) or TMS (δ = 0) as the internal reference.

All of the Ultraviolet (UV) spectra were obtained from a Varian UV-Visible Carry 50 Spectrophotometer at 25.0 ± 0.1 °C. Infrared (IR) spectra were obtained from a Midac FT-IR 5000 Spectrophotometer. IR data were listed with characteristic peaks in wavenumber (cm^{-1}). Varian CP-3800 Gas Chromatography and Varian 2000 GC/MS were used for quantification of contaminants.

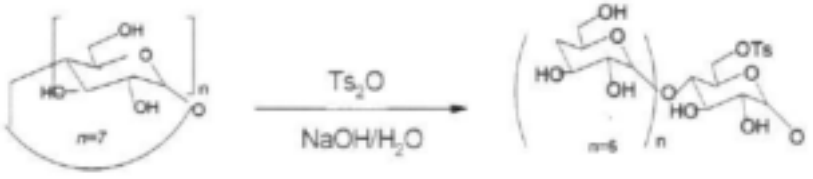
All reactions were performed under nitrogen or argon pressure with dry solvents. *N,N*-Dimethylformamide (DMF) was dried over calcium hydride for 2 days and

then distilled under reduced pressure over calcium sulphate before usage. Acetone and ethanol were stored over sodium sulphate and then distilled and kept in molecular sieves before usage. *p*-Toluenesulfonyl chloride was purified by recrystallisation from petroleum ether prior to use. Unless otherwise indicated, β-cyclodextrin and all the other reagents were utilised without further purification. All reagents and chemicals were obtained from commercial suppliers.

7.2.2 Synthetic procedures

7.2.2.1 Synthesis of mono-functionalized cyclodextrins

a). **Mono-6-tosyl β-cyclodextrin** (**2**): A suspension of β-CD (2.86g, 2.53mmol) and *p*-toluenesulphonic anhydride (1.24g, 3.80mmol, 1.5molar equivalents) in 62.5mL of distilled water was stirred under inert atmosphere for 2 hours at ambient temperature. A solution of NaOH (1.25g in 12.5mL of water) was then added. After 10 minutes unreacted Ts_2O was removed by filtration through silica gel. The filtrate was brought to pH ~ 8 by the addition of ammonium chloride (3.36g), affording **2** as a precipitate that was collected after cooling in the refrigerator overnight followed by drying under vacuum.



ß-CD
1

mono-6-tosyl ß-CD
2

Scheme 7.1

IR/KBr, cm^{-1}: 3414 (O-H), 2929 (C-H), 1654 (C=C), 1599(C-C), 1415 (SO_2, Assy.), 1157, (SO_2, Sym), 1009 (C-O); **^{1}HNMR/ppm, D6-DMSO**: 7.76 (d, H_{ar}), 7.44 (d, H_{ar}), 4.50 (s, OH(6)), 4.20 (m, H6), 4.33 (m, H6), 3.76 (d, H5), 3.29 (t, H4), 5.71 (m, OH(3)) 3.57 (t, H3) 5.71 (m, OH(2)), 3.21 (m, H2) 4.65 (d, H1), 2.42 (s, -CH_3); **^{13}C NMR/ppm, D6-DMSO**: 101.80 (C1), 79.30 (C2), 61.60 (C3), 81.00 (C4), 72.30 (C5), 68.60 (C6), 21.00 (CH3), 1.44.7 1.32.7 129.8 127.5 (C_{ar}); **Yield** = 2.25g (61%); **M.pt** = 172 - 176 °C; **TLC:** Eluant A, R_f = 0.5.

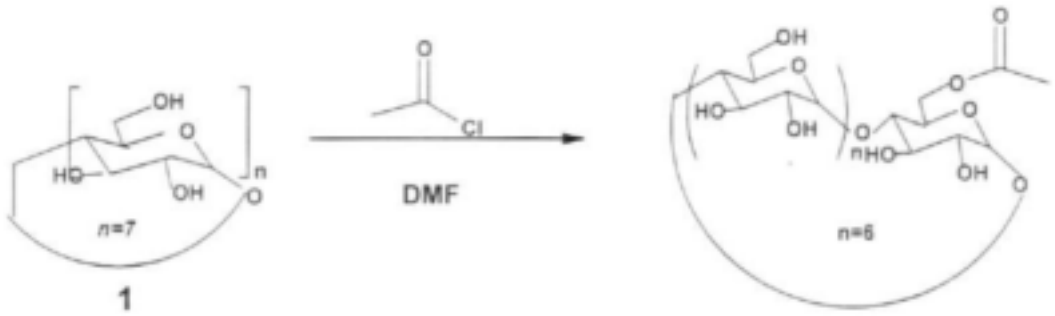
b). **Mono-6-allyl β-cyclodextrin** (**3**): β-CDOTs (1.001g, 0.881mmol) was dissolved in DMF (10mL) and allyl bromide (0.074mL, 0.881mmol) was added dropwise. The reaction mixture was stirred for 24hours at 55 °C under inert conditions. The DMF was concentrated under reduced pressure and the filtrate was added dropwise to acetone (100mL). After filtration and drying, the title compound 0.83g (75%) was isolated.

2 **3**

Scheme 7.2

IR/KBr, cm^{-1}: 3377 (O-H), 2929 (C-H), 1637 (**C=C**), 1599(C-C), 1406, 1151, 1037 (C-O), 943, 571; **^{1}HNMR/ppm, D6-DMSO**: 4.80 - 4.95 (dd, H1), 5.42 - 5.58 (m, OH2, OH3), 3.28 - 3.41 (m, H2, H4), 3.50 - 3.64 (m H5), 3.74 - 3.77 (m, H3, H6), 4.42 - 4.89 (m, OH (6)), 4.16 (dd) 4.28 (dd) 5.18 (dd) 5.27 (dd) 5.68m (Allyl). **^{13}C NMR, D6-DMSO**: 101.92 (C-1), 72.43 (C-2), 73.50 (C-3), 81.25 (C-4), 72.89 (C-5), 60.30 (C-6). **Yield**: 75%; **M.pt** = 268 - 270 °C (dec.); **TLC**: Eluant C, R_f = 0.50.

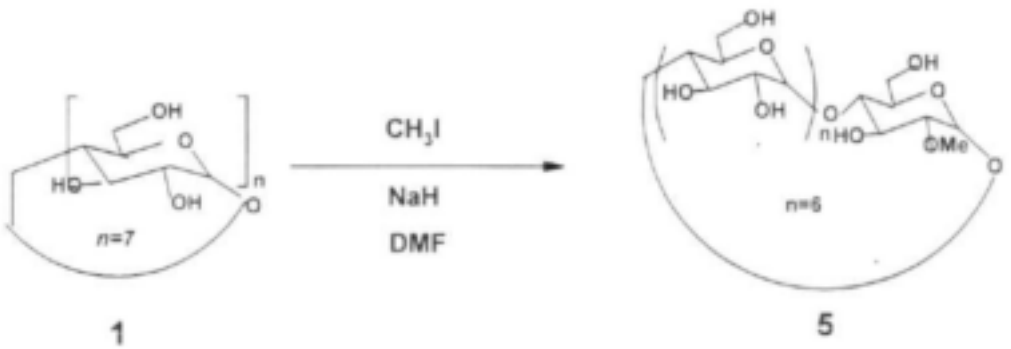
c). **Mono-6-acetyl β-cyclodextrin** (**4**): β-CD (3.005g, 2.64mmol) was dissolved in DMF (50mL) and acetyl chloride (0.19mL, 2.64mmol) was added dropwise. Diisopropylamine (0.45mL, 2.64mmol) was added dropwise to the reaction mixture which immediately changed to yellow brown. This solution was stirred for 2hours at -30 °C under a stream of argon gas. The mixture was then left to stand at RT for 14hours under a weak stream of argon. The solution was concentrated under reduced pressure to about 20mL. Methylene dichloride (200mL) was added to precipitate the CD derivative. The white precipitate formed was filtered off, washed with CH_2Cl_2 and dried in vacuum and 2.901g (76%) of the solid material was obtained.



Scheme 7.3

IR/KBr, cm^{-1}: 3384 (O-H, br), 2925 (C-H, sharp), 1651 (C=O), 1406, 1157, 1032 (C-0), sharp), 937, 750-601 (weak); **^{1}HNMR/ppm, D6-DMSO:** 4.82 - 4.4.83 (d, H1), 5.68 (s, br OH2, OH3), 3.07 - 3.20 (m, H4, H2), 3.60 -3.67 (m, H3, H5, H6), 2.49 - 2.53 (m, DMSO), 1.25 - 1.30 (s, CH3). **^{13}C NMR, D6-DMSO**: 102.00 (C-1), 72.33 (C-2), 73.50 (C-3), 81.99 (C-4), 72.90 (C-5), 59.92 (C-6), 162.2 (C=O); **Yield**: 76%; **M.pt**. = 160-164 °C (dec.); **TLC**: Eluant D, R_f = 0.76.

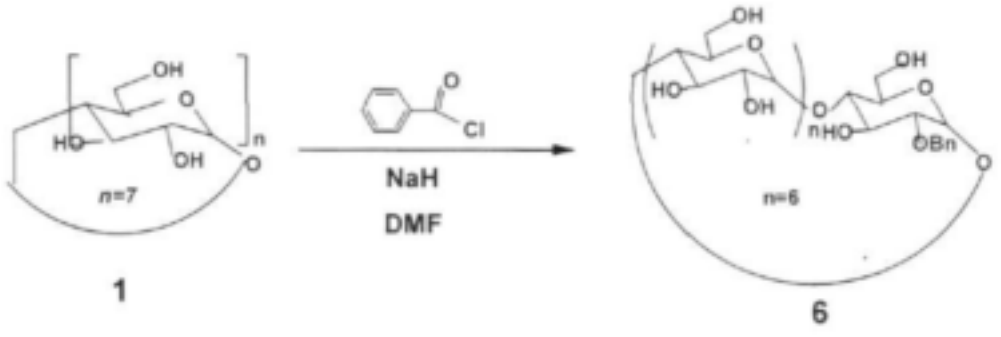
d). **Mono-2-methyl β-cyclodextrin (5):** β-CD (2.001g, 0.00176mol) was dissolved in DMF (20mL) and NaH (0.317g, 0.0176mol) was added in one portion with stirring. The reaction was left at room temperature overnight. Methyl iodide (0.16mL, 0.375g, 2.64mmol, 1.5 molar equivalents) was added to this oxyanion. The reaction was stirred for a further 24hours under argon gas. DMF was then concentrated under vacuum, followed by addition of acetone (100mL) and suction filtration. After washing with acetone and drying 1.35g (50% yield) of the title compound was obtained.



Scheme 9.4

IR/KBr, cm^{-1}: 3380(O-H), 2919(C-H), 1651 (C-C), 1406, 1157, 1032 (C-0), 937, 750-601; **^{1}H NMR, D6-DMSO**: 3.41 (H-2), 3.81 (H-4), 3.74 (H-3), 3.92 (H-5), 4.26 (OH-6) 3.90 (H-6), 4.85 (H-1), 5.68 (OH-3), 5.72 (OH-2); **^{13}C NMR, D6-DMSO**: 102.5 (C-1), 72.43 (C-2), 73.53 (C-3), 82.20 (C-4), 72.90 (C-5), 60.42 (C-6), 53.80 (CH_3); **Yield**: 50%; **M.pt** = 205-207 °C; **TLC**: Eluant A, R_f = 0.38.

e). **Mono-2-benzoyl β-cyclodextrin (6)**: β-CD (2.001g, 0.00176mol) was dissolved in DMF (20mL) and NaH (0.317g, 0.0176mol) was added in one portion with stirring. The reaction was left at room temperature overnight. Benzoyl chloride (0.20mL, 0.25g, 1.76mmol). The reaction was stirred for 24hour at room temperature under nitrogen gas. Addition of acetone (100mL) precipitated the compound which was then filtered and dried.



1 6

Scheme 7.5

IR/KBr, cm^{-1}: 3382(O-H), 2926(C-H), 1660(C=O), 1554, 1403, 1308, 1232, 1016(C-O. **^{1}H NMR, D6-DMSO**: 3.21 (H-2), 3.37 (H-4), 3.57 (H-3), 3.63 (H-5), 3.64 (H-6), 4.30 (OH-6), 4.62 (H-1), 5.48 (OH-3), 5.56 (OH-2), 7.56(d), 7.22(d) (Ar). **^{13}C NMR, D6-DMSO**: 59.91(C-6), 72.02 (C-4), 72.05 (C-3), 72.93 (C-5), 81.50 (C-4), 101.9 (C-1), 127.6, 128.0, 129.9, 145.2 (Car). **Yield**: 1.62 (63%); **M.pt** = 188 - 190 °C (dec); **TLC**: Eluant A, R_f: 0.38.

