Practical Paper

Cyclodextrin nanosponges in the removal of organic matter for ultrapure water in power generation

B. B. Mamba, R. W. Krause, T. J. Malefetse, G. Gericke and S. P. Sithole

ABSTRACT

The water treatment processes employed by coal-fired power stations do not completely remove most of the natural organics (volatile component) from the feed water used for power generation. Currently, polyaluminium chloride, polyelectrolyte and ion exchange resins are used to treat water at power stations. The effectiveness of water-insoluble cyclodextrin (CD) polymers in the removal of natural organics, dissolved organic carbon (DOC) and total organic carbon (TOC) from water collected at a specific power plant is reported. Gas chromatography-mass spectrometry (GC-MS), a total organic carbon combustion analyser and ultra-violet visible (UV-Vis) spectrometry were used in the analysis of the water samples. Results obtained from this study show that, despite the usage of the current treatment processes, natural organic species emanating from raw water still persist throughout the stages of the water treatment process. The polymers on the other hand demonstrated the ability to remove dissolved organic carbon (DOC) from raw water by as much as 84%.

Key words | coagulants, cyclodextrin polymers, dissolved organic carbon (DOC), ion-exchange resin, organic pollutants, total organic carbon (TOC)

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INTRODUCTION

The presence of organic pollutants in raw water is a major concern for a number of power plants and industries requiring ultrapure water such as the pharmaceutical and electronics sectors (Maughan *et al.* 2000). Eskom, the electricity generating utility in South Africa, is no exception, generally acquiring its water from neighbouring surface water sources. This water normally contains inorganic salts as well as natural organic matter (NOM). The concentration levels of organics depend very much on the catchment, soil properties and other industrial and agricultural activities in the area. Seasonal variations are a key factor as they also contribute to the level of organics in water. Following Eskom's chemistry guidelines, the water specifications listed in Table 1 have to be adhered to (Gericke 2002).

To alleviate this problem Eskom has developed a strategy which is aimed at producing water with reduced organic load. Currently, the cost of reducing organics in water is very high; therefore Eskom is looking at alternative technologies such as cyclodextrin polymers. The strategy being used at Eskom in reducing the organic load in water is through conventional treatment processes. These conventional treatment processes which have now been adopted by all power stations, involve coagulation and flocculation of raw water followed by clarification, sand filtration and demineralization (Aspden *et al.* 2002). These processes are illustrated in Figure 1.

The objective of the study was therefore to determine the effectiveness of water-insoluble cyclodextrin polymers, synthesized in our laboratories, in the removal of organic

Table 1 │ Demineralization water specifications for coal-fired power stations measured at the mixed bed outlet (Gericke 2002)

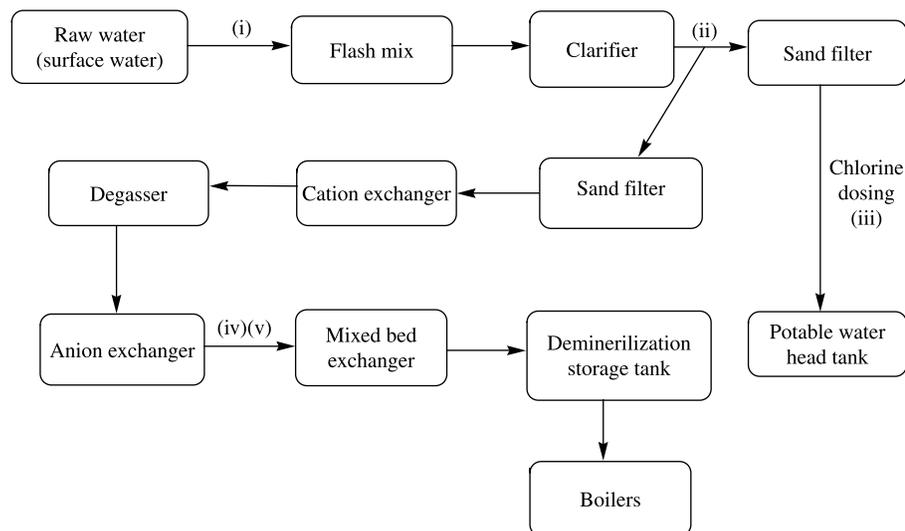| Parameter	Target	Limit
Turbidity (FTU)	<0.1	0.2
Specific conductivity (μs cm^{-1} @ 25°C)	<0.08	0.1
Sodium (ppb as Na^+)	<1	2
Silica (ppb as SiO_2)	ALARA	10
Chloride (ppb as Cl^-)	<1	2
Sulphate (ppb as SO_4^-)	<1	2
TOC (ppb as C)	100	250

ALARA: as low as reasonably achievable.

pollutants from water sampled at a specific coal-fired power station.

