

Removal of organic contaminants from water using nanosponge cyclodextrin polyurethanes

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Abstract: Insoluble nanoporous cyclodextrin (CD) polymers were synthesized using bifunctional isocyanate linkers. The ability of these polymers to remove selected organic pollutants from water at varying concentrations was studied. The investigated pollutants were selected high-priority chlorinated disinfection by-products (DBPs) and a common odour-causing compound in water, 2-methylisoborneol (2-MIB). The unpleasant musty odour imparted by 2-MIB and geosmin in water can be detected by the human nose even at ng L^{-1} (parts per trillion) levels. Pre-concentration and extraction of water samples containing low levels of pollutants was performed using solid phase extraction (SPE) and subsequently quantified by gas chromatography-mass spectrometry (GC/MS). Here we show that the CD polymers demonstrate excellent absorption efficiency (>99%) with respect to the organic pollutants, considerably better than granular activated carbon (GAC). The recyclability efficiency of these CD polymers is also reported.

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Keywords: cyclodextrin nanoporous polymers; water treatment; organic pollutants; gas chromatography-mass spectrometry

INTRODUCTION

Water is a finite and vulnerable resource that is essential for sustaining life. In general, water quality in South Africa and around the world is deteriorating due to contamination by organic substances. The increase in water pollution by these organic compounds is attributable in part to an increased use of chemicals in the advancement of technology.

The removal of organic contaminants from aquatic systems is crucial. Even when not toxic they often produce aesthetically undesirable problems such as colour, odour and bad taste.^{1–4} Even natural organic matter (NOM) can lead to the formation of potentially harmful disinfection by-products (DBPs) such as trihalomethanes, haloaromatic compounds, and other chlorinated organic compounds. Most of these organic compounds are toxic and pose a serious threat to human health, even at very low levels.^{1,3,5}

To date, the removal of organic pollutants to microgram per litre ($\mu\text{g L}^{-1}$) and nanogram per litre (ng L^{-1}) levels remains a challenge to scientists, local governments and industry. Most organic molecules, whether harmless or toxic, have little affinity for common adsorbents, thus making their removal very difficult. The use of materials such as granular activated carbon (GAC) in the removal of odour-causing substances in water has some limitations especially for organic compounds at very low concentrations. These techniques and others such as reverse osmosis, zeolites and molecular sieves are

unsuccessful at removing organic contaminants to parts per billion levels.⁶ Moreover there is some doubt whether these techniques can face the challenges posed by new, emerging contaminants.^{7,8}

Two of the most common taste and odour causing compounds in water are geosmin (*trans*-1,10-dimethyl-*trans*-9-decalol) and 2-MIB (2-methylisoborneol). These semi-volatile organic compounds are produced by planktonic and benthic algae, fungi, bacteria and actinomycetes and are associated with water from spring runoff and/or eutropic systems.^{9,10} The earthy or musty odour of these compounds can be detected by the human nose at very low concentrations (*ca.* 10 ng L^{-1}) and is irritating.¹¹ Possible health hazards posed by these compounds at such low levels have not been reported. However, stringent regulations have been put in place by water authorities to avoid the presence of these compounds from exceeding the threshold for human distaste.^{9,12,13} The removal of odour-causing compounds from drinking water is a serious challenge to many water specialists. Although there have been several advancements in the detection of 2-MIB,¹⁰ techniques to remove these compounds from water on a large scale remain somewhat elusive.

In this study we exploit a new class of nanoporous cyclodextrin (CD) polyurethanes (often referred to as 'nanosponges')⁸ for removing model contaminants from water. These CD polymers have demonstrated the ability to absorb a range of organic compounds

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(Received 20 November 2006; revised version received 12 January 2007; accepted 23 January 2007)

DOI: 10.1002/jctb.1681

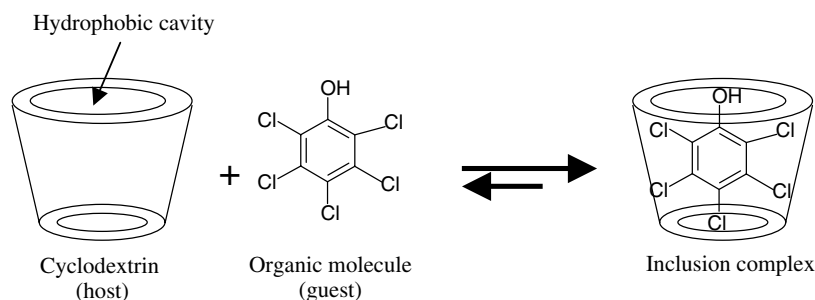


Figure 1. Formation of an inclusion complex of a cyclodextrin with an organic guest molecule in water.