7.2.2.2 General procedure for synthesis of monosubstituted CD polymers

The mono-functionalised CD (**3**, **4**, **5** and **6**) were reacted with hexamethylene and toluene-2,4-diisocynates in a 1:8 molar ratio in DMF solution. The solution was heated at 70°C for 16–24 hours under inert conditions. Filtration and washing of

the resulting material with copious amounts of acetone to remove residual DMF led to the isolation of a solid. These were then dried overnight under high vacuum to generate the target polymers in quantitative yields.

7.2.2.3 Procedure for testing of absorption abilities the polymers with UV-Visible spectroscopy

Water samples containing known amounts of *p*-nitrophenol (PNP) and pentachlorophenol (PCP) were prepared. PNP was dissolved in water and PCP was first dissolved in 1mL of methanol before dissolved in water. Standards of the following concentrations were then prepared: 20 mg/L, 15 mg/L, 10 mg/L, 5 mg/L and 2.5 mg/L and used to plot a calibration curve. Each polymer (0.30g) was then vigorously stirred together with a 100 mL of the 15 mg/L solution. At 15mg/L the yellow colour of PNP was observed and that of PCP cannot be observed with the naked eye. The polymer which had then assumed the colour of the PNP was then filtered off and the absorbance of the filtrate was taken at the absorption wavelength λ = 410nm. A similar procedure was employed for the testing of PCP. However, an absorption wavelength of PCP (λ = 320nm) was employed. The concentration after absorption for each polymer is then computed from the equation; $y = mx + c$.

7.3 Results and Discussions

NMR spectroscopy has been widely used in the characterization of cyclodextrins and their derivatives. Therefore, NMR analysis of the unmodified β-cyclodextrin was very useful in determining whether the substituents were incorporated onto the parent CD skeleton.

The secondary hydroxyl groups of the parent β-cyclodextrin (**Figure 7.1**), at the greater rim of the CD, form intramolecular bonds in which the OH-3 group of one glucose unit is interacting with the OH-2 group of the neighbouring glucose unit.

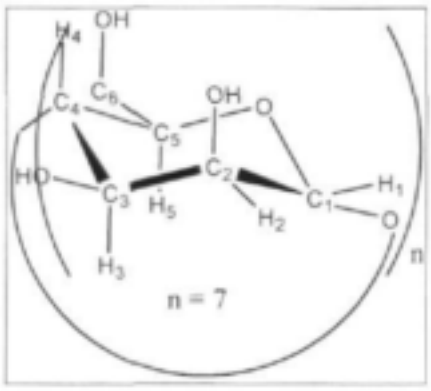


Figure 7.1: Structure of β-cyclodextrin.

This leads to a belt of hydrogen bonds around the secondary hydroxyls that give the whole molecular structure a rather rigid configuration. The primary hydroxyls placed at the smaller rim are not contributing to the intramolecular hydrogen bonding, and thus they can rotate as to partially block the cavity. Protons involved in the hydrogen bonding are much more deshielded than free protons, and therefore appear in different regions of the ^{1}H-NMR spectrum **Table 7.1** shows the chemical shifts of the C-H protons in the unsubstituted β-CD.

Table 7.1: ^{1}H NMR Chemical Shifts, δ (ppm), of C-H Protons in unsubstituted β-CDs in D6-DMSO.

Entry	H-1	H-2	OH-2	H-3	OH-3	H-4	H-5	H-6	OH-6
1	4.82	3.29	5.52	3.64	5.48	3.34	3.59	3.64	4.26

The resonances of OH-3 and OH-2 were found to appear between δ = 5.2 and 5.6 ppm (D_6-DMSO). These were clearly separated from the signals of free and more shielded OH-6 groups that appear between 4.2 and 4.4 ppm. All the other protons, except the anomeric (H-1) at 4.82 ppm, are found in the region 3.29-3.64 ppm.

^{13}C NMR chemical shifts of CDs (**Table 7.2**) extend over a larger range than proton shifts and are especially suitable and useful for identifying these starch-based compounds and their derivatives.

Table 7.2: **^{13}C NMR Chemical Shifts, δ (ppm), of C-H Protons in unsubstituted β-CDs in D6-DMSO**

Entry	C-1	C-2	C-3	C-4	C-5	C-6
1	102.42	72.43	73.53	82.20	72.90	60.42

7.3.1 Characterization of mono-functionalized β-CD derivatives

a). Characterization of the mono-tosylate and its derivatives

Mono-tosylates are generally important precursors to a variety of modified CDs because nucleophiles can attack the electrophilic carbon at the 6-position to produce the corresponding functionalized derivative. The mono-tosylation at the primary side was accomplished (61% yield) by treatment of the β-cyclodextrin with an alkaline solution of *p*-toluene sulfonic anhydride.

The structure of the mono-tosylate **2** was confirmed by ^{1}H and ^{13}C NMR spectroscopy in D6-DMSO. The ^{1}H NMR spectrum showed in the aromatic region the characteristic pattern of a tosyl system. The 6-hydroxyl substitution was also confirmed by the reduction in the integral of the peak due to the hydroxyl protons in position 6, at about δ = 4.5ppm. Furthermore, the IR spectra showed the S=O asymmetric and symmetric stretches at 1295 cm^{-1} and 1157 cm^{-1}, respectively.

Treatment of compound **2** with allyl bromide in DMF led to the formation of the allyl derivative **3**. Recrystallization in hot water afforded this compound **3** in good homogeneity. The structure of this product was satisfactorily determined by ^{1}H NMR studies. The disappearance of the tosyl group in the aromatic region of both the ^{1}H and ^{13}C NMR spectra and the appearance of a new multiplet (5.05-535 ppm) provided evidence for CD allylation. It is astounding however that the carbons of the allyl group could not be traced in the ^{13}C NMR. Further investigations on the characterization of this compound are still being concluded.

b). Characterization of other monosubstituted β-CD derivatives

As noted earlier on, the hydroxyl groups at the 2-position are more acidic than those at the 6-position. This feature is exploited by using sodium hydride (NaH) as

a strong base under anhydrous conditions to deprotonate the hydroxyl groups at position-2. Thus addition of benzoyl chloride produces the ester **6** in a 63% yield. The appearance of the aromatic signals in the region 7.56-7.40ppm (doublet) and a multiplet at about 7.20ppm representing all the protons of the ring and the successive appearance of the carbon at four different regions in the ^{13}C NMR accounted for all the carbon peaks including the quaternary carbon, confirmed successful incorporation of the benzoyl group. There is no doubt that the benzoyl group was successfully built-in to the backbone of the CD in the C2-OH. A carbonyl (C=O) peak was observed in the IR and ^{13}C NMR spectra at 1657 cm^{-1} and 162 ppm, respectively.

The acetylating experiment involved the reaction of a DMF solution of β-CD with acetyl chloride in the presence of hydrogen chloride acceptor (diisopropylamine) Yet again, it was easily concluded from the IR and NMR spectroscopy that the acetyl group was successfully incorporated onto the CD backbone. The emergence of a sharp peak (1657 cm^{-1}) and the appearance of a small signal at δ = 162ppm in the respective IR and ^{13}C NMR spectra of the target compound were assigned to the carbonyl group.

Subsequently, the addition of methyl iodide to the oxyanion yielded the methyl ether **5** at reasonably high yields (63%) under non-optimized conditions. The proton NMR chemical shifts are almost similar to those of the unmodified CD. There is, however, a slight integral change in the OH-2 of the methylated CD with comparison to the OH-6. In the ^{13}C NMR spectra there is an additional peak at δ = 53.80 ppm assigned to the methyl group. Mono-methylation of the β-CD was, therefore, successfully achieved.
All the monofunctionalized CDs were produced at satisfactory yields and were, as shown in **Table 7.3**, obtained either as white powder or solid granules.

Table 7.3: Selected properties β-CD derivatives

CD Derivative	Melting Points	Colour and form	Yield
2	172-176 °C	White fine powder	61%
3	268-270 °C	White solid	75%
4	160 -164 °C (dec.)	White fine powder	76%
5	205-207 °C	White solid material	50%
6	188-190 °C (dec)	White solid granules	63%

dec = the material was decomposing at its melting point.

7.3.2 Characterization of the functionalized CD polymers

Cyclodextrin chemistry continues to present an assortment of possibilities to produce diverse derivatives, including polymers, with different functionalities. Efficient cross-linkers convert the molecular nanocavities of parent CDs into three dimensional, nanoporous polymers. The degree of cross-linking can be fine-tuned to give either hydrophilic or hydrophobic (reject water but attract organic molecules) polymers with "molecular hosts" that can trap targeted organic compounds.

Cross linkers used in this research work have been successfully employed in the synthesis of insoluble cyclodextrin polymers from the corresponding monofunctionalized β-cyclodextrin (**Figure 7.2**). The linkers used in this work are HMDI (Hexamethylene diisocyanate) and TDI (Toluene-2,4-diisocynate).

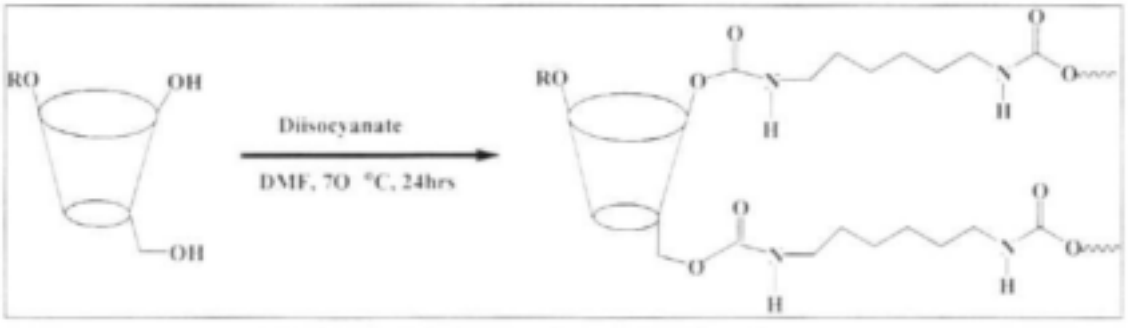


Figure 7.2: Preparation of CD polymers.

Since all the polymers formed are insoluble in water; it is impossible to do the characterization of these compounds with the NMR instruments at our disposal. Solid state NMR, however, supports the characterization of these compounds. The characterization has so far been performed by IR spectroscopy. The complete disappearance of the isocyanate peak at 2270cm^{-1} and the development of vibration bands at 3370 (N-H), C=O at 1600cm^{-1} and NH-CO groups at 1530 cm^{-1} for all these nanosponges confirmed the successful synthesis of these compounds. **Table 7.4** summarizes the yields, solubility properties and absorption capacity for PNP of the polymers that were synthesized.

Table 7.4: A summary the properties of monofunctionalized CD polymers and their absorption capacity.

CD Polymer	R Group	Bifunctional Linker	Yields obtained (%)	Solubility/ Water	*Final Conc of PNP (mg/L)
7		HMDI	~100	Insoluble	7.52
8		TDI	95	Insoluble	8.75
9	$COCH_3$	HMDI	89	Insoluble	7.73
10	$COCH_3$	TDI	89	Insoluble	8.77
11	CH_3	HMDI	~100	Insoluble	7.98
12	CH_3	TDI	~100	Insoluble	7.90
13		HMDI	95	Insoluble	12.90
14		TDI	95	Insoluble	7.80

*Initial conc OF PNP = 15 mg/L.

Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) are currently being used to study the thermal properties of these polymers. Preliminary studies indicate that they may offer improved thermal qualities compared to the polymers made from native CDs.

7.3.3 Preliminary studies on the testing of absorption abilities of the monofunctionalized nanoporous polymers

All the polymers formed thus far are insoluble in water (a very important characteristic in the removal of organic from water). An investigation of the absorption capability of these polymers is continuing. This is accomplished by modelling contamination experiments. Such experiments involve deliberately placing solid nanoporous polymers into an aqueous solution containing known concentration of organics. The degree of absorption is then quantified and measured using UV- Visible Spectroscopy and GC-MS analysis. In this part of the project only UV-visible Spectroscopy was employed in these investigations.