EXPERIMENTAL

Sampling site

Water samples (20 l) were collected from each of the different sampling points at a coal-fired power station (raw water outlet, clarifier outlet, potable water head tank inlet, sand filter outlet, cation exchanger outlet, weak base and strong base outlet and mixed bed outlet) as shown in Figure 1. It should be noted that only raw water was used in total organic carbon (TOC) and ultraviolet-visible (UV-Vis) analyses.

Treatment of water samples with cyclodextrin polymers

β-Cyclodextrin/hexamethylenediisocyanate (β-CD/HMDI) and β-cyclodextrin/toluenediisocyanate (β-CD/TDI) polymers (500 mg each) were loaded into an empty cartridge (6 cm^3) and 500 ml of the water samples were passed through (Mamba *et al.* 2007). Filtration was enhanced by the use of a vacuum pump or water aspirator. Water samples treated with cyclodextrin polymers were extracted using solid phase micro-extraction (SPME) and analysed using gas chromatography-mass spectrometry (GC-MS). The procedure for these analyses is described in the following sections. UV-Vis and TOC analyses were also carried out before and after treatment with polymers. These polymers were first washed with deionized water several times in order to remove unreacted cyclodextrin. While the full UV spectrum was analysed, the industry prefers the use of UV absorbance readings at 254 nm, as detailed below (Gericke 2002).

Ultraviolet-visible (UV-Vis) spectroscopy analysis of water samples

A CARY-UV 50 was used for the analysis of raw water. The water sample was filtered through a 0.45 μm polyethylene filter paper. A full UV scan (200–800 nm) was done and

Figure 1 │ Representation of a power station water treatment pathway showing the sampling points: (i) raw water outlet; (ii) clarifier outlet; (iii) potable water inlet; (iv) weak base outlet and (v) strong base outlet.

no significant difference in the spectra was observed. The measurements were determined at a UV wavelength of 254 nm according to Eskom's procedure since it gives an indication of dissolved organic carbon (DOC) present in the water samples (Gericke 2002). An overall reduction of the other absorbance maxima confirmed that while UV_{254} only gives an accurate indication of the aromatic portion of the sample, the trends observed at this wavelength were representative of the spectrum as a whole.

Total organic carbon (TOC) analysis of the water samples

A Tekmar Dohrmann Apollo 9000, TOC combustion analyser was used for the analysis of the raw water sample. Aliquots of the water samples were poured into sample vials that have pierceable teflon septum caps. The vials were then placed on the TOC analyser autosampler rack for analysis. Three replicates were run. Standard potassium phthalate samples of 1, 2, 5, 10 and $15 \, mg \, l^{-1}$ were prepared and a calibration curve was plotted. TOC concentrations were deduced from the calibration curve.

Extraction technique

A solid phase micro-extraction (SPME) device was used for the extraction of the analytes from the water samples collected from sampling points shown in Figure 1. The device has a polymer-coated fibre that is fused within a syringe. The type of polymer coating is chosen in order to match the characteristics of the analytes of interest (Nakamura & Daishima 2005). In this procedure, a fibre coated with polydimethylsiloxane/divinylbenzene (PDMS/DVB) with film thickness of 65 μm was used. PDMS/DVB is a non-polar polymer that is designed for the absorption of non-polar organic compounds (Lin *et al*. 2003).

To ensure that the fibre was clean before performing an analysis it was first conditioned. The conditioning was performed by exposing the fibre to a similar injector analysis temperature of 220°C for 30 minutes. This was followed by a blank analysis which was done by desorbing the fibre for a further 5 minutes at similar analysis temperature. Water samples (before and after treatment with cyclodextrin polymers) were extracted by immersing the fibre in 10 ml

aliquots for 30 minutes at 60°C. It was necessary to constantly stir the sample at the required temperature in order to enhance the extraction efficiency.

