February 2016
The WRC operates in terms of the Water Research Act (Act 34 of 1971) and its mandate is to support water research and development as well as the building of a sustainable water research capacity in South Africa.

TECHNICAL BRIEF

Industrial water treatment

Advancing oxidation technology for improved water treatment

A newly-completed Water Research Commission (WRC) study has advanced water treatment using electrohydraulic discharge.

Background

Water pollution has become a global problem as a consequence of growing accumulation of persistent organic pollutants caused by natural and anthropogenic activities. Many of these contaminants are highly recalcitrant, toxic and non-biodegradable with grave, environmental consequences.

With the growing demand for safe drinking water and perpetually increasing water pollution, urgent practical and strategic water treatment solutions are required. Currently, available conventional water treatment approaches are less capable of producing the desired results and often generate toxic intermediate products.

These disadvantages have driven research interest into the development of new water treatment technologies that will supplement the existing approaches. Thus, the use of advanced oxidation technologies such as the electrohydraulic discharge (EHD) system for decomposing organics and inactivating microorganisms was considered due to its greater efficiency, energy saving, high speed, use of few or not chemicals, and non-destructive impacts upon the ecosystem.

This WRC project investigated the design and methods for applying electrical energy to single or multiple electrodes. An assembly having a single or more electrodes may be configured such that the high voltage electrodes are submerged into the setup of the water to be treated for production of a cocktail of active chemical species.

The combination of these reactive species has been reported to be capable of degrading biological and chemical pollutants rapidly and efficiently. This technology development of advanced oxidation was initiated under a previous WRC project (see **Report No. 1897/1/12**).

This latest project aimed to investigate optimisation of the whole EHD system, as well as detection and quantification of the free reactive species, both of which have been some of the most challenging tasks in previous projects.

Methodology

The EHD system was optimised by investigating the effects of physico-chemical, electrical parameters and reactor configurations on methylene blue (MB) degradation efficiency. The physico-chemical parameters included MB concentration (0.5-10 mg/L), solution pH (2.5-10.5) and conductivity (5-20 mS/cm), solution volume (500-2000 mL), NaCl electrolyte concentration (10-50 g/L) air gap (2-6 mm) and air flow rate (2-4 L/min).

As for electrical parameters, the effects of applied voltage (20-25 V), current (2-4 A), electrode type (copper, silver and stainless steel) and electrode size (0.5-1.5 mm) on MB degradation efficiency were evaluated. The effects of these parameters on MB degradation efficiency was assessed by varying one parameter at a time at the following fixed/constant conditions: reactor air gap 2 mm, solution volume 1500 mL, NaCl electrolyte concentration 50 g/L in electrode compartment, voltage 25 V (7.8 kV), airflow rate 3 L/min, 0.5 mm silver electrode and a running time of 60 minutes.

In comparison to the preliminary experimental conditions the following optimum results were obtained based on the investigated parameters: optimum MB concentration (5 mg/L), solution pH (2.5), solution volume (1500 mL), air flow rate (3 L/min), 1.5 mm silver electrode, applied voltage

(25 V), current (4 A), NaCl electrolyte (50 g/L) a contact time of 60 minutes.

In order to utilise the UV radiation generated during the operation of the EHD, supported photocatalysts were developed. In the previous WRC funded studies, it has been shown that titanium dioxide loaded carbon nanotube (CNT) nano-composites modified with silver nanoparticles was an effective photo-catalyst for the degradation of contaminants, using methylene blue (MB) as a model pollutant. In that work 1 g/L of catalyst with loading of 20 wt. % TiO_2 on CNT was enough to achieve a degradation rate of 83% of 500 mL of 50 mg/L aqueous MB solution in 10 h using UV light and at pH 8. The deposition of 2 wt. % Ag on 20 wt. % TiO_2/CNT resulted in a greater and faster degradation of MB of 92% in 4 h under the same conditions. Furthermore, the powder TiO_2 decoloured 68% of the solution after 8 hrs.