Preliminary results reveal that these polymers are capable of absorbing organic guest, especially *p*-nitrophenol (PNP), from water (see **Table 7.4**). A much more reliable method for detection of the contaminants involves the use of GC-MS and is in progress.

8.1 Conclusions

The project was successfully completed in accordance with the set objectives. The following conclusions were drawn from the fundamental work done and results that emanated from this project:

- Toluene-2,6-diisocyanate (TDI) and hexamethylene diisocyanate (HDI) linked α-, β- and γ-cyclodextrin polymers were successfully prepared in the laboratory giving a 100% percent yield of the product. The products were characterized mainly by infra-red spectroscopy due to the insoluble nature of the nanoporous polymers.

- Polymers with different physical properties were synthesized from the same parent cyclodextrin and a complementary linker by varying the reaction conditions. It was shown that these polymers have different affinities for organic compounds in water.

- Water samples with concentrations of contaminants as low as 10ng/L were prepared. These were pre-concentrated by solid phase extraction (SPE) or purge/trap cycles and successfully analyzed using Gas Chromatography-Mass Spectrometry (GC/MS).

- When water samples containing a high concentration of organic pollutant (concentrations of 10 mg/L) were treated, the polymers were not as effective at removing organic contaminants as granular activated carbon (GAC) at such high levels of concentration.

- The polymers were however extremely effective when lower concentrations (10 ng/L) of water samples spiked with known organic contaminants were treated. By contrast, the organic pollutants could still be detected after treating the same sample with GAC.

- The polymers were recycled and tested for durability. It was observed that the polymers could still be effective even after 20 cycles. The measure of such

effectiveness was achieved by washing the polymers with ethanol to clean their cavities.

- While the study was performed at laboratory scale, it was observed from the regeneration studies that the polymers did not reach the breakthrough stage.

- The parameters used for the determination of the iodine number, phenol value and methylene blue number for GAC were not ideal for the assessment of the CD polymers. The concentrations of solutions treated were relatively high and these had to be reduced particularly in the determination of the phenol number.

- Analyses of samples using Total Organic Carbon (TOC) method of analysis and Ultraviolet (UV) Visible Spectroscopy were successfully accomplished. Reduction in TOC and UV absorbance was observed after treatment of the water samples with CD polymers. However, only a small amount of humic acid (HA) was removed in all experiments using a 10 mg/L HA sample.

- Problems of consistency were encountered with TOC analysis especially at higher concentrations and measures to overcome these were implemented.

- The polymers were absolutely effective at removing 2-MIB (and geosmin) from water at the ng/L level. GAC on the other hand failed to remove it completely.

- The preparation of the polymers is inexpensive and simple. From 10 g of β-CD, 10 mL of HMDI linker and 150 mL of DMF, approximately 18 g of polymer material is obtained. Although the CD polymers are more expensive to produce compared activated carbon, they can be used in industries or applications where ultra pure water is an imperative.

- TGA and DSC analysis showed that the polymers are stable within a wide temperature range. The techniques were not suited for studying the inclusion complexes of such compounds due to the fact that host-guest ratios could not be ascertained given the low levels of contaminant. The possibility of inclusion

complex formation was however confirmed through the qualitative comparison of the TGA thermograms and DSC curves obtained.

- We have demonstrated a practical and a simple procedure for monofunctionalization of the hydroxyl groups of the CDs. A wide variety of monosubstituted CDs have been prepared in high yields using straightforward work-up procedures. Sulfonation, methylation, allylation, benzoylation and acetylation procedures were all carried out using efficient modification strategies. All the novel monosubstituted CDs obtained were in satisfactory yields and were characterized with IR spectroscopy and NMR techniques.

- The methods used for the polymerization reactions successfully tailored the CDs into highly cross-linked nanosponges. These nanoporous polymers have shown excellent absorption abilities when tested for *p*-nitrophenol absorption from an aqueous medium using UV-Visible spectrophotometer. We are currently in the process of testing the absorptive capabilities on low-concentrations of contaminants using GC/MS. An investigation of the effect of the substituents on the absorption properties of the resultant polymers will also be carried out.

8.2 Recommendations for future work

Several recommendations that emanated from the findings of the project are the following:

- A study that would investigate the minimum contact time required for the absorption of organic contaminants by varying the flow rates at which water is passed through the polymer may be crucial.
- A mini-scale column setup that resembles a real situation where CD polymers could be applied in conjunction or as a substitute for GAC may be designed for further studies.

- Small scale commercialization of CD polymers such as the manufacturing of small filtering gadgets may be an ideal step in the utilization of these polymers.

- Pilot studies may have to be performed to investigate how these could be effectively implemented in large scale applications such as in water treatment plants.

- The polymers may be used as the last clean up step in water treatment processes after all conventional technologies have played their role.

- Studies may be undertaken to investigate any adverse effects that the polymers could have on humans and the environment. None have been discovered so far.

- Specific applications of these polymers (such as removal of endocrine disrupting compounds, EDC's) should be conducted on real-water samples to investigate the efficacy of the polymers in the presence of interfering pollutants.

- Funding of the project may enhance further work on the applications of the polymers which, with the sharing of knowledge both from local and international sources, may see the implementation of these come into effect sooner than anticipated.

APPENDIX A

A1: GC/MS identification of selected organic compounds

Selected chromatographs and mass spectra of the investigated organic contaminants are shown in **Figure A1 – A6**. Each figure shows the characteristic peak together with the retention time as well as the ion fragments from the mass spectra. **Figure A5** is a depiction of the compounds in a megamix standard.