The main reason for extracting organic compounds was that organics have an impact on the overall performance of the treatment plant. They interfere with various processes: for example, they can foul the anion exchange resins, hence leaching silica and sodium (Gericke 2002). Some of the organics also seep through the treatment system and find their way to the turbines where they cause corrosion. Analysis of the extracted organics was done in order to find out which organics cause an impact in the treatment system and the nature of these compounds.

Analysis of water samples using gas chromatography-mass spectrometry

GC-MS analysis was carried out using a Varian CP-3800 capillary gas chromatograph coupled with a Varian Saturn 2000 mass spectrometer. This technique was used because of its ability to separate and uniquely identify organic compounds from a complex mixture. The one drawback of GC-MS is that only part of the organic load (semi-volatile organics) is analysed; nonetheless it gives a good indication of the effectiveness of the cyclodextrin polymers.

Water samples before and after treatment with cyclodextrin polymers were first extracted using SPME as described above. After the extraction of organic compounds the SPME fibre was retracted from the sample and placed in

Table 2 | GC-MS conditions for the analysis of organic pollutants extracted by SPME for treated and untreated water samples

Parameter	Condition
Column type	VF, 5 ms, 30 m × 0.25 mm, 0.25 μm
Injector	Splitless, 3 min sample exposure
Injector temperature	220°C
Oven temperature	50°C (hold for 1 min) to 270°C at 10°C min^{-1} hold for 10 min
Ionization	Electron impact
Carrier gas	Helium
Flow rate	1 ml min^{-1}
Detector	Mass spectrometer (ion trap)
Mode	Full Scan (m/z = 40–650)

the gas chromatograph injector port to desorb for 3 minutes. The GC-MS instrument conditions used for the analysis are indicated in Table 2.

RESULTS AND DISCUSSION

Ultraviolet-visible (UV-Vis) and total organic carbon (TOC) analysis

The UV-Vis analysis demonstrated the effectiveness of the cyclodextrin polymers in the removal of dissolved organic carbon from the raw water sample (Table 3). β-CD/TDI polymer removed about 84% of DOC while β-CD/HMDI removed about 73%. These findings are comparable to those obtained from a water treatment plant when enhanced coagulation was applied. In that case, DOC removals of up to 90% were achieved (Gericke 2002). The TOC results shown in Table 4 demonstrate low levels of TOC removal from raw water, far below the 60% removal achieved using enhanced coagulation.

We suspect that the low TOC removal values are due to some unreacted cyclodextrin leaching out of the polymers thereby contributing to the TOC. Since the polymers effectively have no UV-chromophore they do not contribute to the UV absorbance values, especially not at UV_{254}, but even a small amount of cyclodextrin adds a significant amount of carbon to the TOC values. Cyclodextrin polymers fabricated in pellet form, beads and membranes are being investigated as a means to reduce leaching problems. Therefore, we propose that the cyclodextrin polymer technology could be positioned between the sand filter and the cation exchanger. By doing so the clarifier would remove the solid particles while the polymer would remove DOC that cannot be properly removed by the clarifier.

Table 3 | Dissolved organic carbon removal from raw water

Polymer	Initial absorbance cm^{-1}	Final absorbance cm^{-1}	% DOC removal
β-CD/TDI	0.268	0.044	84
β-CD/HMDI	0.268	0.073	73

Table 4 | Total organic carbon removal from raw water

Polymer	Initial TOC (mg l^{-1})	Final TOC (mg l^{-1})	% TOC removal
B-CD/TDI	3.01	2.84	6
B-CD/HMDI	3.01	2.48	18