Due to the toxicity problem, separation and light penetration issues of free floating nanoparticles in water, much effort was directed to preparing high surface area supported TiO_2 anatase nanocrystals. By combining photocatalysis with advanced oxidation systems much more complete degradation is possible. Methods to prepare high surface area TiO_2 anatase nanocrystals supported on a stainless steel mesh were developed.

These new composite materials were used to remove methylene blue (MB) from aqueous solutions. The supporting procedure involved the thermal decomposition of a sol gel solution coated upon stainless steel mesh. The nanocrystalline anatase phase was formed by thermal decomposition of stainless steel mesh coated with 8% PAN/DMF/TiO2 sol gel formation calcined at varying temperatures of 300°C, 400°C, 500°C and 600°C.

The heating rate of 50°C/min and holding times of 1 h, 2 h, 3 h and 4 h were applied to find the optimum supporting conditions. The synthesised TiO_2 nanocomposites materials were characterised using the following analytical techniques: XRD, HRSEM, EDS, HRTEM, SAED, FTIR and UV-Vis absorption spectroscopy. The photocatalytic activity of the TiO_2 nanocrystals supported on a stainless steel mesh were tested using 50 mg/L methylene blue solution under UV irradiation for 30, 60 and 90 minutes.

The specific EHD system developed, namely a dielectric barrier discharge (DBD) system was also employed for the treatment of real textile effluent and to inactivate *E. coli* bacteria in water at room temperature.

Main results

No corrosion was observed with silver electrodes, whereas previously used copper electrodes showed significant corrosion after a few electrohydraulic cycles. Further increase in MB concentration above 5 mg/L resulted in a decrease in the decolourization rate under the optimised conditions.

With regards to the reactive species responsible for the decomposition of the organics, two of the active species, hydrogen peroxide and ozone (H_2O_2 and O_3), in the effluent were detected and quantified. It was observed that within the first 20 minutes, no significant amount of ozone was produced in solution.

However, the concentration of generated hydrogen peroxide reached 6.05×10^{-7} mol/L in solution after 10 minutes and decreased to 4.76×10^{-7} mol/L after 20 minutes. This demonstrates that hydrogen peroxide rather than ozone is the first species to be formed and is possibly responsible for the initial MB degradation. After 20 minutes, the concentration of generated ozone increased to 0.5×10^{-7} mol/L.

The complete decolourization of MB was ascribed to the combined effect of hydrogen peroxide and ozone within 40 minutes. Beyond this time, the concentration of hydrogen peroxide decreased continuously whereas that of ozone continued to rise in a sinusoidal fashion.

Furthermore, with application of the optimised conditions on MB decolourisation/degradation, 99.99% MB decolourisations rate was achieved within 20 minutes of contact time. Therefore, the optimized EHD system showed an improvement in reduction of the treatment time with a corresponding 53% total organic carbon (TOC) reduction.

The free reactive species (H_2O_2 and O_3) were also detected and quantified. After 10 minutes of experiment, about 3.73×10^{-5} mol/L H2O2 was produced which decreased to 2.93×10^{-5} mol/L with a low concentration of O_3 concentration. However, 0.5 mol/L of O_3 was detected after 20 minutes of contact time, thereafter, H_2O_2 concentration decreased continuously with time while that of O_3 fluctuated as the treatment time increased.

Thus MB degradation in the optimized EHD configuration was mostly initiated by generated H_2O_2 and O_3. The report also demonstrates the details of the degradation mechanism of methylene blue. The effects of the physicochemical parameters (pH, conductivity of the water, additives) and discharge conditions (applied voltage polarity and pulse repetition rate) on hydrogen peroxide production were investigated.

It was found that MB dye decolorized but decomposed to various intermediate by-products and the resulting aliphatic compounds such as carboxylic acids, aldehydes, amines, amides, were not fully oxidised into CO_2 and H_2O but remained in the solution. Hence it is necessary

for the further identification of intermediate products using Liquid chromatography Mass Spectroscopy or Gas Chromatography Mass Spectroscopy.