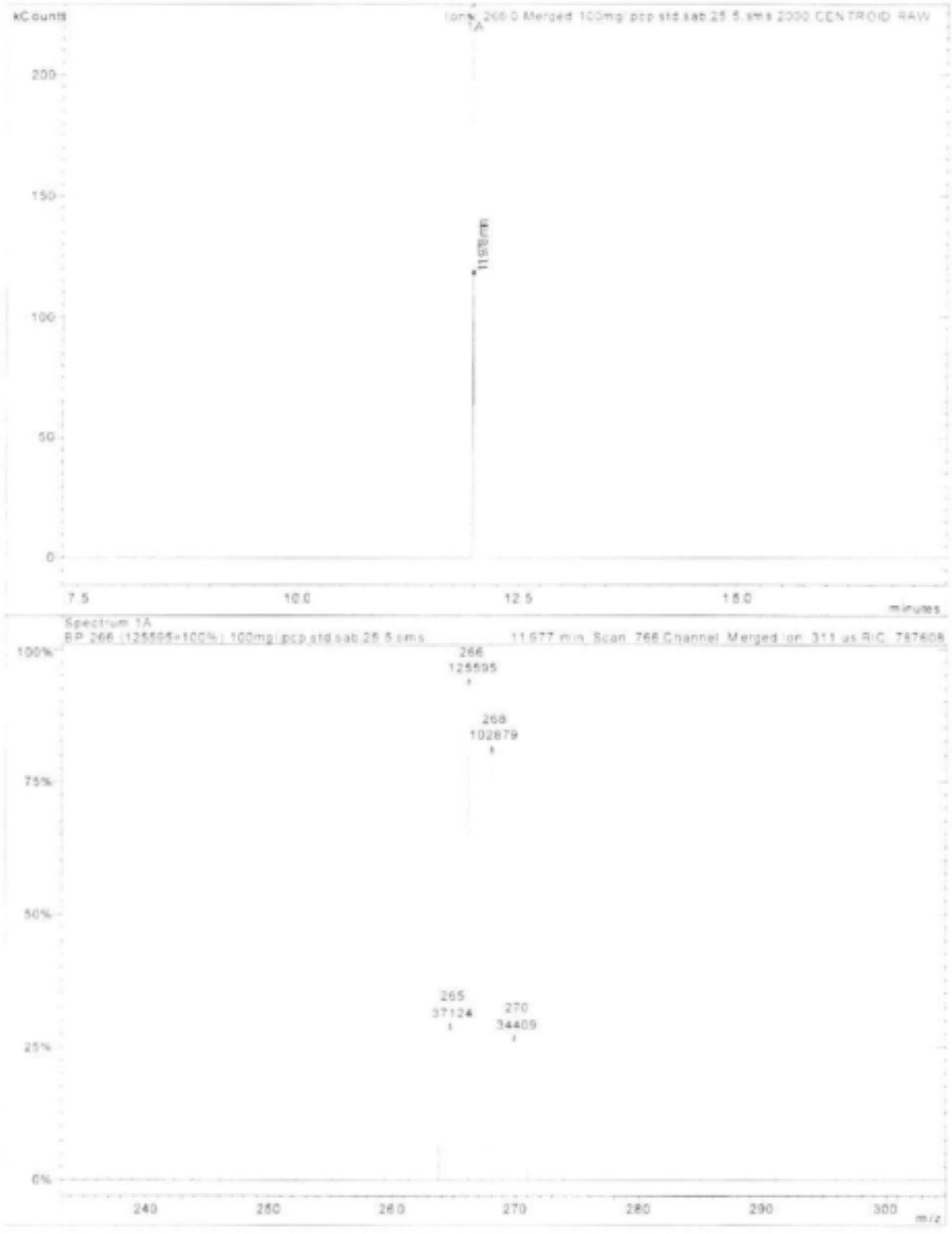


Figure A1: Pentachlorophenol

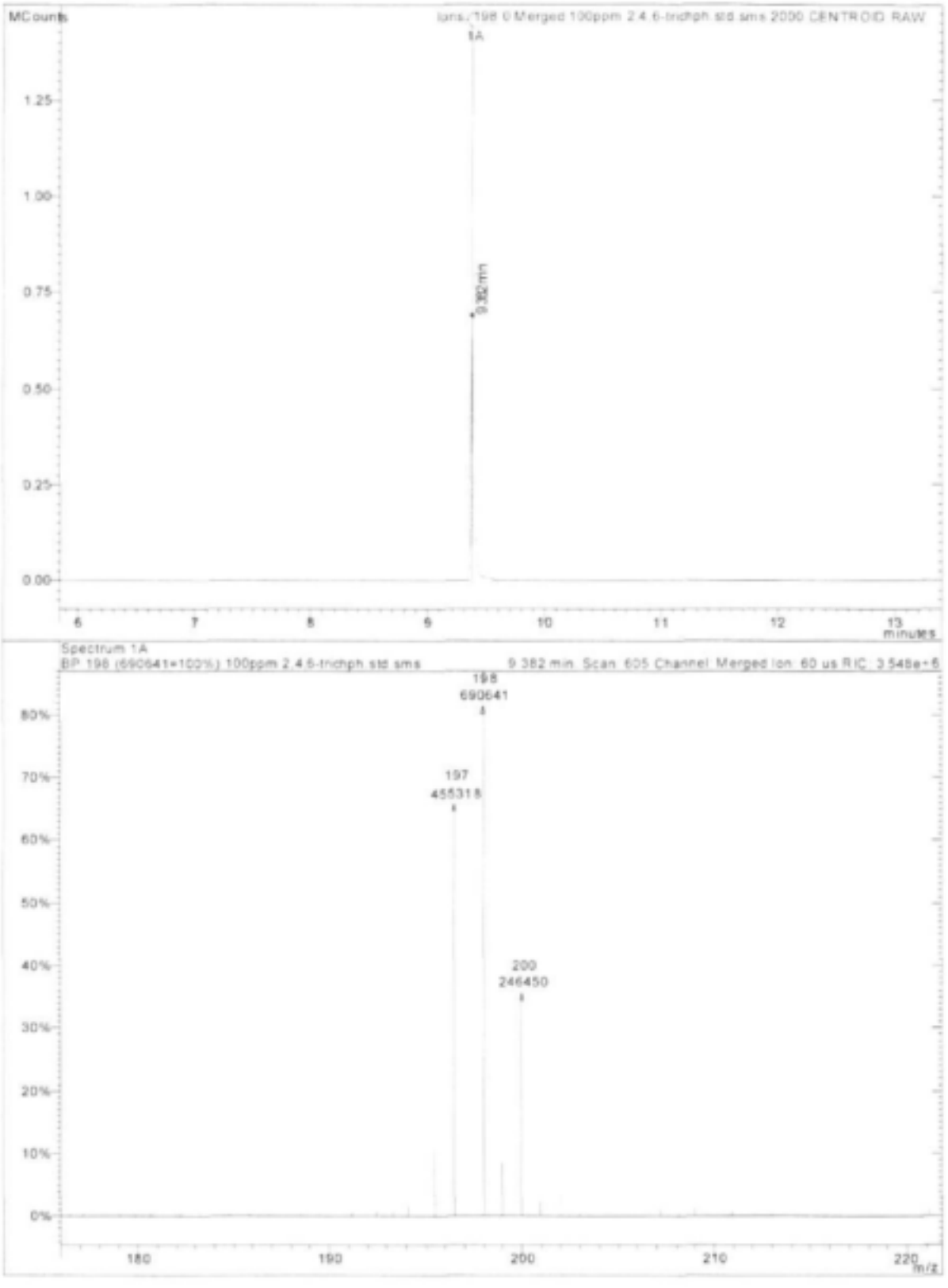


Figure A2: 2,4,6-trichlorophenol

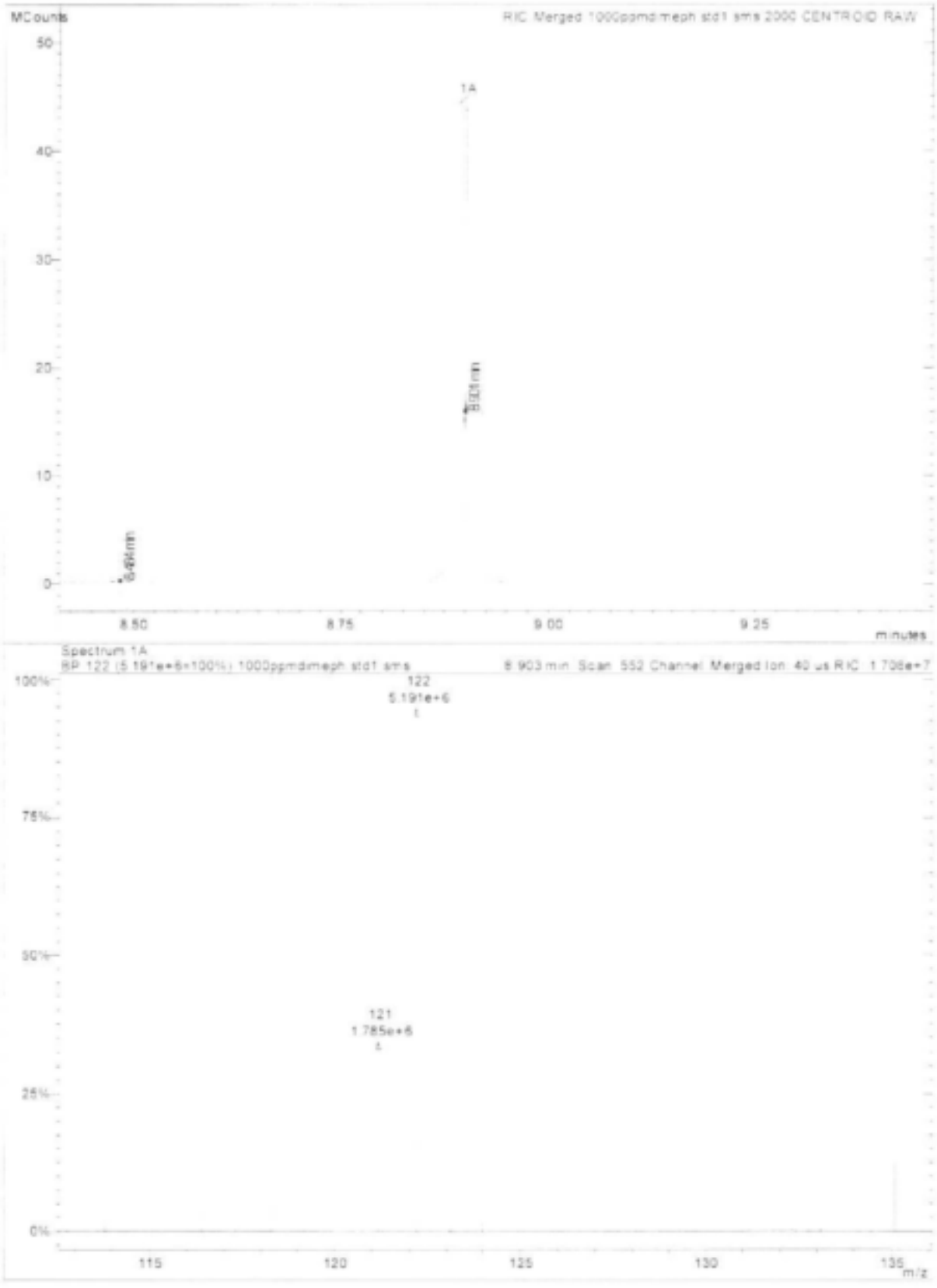


Figure A3: 2,4-dimethylphenol

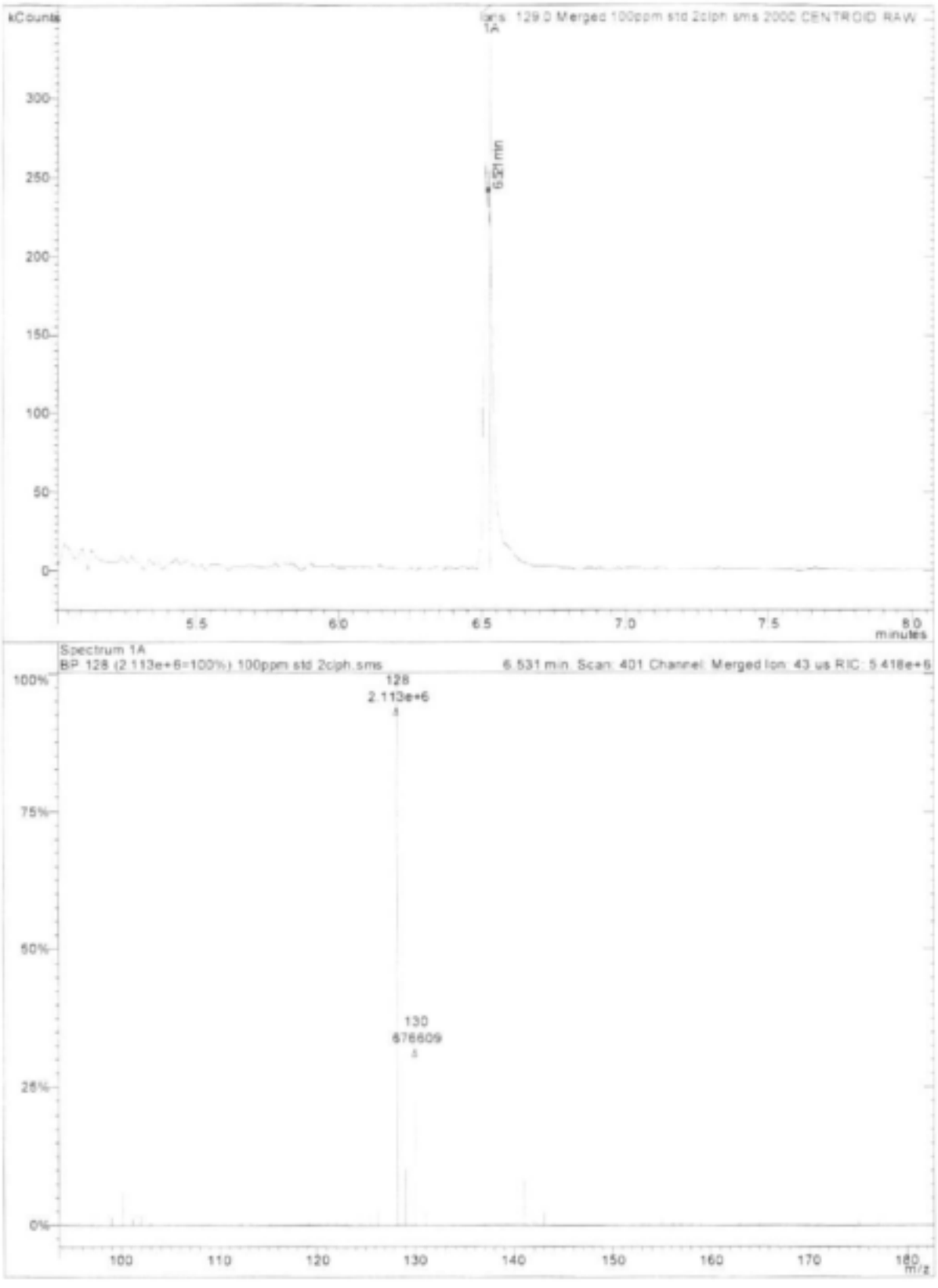


Figure A4: 2-chlorophenol

Figure A5: Standard MegaMix with 76 organic compounds

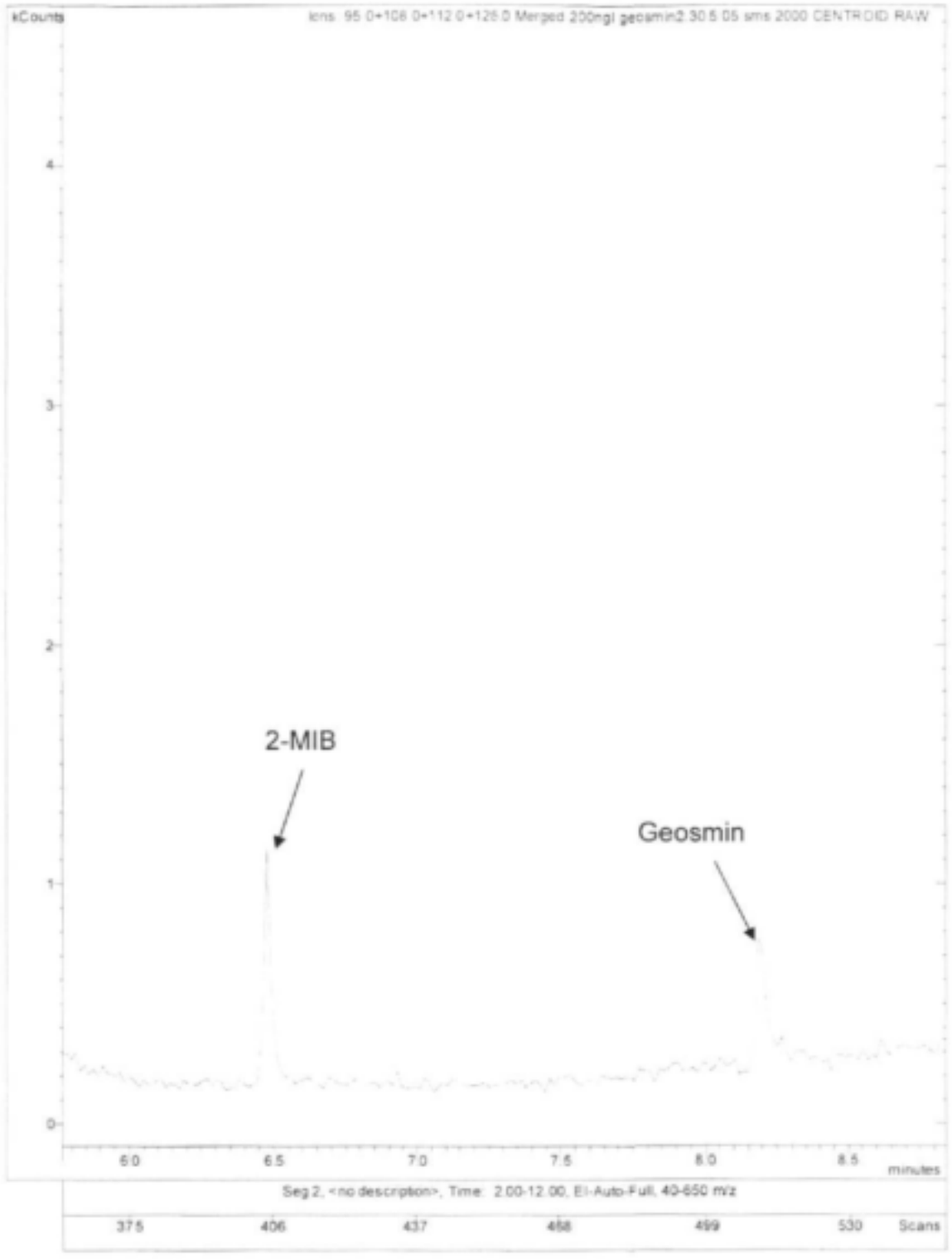


Figure A6: Geosmin and 2-MIB

A2. Selected TGA curves

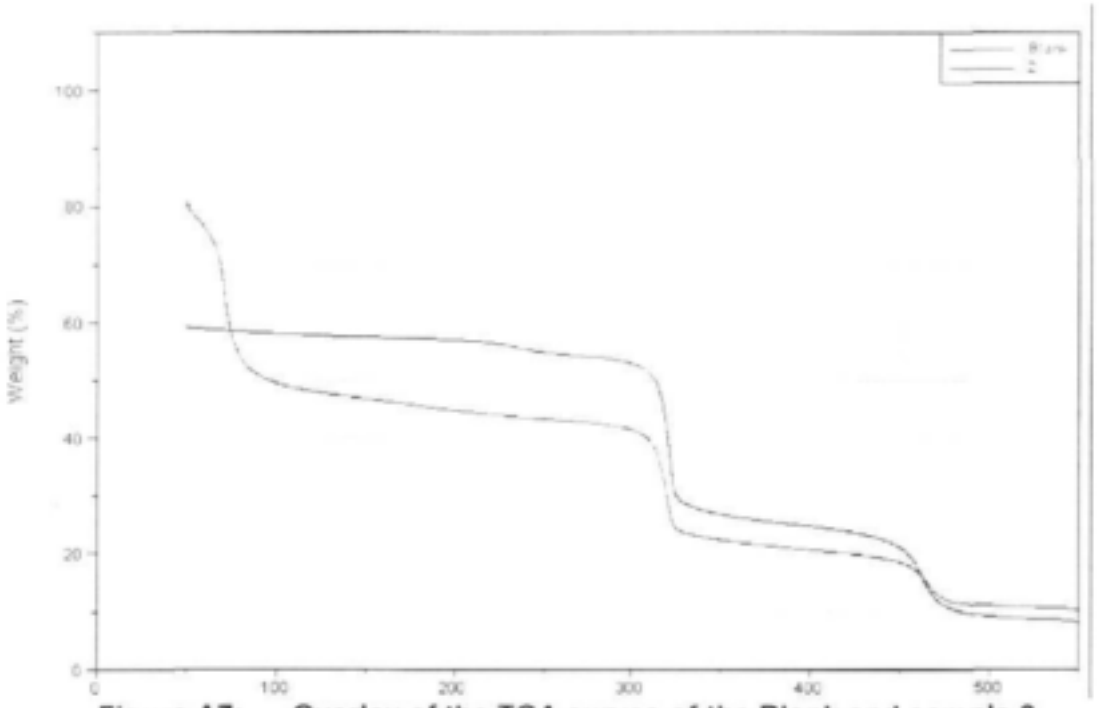