Quantitative analysis of the water samples using SPME and GC-MS

The presence of semi-volatile organic compounds in raw water before treatment with cyclodextrin polymers was confirmed by the appearance of signals in the GC-MS chromatogram illustrated in Figure 2(a). The chromatogram showed reduced intensities after the coagulation and flocculation process (Figure 2(b)). About 50% removal was obtained when taking into account the reduction in ion counts from raw water to the clarifier outlet. It should be noted that quantification was not done since no standards
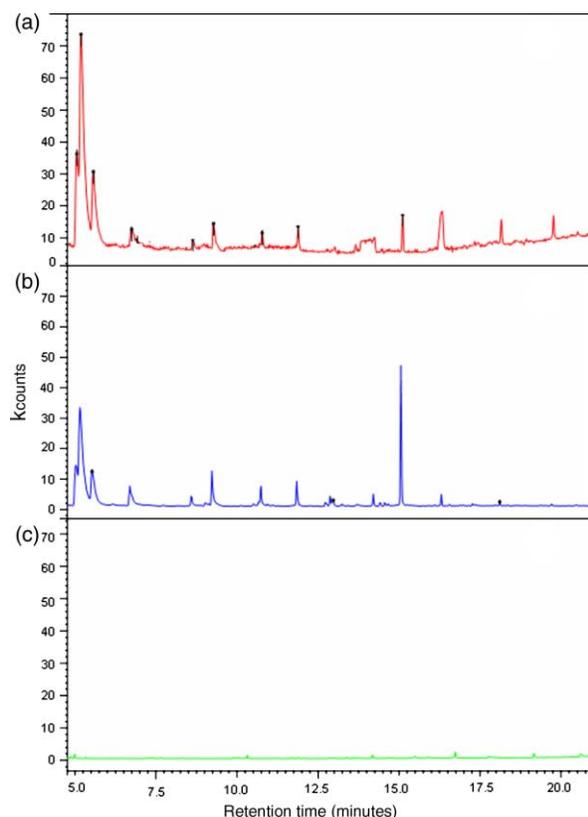

Figure 2 | GC-MS chromatograms of (a) raw water before treatment with cyclodextrin polymers and polyaluminium chloride with minimal polyeclectrolyte; (b) clarifier after treatment with polyaluminium chloride and minimal polyelectrolyte; (c) raw water outlet after passing through β-CD/TDI polymer.
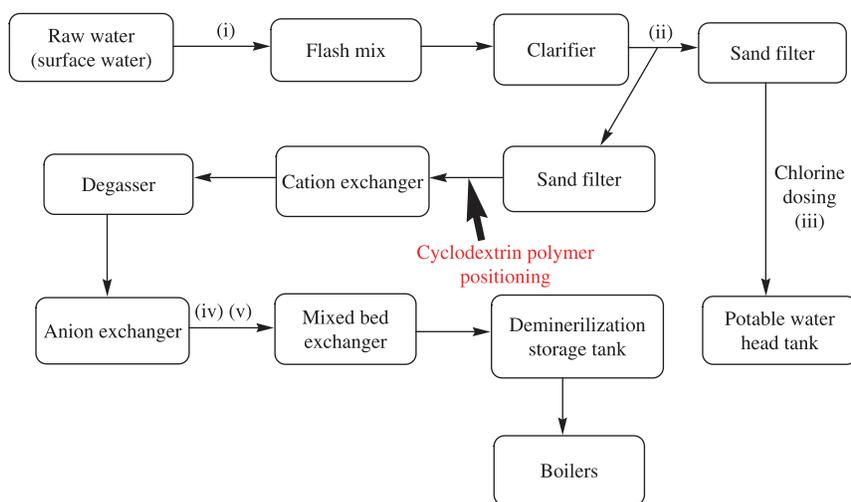
Figure 3 │ Positioning of cyclodextrin polymer along the demineralization treatment trail.

were used in this study. Characterization of the pollutants is still ongoing. However, the persistence of these signals from water sampled at the clarifier outlet (Figure 2(b)) even after treatment with polyaluminium chloride and the polyelectrolyte demonstrated that the coagulation and flocculation processes do not completely remove these pollutants from the water. GC-MS chromatograms of the other three sampling points (potable water inlet, strong base and weak base outlets) showed a similar trend. This indicates a persistent presence of semi-volatile organics in both potable and demineralized water. Additionally, this serves to demonstrate that the water treatment methods used in the removal of organic impurities need to be improved.