Because the single reactor tube was applied in EHD optimization, gas bubbles containing reactive species escaped the system, and a strong odour of ozone arose around the working system which could not be quantified. It is likely that other reactor configurations that sparge the bubbles more finely into the fluid, and utilise the reactive species more effectively and can handle higher volumes will show an effective maximum removal depending upon the applied conditions.

A redesigned multiple tube reactor is presented in this report. Future work will focus on developing a new continuous mode reactor system that will recirculate the fluid, thus allowing better contact between reactive species in the gaseous phase and the liquid effluent to be treated.

The results of the characterisation of the synthesized TiO_2 nanocrystals supported on a stainless steel mesh indicated that they were in the anatase form, polycrystalline in nature, and contained additional carbon-carbon bonds from the polymer used during preparation with TiO_2 particle sizes ranging from 13.60±0.0091 nm to 2285.43±0.0010 nm depending upon the thermal conditions applied.

The percentage degradation of MB achieved was 96.02% after 30 min under UV radiation in the presence of 0.3 g stainless steel mesh supported TiO_2 nanocrystals prepared by decomposition at 400°C for 2 h.

This study clearly demonstrated that TiO_2 anatase nanocrystals supported on a stainless steel mesh effectively removed methylene blue from aqueous solution, hence can effectively utilize the UV radiation generated from the EHD system. This study has successfully produced stably adhered, supported TiO_2 anatase nanocrystals with a high surface area that eliminated the post separation problem of powdered forms of TiO_2 and which photocatalysts were highly effective for the degradation of complex organics such as methylene blue.

In terms of real textile effluent containing a plethora of dyes, it was demonstrated that a combination of coagulation-flocculation and electrohydraulic discharge treatment was able to remove the colour and lower the COD value of a real textile effluent to well below the discharge limit, depending upon the treatment process combination.

The preliminary investigation conducted on the textile effluent indicated that removal of COD below the detection limit remains unrealistic via a single treatment system such as EDH alone. Thus, process integration was considered to be more economically advantageous and beneficial for the maintenance of environmental sustainability and protection. However, the application of the single cell configuration of the electrical discharge system for industrial wastewater treatment is costly to scale up thus may limit its full scale application for effluent treatment.

The treatment of wastewater containing microorganisms originating from different point and non-point sources has remained one of the cardinal objectives of most researchers. Most of these microorganisms, particularly bacteria, are not readily biodegradable and pose a serious threat to human health.

Thus, it becomes imperative to develop an appropriate and effective treatment technique that could be used to remove the enteric bacteria from water. The specific EHD system developed, namely a dielectric barrier discharge (DBD) system was employed to inactivate E. coli bacteria in water at room temperature. Air was used as a feeding gas to raise the concentration of ozone generated during the plasma process.

The obtained results indicate an increase in the optical density of the bacteria during the first 10 minutes which drastically decreased with an increase of treatment time. After the first 10 minutes of exposure of **E. coli** to plasma discharge, the bacterial inactivation percentage increased from 11.3 to 59.4%. The increase in inactivation percentage was due to the combination of physical and chemical properties of the plasma generated within the discharge zone of the DBD system.

In summary, the DBD system was shown to be a viable technique for decomposing non-biodegradable organic pollutants and microorganisms such as E. coli commonly detected in water. This study developed an optimized single cell EHD system that can incorporate a supported UV active TiO_2 photocatalyst and the system is capable of degrading organic pollutants in wastewater within 20 minutes without chemical additives therefore presenting an advantage over current technologies.

Further reading:
To obtain the report, *Advanced oxidative water treatment process for water disinfection using an electrohydraulic discharge reactor and TIO_2 immobilised on nano fibres* (**WRC Report No. 2132/1/15**), contact Publications at Tel: (012) 330-0340; Fax: (012) 331-2565; Email: orders@wrc.org.za or Visit: www.wrc.org.za to download a free copy.