Figure A7: Overlay of the TGA curves of the Blank and sample 2

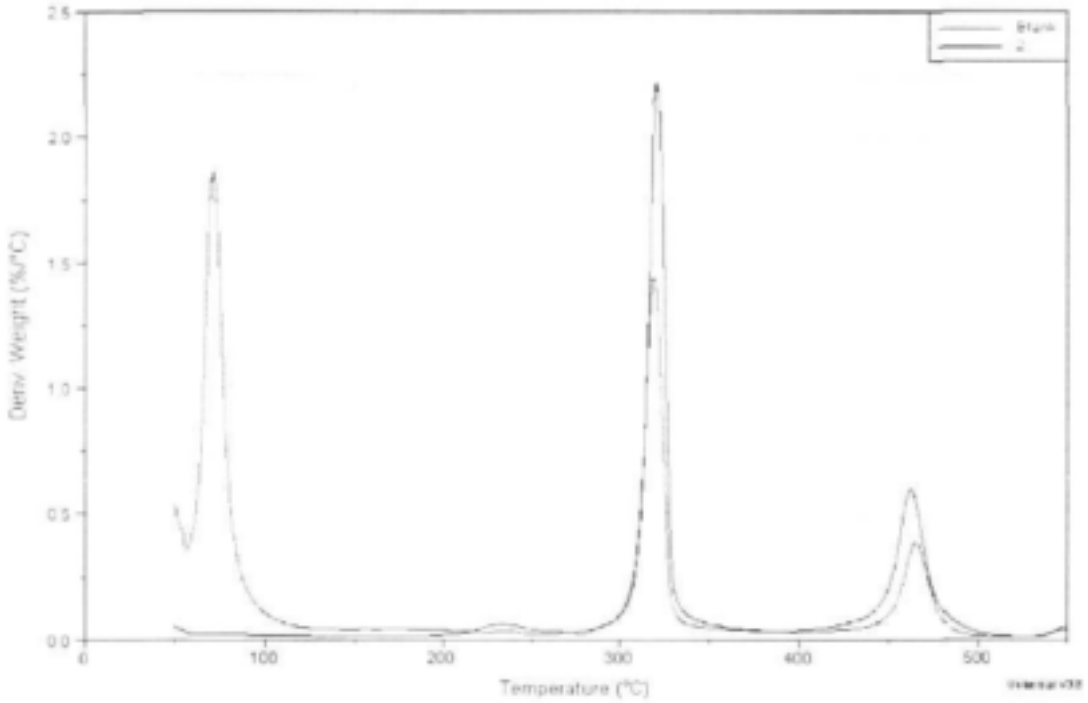


Figure A8: Overlay of the Derivative TGA curves of the Blank and sample 2

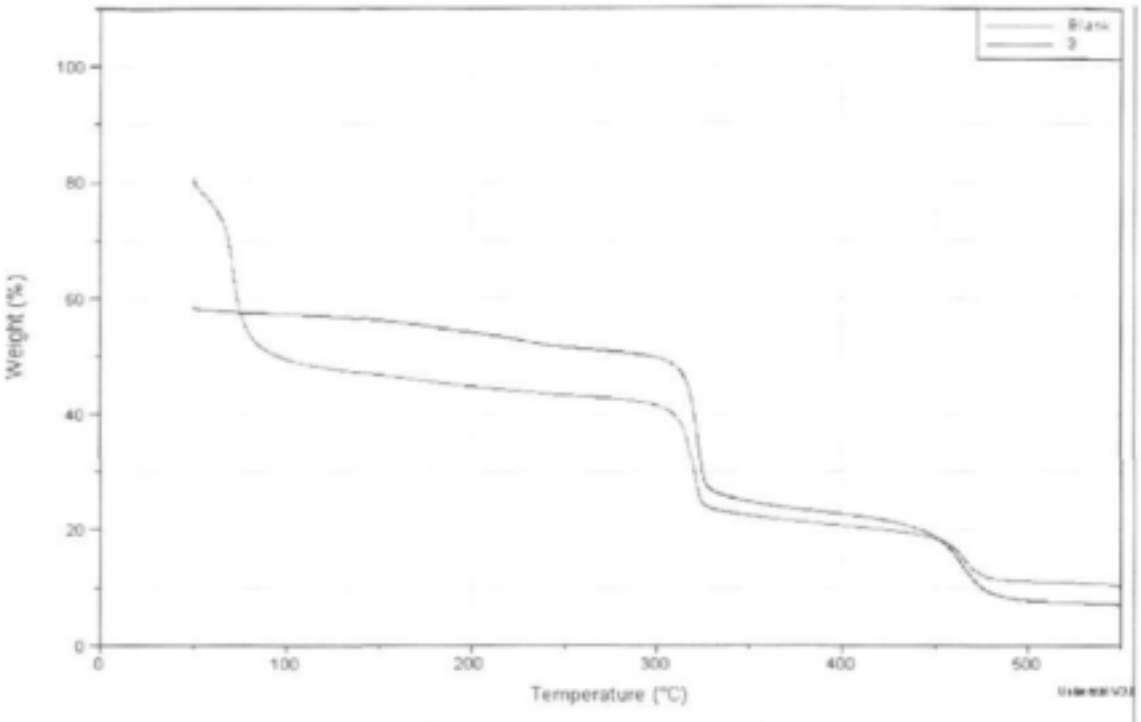


Figure A9: Overlay of the TGA curves of the Blank and sample 3

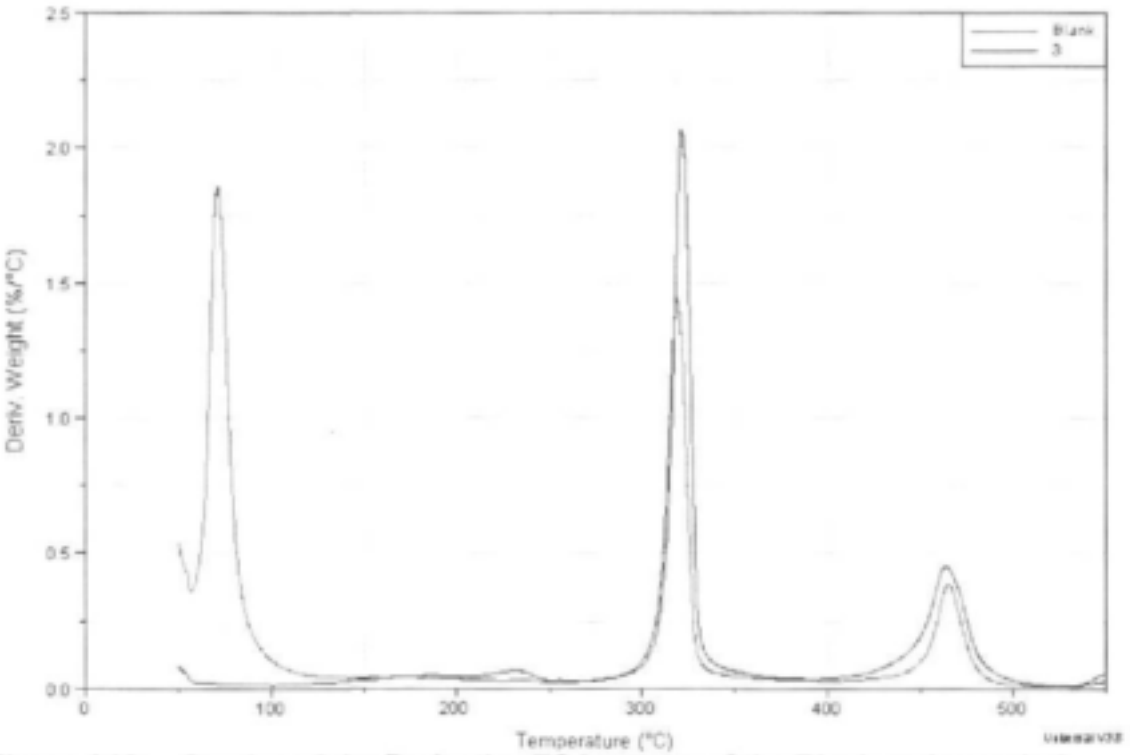


Figure A10: Overlay of the Derivative TGA curves of the Blank and sample 3

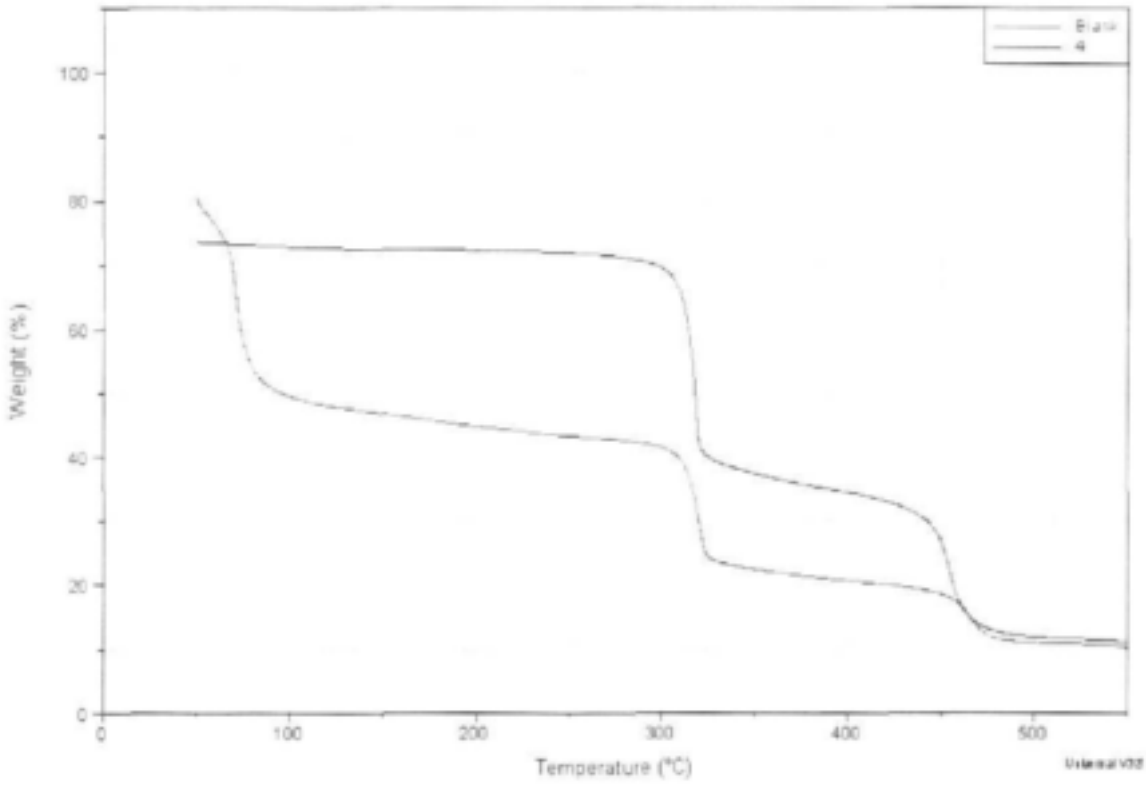