It can be noted that, after passing the raw water through β-CD/TDI polymer, an almost complete removal of the volatile organics was observed as shown in Figure 2(c). A similar trend was noted when the raw water was passed through β-CD/HMDI polymer. A removal efficiency of 90% (volatile and semi-volatile organics) was estimated based on the ion counts before (Figure 2(a)) and after treatment (Figure 2(c)) with the cyclodextrin polymers when taking into account the GC/MS analysis.

Qualitative analysis of the water samples using SPME and GC-MS

The presence of three semi-volatile organics was inferred using the MS online library (NIST library). The compounds

are 4-Chlorophenyl-phenylether ($T_R = 4.01$ minutes), 5-Hydroxyindole ($T_R = 6.07$ minutes) and ethoxyquin ($T_R = 15.01$ minutes). While 5-Hydroxyindole and ethoxyquin were detected in all sampling points the presence of 4-Chlorophenyl-phenylether was only observed in the last two sampling points (weak base and strong base outlet). 4-Chlorophenyl-phenylether is generally used as a dielectric fluid and can be released to the environment through its use in capacitors. Ethoxyquin is utilized as a fungicide, preservative in animal feed and as an antidegradation agent. 5-Hydroxyindole is found in dye making industries, agrochemicals and perfumes. All these compounds are probably from other industrial activities, including agriculture, and eventually get released into the river systems through run off and soil leaching.

CONCLUSION

The results obtained from the DOC and TOC analysis of the raw water after the use of the cyclodextrin polymers suggest that the cyclodextrin polymer can be utilized at site points between the sand filter and cation exchanger (see Figure 3). Positioning this technology before the ion exchanger would protect the life of the ion exchanger and reduce the impact of the organics in the turbines.

The clarifier would remove the bulk of the particulate and dissolved organic carbon while the rest could be removed by the cyclodextrin polymer before the water enters the

demineralization plant. Also, unlike the previously considered alternative technologies (activated carbon, membrane processes, organic scavenging resin and advanced oxidation processes), cyclodextrin polymers are not widely manufactured or available commercially; hence it is presently difficult to make an estimation of the cost of application of this technology. The advantages of this technology, however, are that the polymer can be recycled several times without losing its efficiency, it is effective at removing organics at low concentrations and it can be formed in different shapes to suit any application unlike activated carbon. Ongoing work entails the use of techniques such as high performance liquid chromatography (HPLC), liquid chromatography-mass spectrometry (LC-MS) and ^{1}H, ^{13}C nuclear magnetic resonance (NMR) in characterizing the organic acids and humics present in the water obtained from the specific sites of the coal-fired power station water treatment train. In addition, adjustment of the polymer formulation and synthesis procedure should allow us to prevent any of the polymers or cyclodextrin monomer from leaching into the water, and therefore improve TOC removal.

REFERENCES

Aspden, J. D., Dendekind, I., Gericke, G. & Wilshire, S. 2002 The impact of natural organic matter and chemical selection on the water treatment plant at Kendal power station. *VGB PowerTech.* **82**(8), 82–85.

Gericke, G. 2002 Plant optimization: A key factor in minimising natural organic matter in power station make-up water. *VGB PowerTech.* **3**, 93–96.

Lin, T., Liu, C., Yan, F. & Hung, H. 2003 Effect of residual chlorine on the analysis of geosmin, 2-MIB and MTBE in drinking water using the SPME technique. *Water Res.* **37**(1), 21–26.

Mamba, B. B., Krause, R. W., Malefetse, T. J., Mhlanga, S. D., Sithole, S. P., Salipira, K. L. & Nxumalo, E. N. 2007 Removal of geosmin and 2-methylisorboneol (2-MIB) in water from Zuikerbosch Water Treatment Plant (Rand Water) using β-cyclodextrin polyurethanes. *Water SA* **33**(2), 223–228.

Maughan, E. V., Gericke, G. & Roscoe, G. 2000 The measurement of TOC in the cycle fluid modern power plants and correct selection of monitoring equipment. *Power Plant Chem.* **2**(4), 219–222.

Nakamura, S. & Daishima, S. 2005 Simultaneous detection of 22 volatile organic compounds, methyl-tertbutyl ether, 1, 4-dioxane, 2-methylisoborneol and geosmin in water by headspace solid phase microextraction-gas chromatography-mass spectrometry. *Anal. Chim. Acta* **548**(1–2), 79–85.

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