Figure A11: Overlay of the TGA curves of the Blank and sample 4

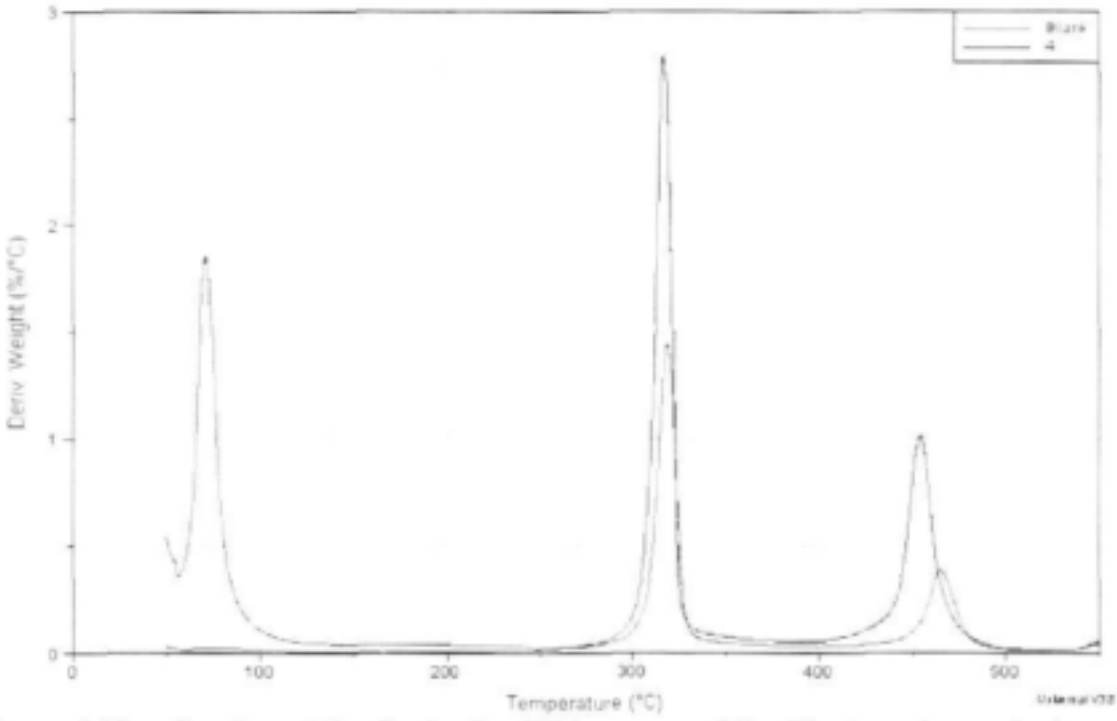


Figure A12: Overlay of the Derivative TGA curves of the Blank and sample 4

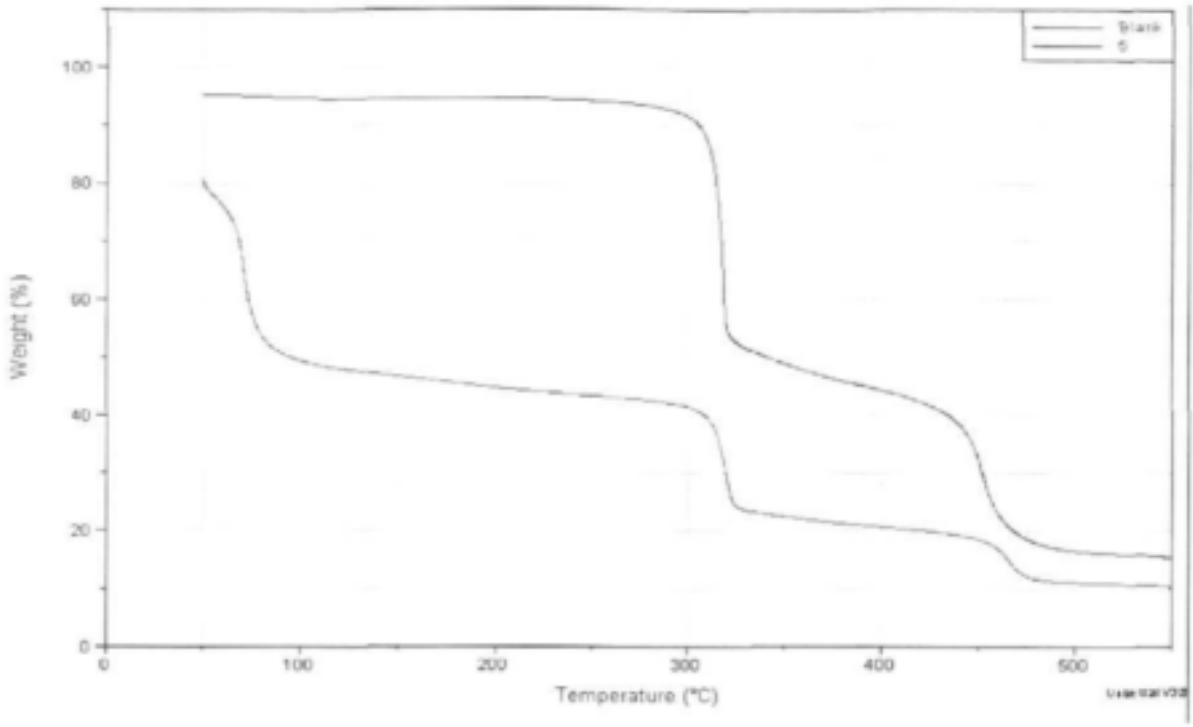


Figure A13: Overlay of the TGA curves of the Blank and sample 5

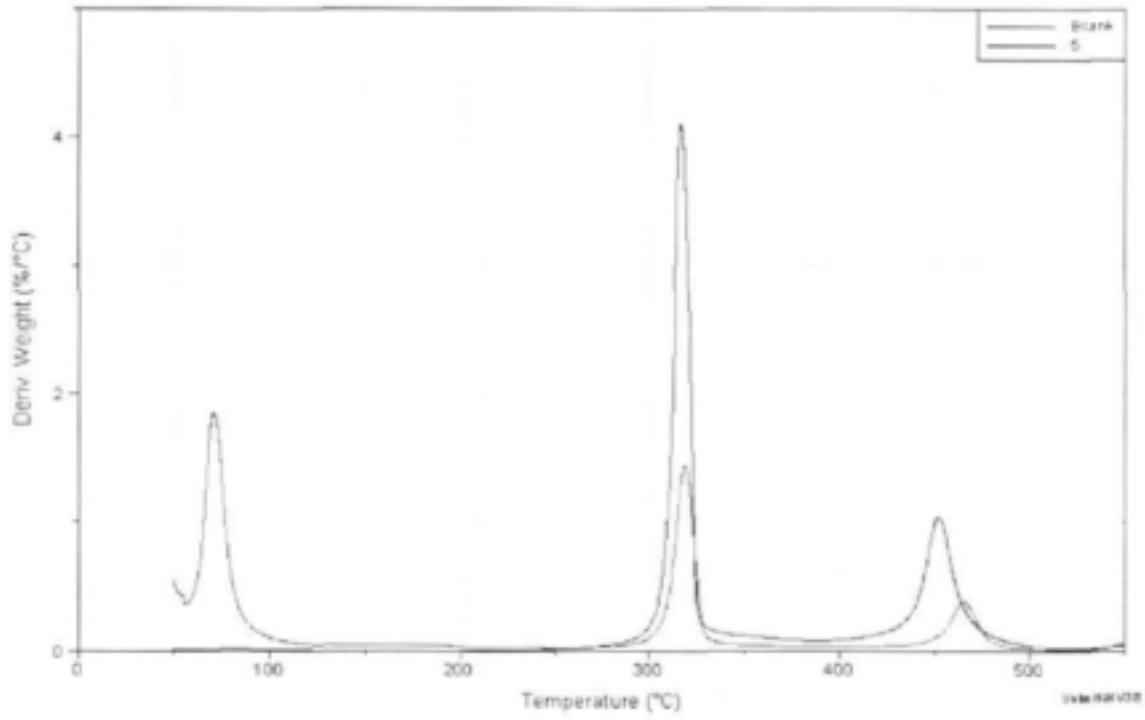


Figure A14: Overlay of the Derivative TGA curves of the Blank and sample 5

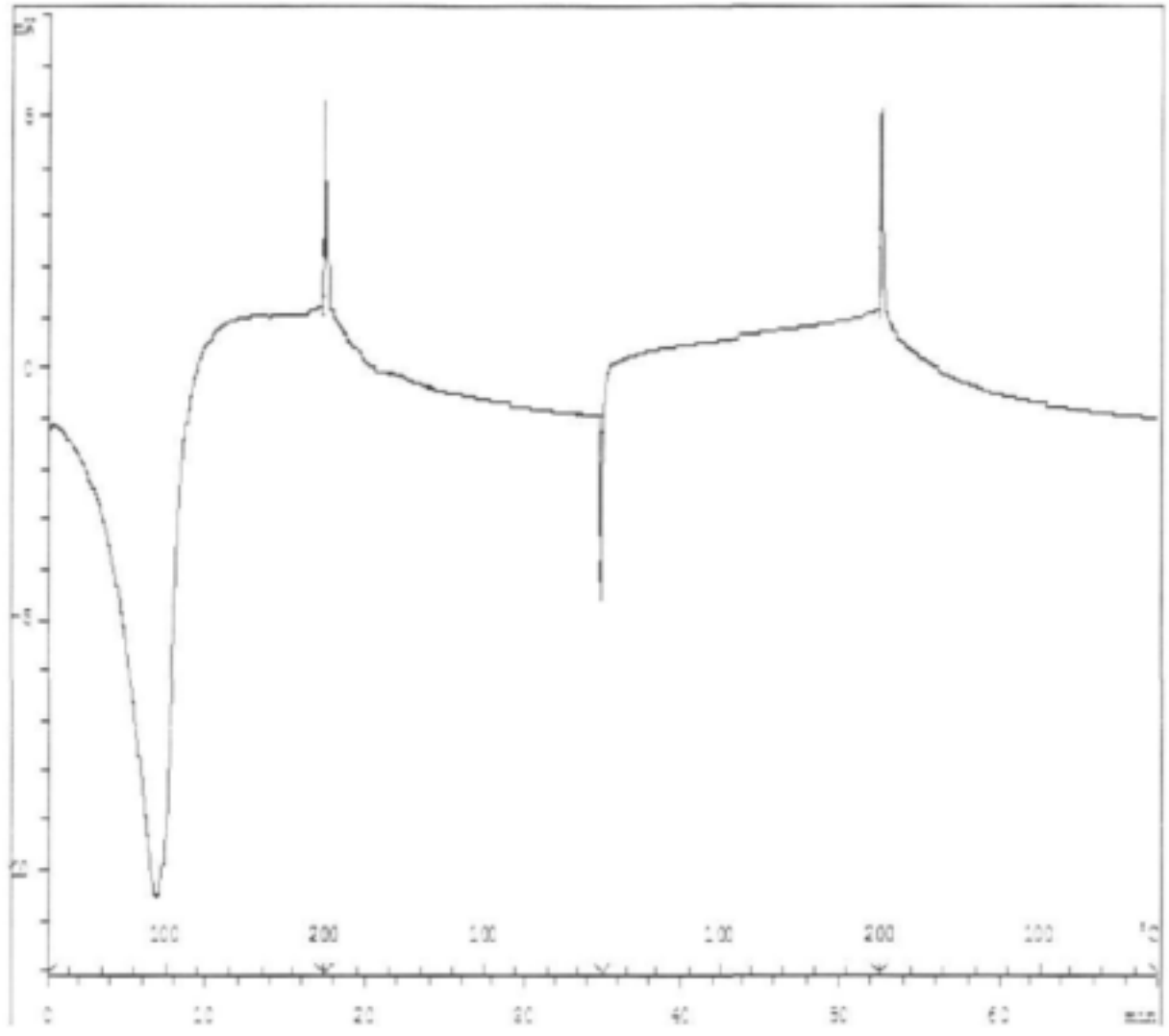


Figure A15: DSC curve of [β-CDHDI·2-Chlorophenol]

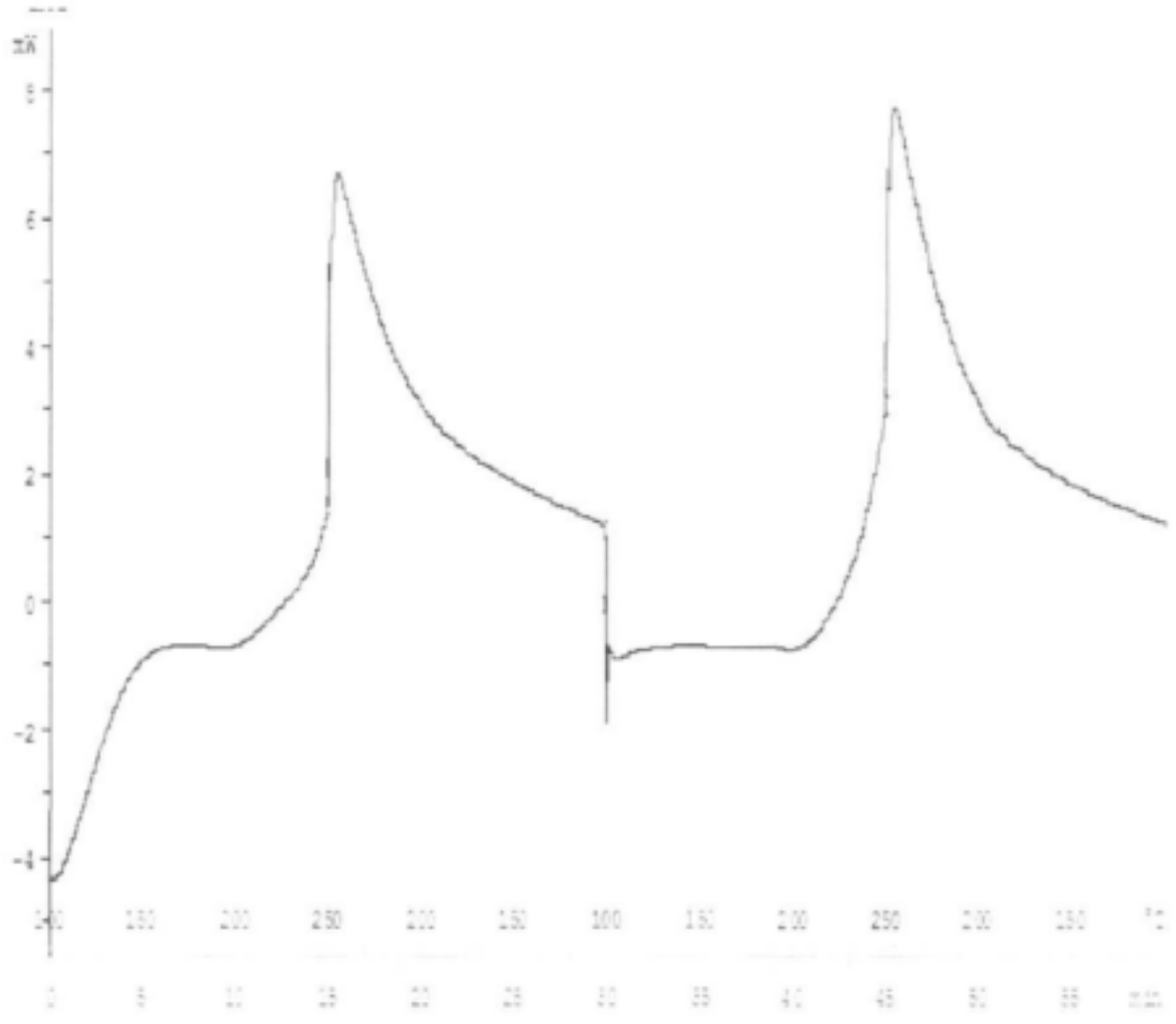


Figure A16: DSC curve of [β-CDHDI·2-MIB]

APPENDIX B

Laboratory Experimental Procedures

B1. Introduction

The laboratory testing of activated carbon commonly involves carrying out isotherm tests in which reductions in target contaminants are measured at different carbon concentrations and after a specific contact time. However according an Umgeni Water report, these tests tend to be laborious and they often involve complicated adsorption models, apart from the fact that they provide nothing more than a rough estimate of the suitability of the carbon for the intended application.

The tests that were performed in this study are the iodine number, phenol value and methylene blue number. Similar procedures to those conducted for activated carbon assessment by Umgeni Water were adopted and applied. Slight modifications were done on these tests in order to suit the working conditions and/ or apparatus available in the laboratory. This section describes in detail, the analytical methods that were used for each of the tests and examples of how calculations were done. It may be noted that in all experiments where a certain volume of activated carbon is used, equivalent amounts of CD polymers were used instead.

B2. Iodine number

B2.1. Apparatus

1. A-Grade pipettes
2. Burette
3. Beakers
4. Conical flasks 250 mL
5. Glass funnels
6. Graduated measuring cylinders
7. Whatman No. 2V filter paper or equivalent

8. Whatman No. 3 filter paper or equivalent
9. Analytical balance

B2.2. Reagents

1. 5% Hydrochloric Acid
   - Add 70 mL of concentrated hydrochloric acid to 550 mL of distilled water, and mix well.
2. 0.1 N sodium thiosulphate
   - Dissolve 24.82 g of sodium thiosulphate in approximately 75 mL of freshly boiled distilled water.
   - Add 0.1 g of sodium carbonate to minimize bacterial decomposition of the thiosulphate solution.
   - Quantitatively transfer the mixture to a 1 L volumetric flask and dilute to the mark. Allow the solution to stand for at least 4 days before standardizing. The solution should be stored in an amber bottle.
3. 0.1 N Iodine
   - Weigh 12.7 g of iodine and 19.1 g of potassium iodide, KI into a beaker and mix the dry iodine and potassium iodide.
   - Add 2 to 5 mL of water to the beaker and stir well. Continue adding small increments of water, while stirring, until the total volume is 50 to 60 mL.
   - Allow the solution to stand a minimum of 4 hours to ensure that all the crystals are thoroughly dissolved.
   - Quantitatively transfer to a 1 L volumetric flask and fill to the mark with distilled water. Store the solution in an amber bottle.
4. Potassium iodide
5. Starch
6. Sodium carbonate
7. Sulphuric acid
8. 0.1 N Potassium dichromate
   - Weigh out 4.940 g potassium dichromate (previously dried to constant weight at 105° C, cooled and stored in a desiccator) into a beaker.

- Quantitatively transfer to a 1 L volumetric flask and make to the mark.

B2.3. Analytical Procedure

1. This procedure can be used for both powdered and granular activated carbons. Granular carbon must be ground until at least 95 wt% passes through a 325 mesh (50 µm) screen. Powdered carbons may also require additional grinding in order to meet this size requirement.
2. Standardization of 0.1 N sodium thiosulphate
   - Pipette 10 mL of 0.1 N potassium dichromate into a 250 mL conical flask.
   - Add 90 mL of distilled water, 1 mL of concentrated sulphuric acid, and a spatula tip of KI.
   - Place in a dark cupboard for 5 minutes. Titrate against 0.1 N sodium thiosulphate, using starch as indicator.
3. Standardization of 0.1 N Iodine
   - Pipette 20 mL of ± 0.1 N Iodine into a 250 mL conical flask. Titrate against standardized sodium thiosulphate, using starch as indicator.
4. Grind a representative sample of carbon until 95% or more will pass through a 50 µm sieve.
5. Dry the carbon in a 110° C oven for 3 hours.

Part A: Iodine number (Single-point isotherm)

6. Weigh out approximately 1 g of carbon into a 250 mL conical flask.
7. Add 10 mL of 5% hydrochloric acid, and swirl until the carbon is wetted.
8. Place the flask on a hotplate, and bring the contents to the boil for 30 seconds only.
9. Allow to cool to room temperature and then add 100 mL of standardized Iodine.
10. Immediately stopper the flask, and shake vigorously for 30 seconds.
11. Filter through a Whatman No. 3 filter immediately after shaking.
12. Discard the first 20 to 30 mL and collect the remainder of the filtrate in a clean conical flask.

13. Transfer 50 mL of this filtrate to a clean conical flask, and titrate the sample with the standardized sodium thiosulphate, using starch as indicator.
14. Calculate the estimated iodine number (E), using the attached graph.

Part B: Iodine Number (Three-point Isotherm)

15. Using three masses of carbon spanning the expected concentration range required (use the iodine number, E determined in Part A to estimate these three masses) add 10 mL of 5% hydrochloric acid to each, and swirl until the carbon is wetted.
16. Place the three flasks on hotplates, and bring the contents to the boil for 30 seconds only.
17. Allow to cool to room temperature and then add 100 mL of standardized 0.1 N iodine to each flask.
18. Immediately stopper each flask, and shake vigorously for 30 seconds.
19. Filter the contents of each flask through Whatman 2V immediately after shaking.
20. Discard the first 20 to 30 mL from each flask and collect the remainder of the filtrates in clean conical flasks.
21. Transfer 50 mL of each filtrate to clean conical flasks, and titrate each sample with standardized sodium thiosulphate, using starch as indicator.

B2.4. Calculations

$$N\ (Na_2S_2O_3) = \frac{10 \times 0.1}{\text{Titre } Na_2S_2O_3\ (mL)\ (\text{Part A})}$$

$$N\ (I_2) = \frac{\text{Titre } Na_2S_2O_3\ (mL)\ (\text{Part A}) \times N\ (Na_2S_2O_3)}{20}$$

Part A:

$$N\ (I_2)\ (\text{Residual filtrate}) = \frac{N\ (Na_2S_2O_3) \times \text{Titre } Na_2S_2O_3\ (mL)\ (\text{Part A})}{50}$$

N (I_2) (Residual filtrate) is used to obtain F, the correction factor from the iodine correction graph (**Figure 4.4**).

$$E_{Part\ A} = \frac{F \times A - (DF \times B \times \text{Titre } Na_2S_2O_3\ (mL))}{\text{Sample mass (g)}}$$

Where:

$E_{Part\ A}$ = Iodine Number calculated from Part A

A = N (I_2) x 12693.0

B = N ($Na_2S_2O_3$) x 126.93

F = Correction factor obtained from iodine correction graph

DF = Dilution Factor = $\frac{100\ mL\ I_2 + 10\ mL\ HCl}{50} = 2.2$

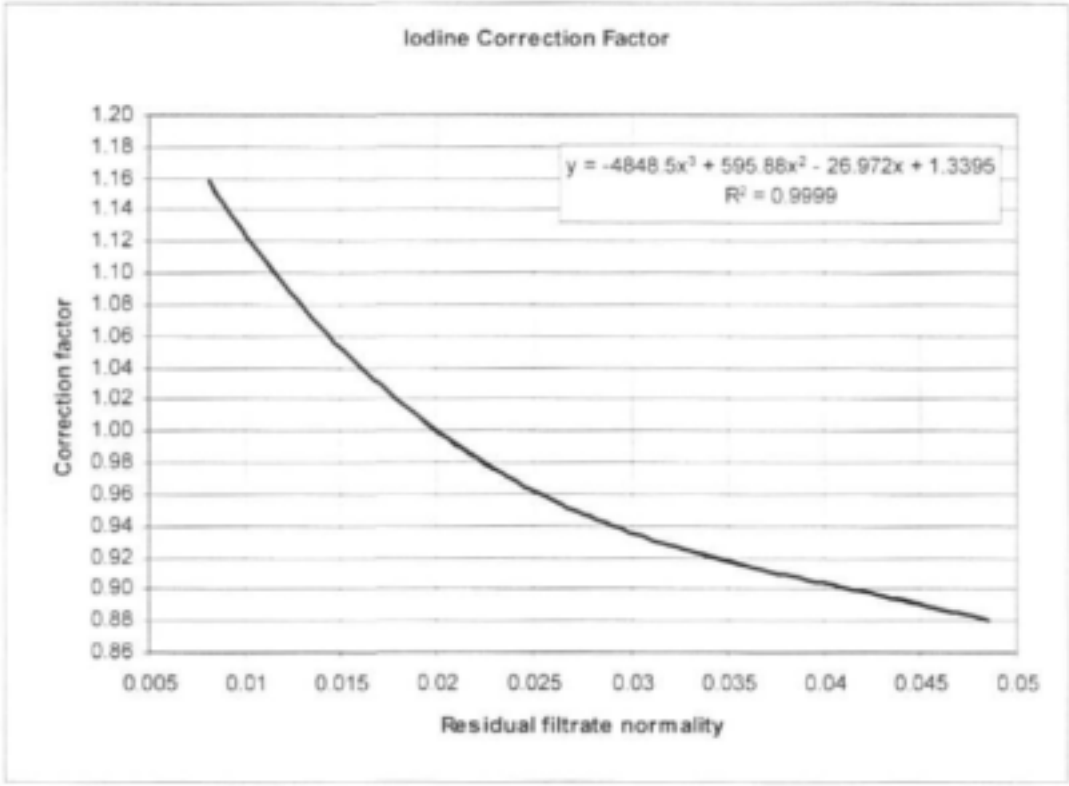


Figure B1: Iodine Correction Curve

Part B:

Estimation of the three carbon doses:

Use N (I_2) residual filtrate as the middle of a range of three residual filtrate normalities to calculate the three carbon doses.

Estimated masses for Part B (g) =

$$\frac{A - (13\,962{,}3 \times \text{residual filtrate normality [in this case 0,01; 0,02 or 0,03]})}{E_{\text{Part A}}}$$

After obtaining the 3 estimated doses, continue with **Part B**:
Calculate X/m (iodine adsorbed per gram of carbon), for each mass:

$$X/m = \frac{A - (2.2 \times B \times \text{Titre } Na_2S_2O_3 \text{ (mL)})}{\text{Sample mass (g)}}$$

Calculate C, the residual filtrate normality:

$$C = \frac{N\ (Na_2S_2O_3) \times \text{Titre } (Na_2S_2O_3) \text{ (mL)}}{50}$$

The values of C (as the abscissa) are plotted against X/m (as the ordinate) as a logarithmic graph for each of the three carbon dosages. Calculate the least squares fit for the three points. The Iodine Number is the X/m value at a residual iodine concentration of 0.02N. The regression coefficient for the least squares fit should be greater than 0.995.

B2.5. Source

(i) Process Services, Umgeni Water.

(ii) ASTM D4607- 86.

B3. Phenol value

B3.1. Apparatus

1. Whatman 2V filter paper
2. Analytical balance
3. Iodine flasks
4. Erlenmeyer flasks

5. Spectrophotometer
6. 10 mm quartz cells
7. 200 mL volumetric flasks

B3.2. Reagents

1. Stock phenol solution
   - Weigh 1.0 g of reagent grade phenol into a glass beaker.
   - Transfer to a 1 L volumetric flask and make to mark. Rinse the beaker well.
   - Discard solution after two weeks.
   - Remember to store reagent grade phenol in the refrigerator.
2. 0.1 N Sodium thiosulphate
   - Place 25 g $Na_2S_2O_3.5H_2O$ in a 1 L volumetric flask and dissolve in freshly boiled distilled water. Make up to the make with boiled distilled water. Store in an amber bottle. Standardize before use.
3. 0.1 N Potassium bromate-bromide
   - Dissolve 2.784 g of potassium bromate and 10.0 g of potassium bromide (bromate free) in distilled water and dilute to 1 L. Store in and amber bottle.
4. Potassium iodide crystals
5. Starch solution
6. Sulphuric acid
7. 0.1 N Potassium dichromate
   - Weigh out 4.940 g potassium dichromate (previously dried at 105° C to constant weight, cooled and stored in a desiccator) into a beaker.
   - Quantitatively transfer to a 1 L volumetric flask and make to the mark.
8. Buffer solution (8 strength)
   - Dissolve 728 g of anhydrous disodium phosphate (Na_2HPO_4) or equivalent weight of crystalline phosphate, in 2 L of hot distilled water.
   - When the phosphate is completely dissolved, acidify with approximately 100 mL of phosphoric acid, check using a pH meter, and make up to 7 L. The final pH should be 6.5.

- Single strength buffer solution is prepared by diluting 100 mL of 8 strength buffer solution with 700 mL of distilled water.

B3.3. Procedure

Standardization of phenol solution

- Pipette 25 mL of stock phenol solution into a 500 mL iodine flask.
- Add 25 mL of potassium bromate-bromide using either a burette or pipette.
- Shake flask.
- Add 5 mL concentrated HCL.
- Wait 3 minutes.
- Add 8 mL of 12.5% KI.
- Stand for 3 minutes, and then titrate the liberated iodine with ±0.1 N sodium thiosulphate, using starch as an indicator.

Standardization of 0.1 N sodium thiosulphate

- Pipette 10 mL of 0.1 N potassium dichromate into a 250 mL conical flask.
- Add 90 mL of distilled water, 1 mL of concentrated sulphuric acid, and a spatula tip of KI.
- Place in a dark cupboard for 5 minutes. Titrate against 0.1 N sodium thiosulphate, using starch as indicator.

Phenol test

1. Prepare a 200 mg/L phenol test solution by diluting one volume of stock phenol (1 000 mg/L) with four volumes of single strength buffer solution i.e. for 1 L of phenol test solution dilute 200 mL of stock phenol with

800 mL of single strength buffer solution. If the stock phenol solution concentration is not exactly 1 g/L adjust the volume used so that the test solution is maintained at 200 mg/L phenol.

2. Enough test phenol solution must be prepared to conduct all the samples for the day (200 mL per each carbon dose).
3. Use the activated carbon as received and determine the moisture content.
4. For each carbon sample, 4 carbon weights are used. Start the test with weights of 0.4, 0.5, 0.6, and 0.7 g. One of these weights should absorb 90% or more of the phenol in the test phenol solution. If the weights do not give the correct absorption adjust the weights by using higher or lower weights.
5. Weigh each carbon dose into an Erlenmeyer flask.
6. Pipette 200 mL of phenol test solution (200 mg/L phenol) into flask, using 100 mL to wet the carbon first and then rinse the sides of the flask with the remaining 100 mL.
7. Stopper flasks with rubber caps and place on a shaker at ambient temperature for 30 minutes.
8. Gravity filter the samples through a Whatman 2V, 24 cm diameter filter paper. Allow samples to filter completely.
9. Prepare 1 500 mL of buffer solution consisting of 1 volume of 8 strength buffer and 9 volumes of distilled water.
10. This solution is used as a reference solution in the spectrophotometer and as the diluent in preparing the phenol standard.
11. Pipette or use a burette to add 4.0, 8.0, 12.0, 16.0, 20.0, and 24.0 mL stock phenol solution to each of six 200 mL capacity volumetric flasks, to give standards with concentrations of 20, 40, 60, 80, 100 and 120 mg/L phenol respectively. Make up to volume with the buffer solution mixture and mix thoroughly.
12. Set the wavelength of the spectrophotometer to 270 nm.
13. Zero the spectrophotometer using the buffer solution mixture.
14. Use quartz cells and measure the absorbance of the samples and the standards.
15. For the phenol reference curve, plot mg/L phenol versus absorbance.

16. Determine the residual phenol concentration for each activated carbon treated filtrate from the phenol reference curve.

B3.4 Calculation

Determine % residual filtrate concentration (remaining phenol) in each activated carbon treated filtrate:

$$\% \text{ Residual filtrate concentration} = \frac{\text{Residual phenol (mg/L)} \times 100}{200 \text{ (mg/L)}}$$

Determine % of X (adsorbed phenol):

% X = 100 - % residual filtrate concentration

Activated carbon dosages/200 mL phenol solution, are multiplied by 5 to obtain activated carbon dosage, M g/L.

Plot % X versus M (carbon dosage) (g/L).
Read off M (carbon dosage) for X = 90.

$$\text{Phenol value} = M \text{ (at } X = 90) \times \frac{100\% - \% \text{ moisture}}{100\%}$$

B3.5. Source

(i) Process Services – Umgeni Water

(ii) AWWA Standard Methods for Activated Carbon, ANSI/AWWA B600-96, 1996.

The phenol concentration used for the assessment of activated carbon was very high. The concentration of the phenol test solution was reduced to 1mg/L.

B4. Methylene Blue Number

B4.1. Apparatus

1. Analytical balance
2. Whatman 44 or No 3 filter paper
3. Spectrophotometer
4. Volumetric flasks

B4.2. Reagents

1. Acetic acid 0.25%
   - Add 2.50 mL of glacial acetic acid to 900 mL of distilled water. Dilute to 1 L in a volumetric flask.
2. Standard Methylene Blue solution (1 200 mg/L)
   - Weigh out 1.20 g methylene blue (previously dried to a constant weight, cooled and stored in a desiccator).
   - Dissolve in 100 mL 50% acetic acid.
   - Dilute to 1 L in a volumetric flask
3. Working methylene blue standards
   - Prepare a 120 mg/L intermediate methylene blue standard by diluting the stock 1:10 with 0.25% acetic acid into 100 mL volumetric flasks.
   - Pipette 10.0, 7.5, 5.0, and 2.5 mL of the intermediate methylene blue standard into each of four 100 mL volumetric flasks and make up to volume with 0.25% acetic acid. These standards are equivalent to residual methylene blue concentrations of 12 000, 9 000, 6 000 and 3 000 µg/L.

B4.3. Procedure

1. Granular carbon must be ground until at least 95wt% passes through a 325 mesh (50 µm) screen. Powdered carbons may also require additional grinding in order to meet this size requirement.
2. Set the wavelength of the spectrophotometer to 620 nm and using a 10 mm cell read the working standards and record the absorbances.
3. Plot a calibration curve of methylene blue concentration versus absorbance and calculate the slope of the regression line.
4. Weight out 0,100 g of dried, ground carbon sample into a 100 mL beaker.
5. Add 25.0 mL of 1200 mg/L methylene blue solution and stir on a mechanical stirrer for 30 minutes.
6. Filter through Whatman 44 or No 3 filter paper and discard the first 5 mL of filtrate.
7. Measure the absorbance of the filtrate at 620 nm (this gives R, the residual methylene blue concentration from the calibration curve)

B4.4. Calculations

$$\text{Methylene Blue absorption g/100g carbon} = \left(\frac{30 - R}{40}\right)$$

Where:

R = residual methylene blue concentration.

B4.5. Source

1. Process Services, Umgeni Water.
2. European Council of Chemical Manufacturer's Federations (CEFIC), Test Methods for Activated Carbon, Belgium, 1986.

APPENDIX C

Estimation of laboratory scale production of standard CD polymers

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The estimated cost of producing cyclodextrin polymers used in this study is given below. This is calculated from the cost of the starting materials used during the preparation of these polymers. The calculation below is an estimation cost for producing β-CD polymers.

Material	Quantity	Cost (R)
β-cyclodextrin	1kg	1 500.00
HDI	100g	140.00
DMF	1L	115.00

10g of β-CD costs R15.00
1g HDI costs R1.40
15mL DMF costs R1.70
Total cost = **R18.10**

The yield of polymer obtained after using the amounts above ≈ 17 g (a 100% yield) with an approximate cost of R18.00.

The cost of producing the polymers may reduce significantly when the polymers are commercialized. It was mentioned also that these polymers can be reused many times without losing their effectiveness and this element renders them suitable for commercial applications.

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