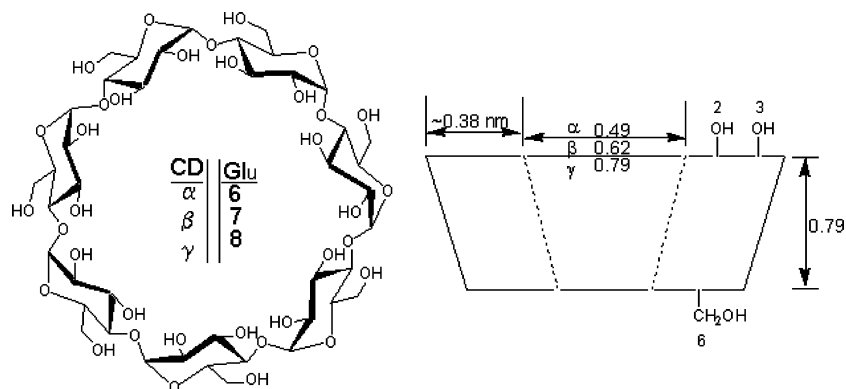


Figure 2. Structures of α -, β - and γ -CDs with different cavity sizes.

through the formation of inclusion complexes of the guest–host type (Fig. 1).^{14,15} This process of absorption involves the uptake of the organic molecules into the cavities of the CDs to form a guest–host complex, and is different from adsorption where molecules are attached to the surfaces of materials. Most frequently in CDs the complex formed is in a 1:1 ratio with the guest.^{15–18} It is also possible to form inclusion complexes where the guest molecules are significantly larger than the CD cavity where only part of the guest molecule or side chains penetrate into the cavity. In some cases a 2:1 complex (CD:guest) may be formed,^{15,16} while even more complicated associations have been reported.¹⁷ Determining the complex is usually done in solution using nuclear magnetic resonance (NMR) spectroscopy or circular dichroism, and this was not possible with our solid, insoluble CD-polymers. Hence, while we believe the pollutants are being *absorbed* by the polymers we have not yet been able to confirm this. We anticipate that *adsorption* may play an important role in removing large or polar pollutants from water, and are currently investigating this further. Apart from removing a variety of organic compounds to ng L^{-1} levels the polymers can be synthesized in a number of forms, thus providing ease of use.^{6,8} This work is part of an ongoing effort in our laboratories to develop this polymer-based water-treatment technology assist industries and municipalities in solving problems of water contamination by organic compounds.

CDs are simple low molecular oligosaccharides that are commercially produced by treating starch with the amylase of *Bacillus macerans*.^{19,22,23} Three common CDs (α -CD, β -CD and γ -CDs) are available,

possessing six, seven and eight glucose (Glu) units, respectively, with α -(1,4)-linkages forming a ring (Fig. 2).

Since CDs are soluble in water, they cannot be used directly for water treatment purposes. As a result, bifunctional linking reagents such as hexamethylene diisocyanate (HMDI) and toluene-2,4-diisocyanate (TDI) were used to synthesize water-insoluble CD polyurethanes from both un-functionalized as well as mono-functionalized CD monomers. Since β -CD is the most accessible, both in cost and reactivity, it was used extensively in this study.

EXPERIMENTAL

Preparation of water samples

Model water samples were prepared by spiking ultra-pure doubly deionized water with a known concentration of organic contaminant (10 mg L^{-1} , $20 \mu\text{g L}^{-1}$ and 100 ng L^{-1}).

Raw water samples were also obtained from the Rietvlei Dam (an important water reservoir in the Gauteng province north of Johannesburg). Samples were transported in a cooler box and stored in a refrigerator at 4°C prior to analysis.

Analytical methods

Solid phase extraction (SPE) was used for the pre-concentration of all water samples using an Autotrace SPE Workstation (Zymark Corp., Hopkinton, MA, USA) fitted with C18 SPE cartridges containing 500 mg of bonded, reversed phase silica gel. Due to the nature of compounds isolated, an approved

Environmental Protection Agency (EPA) method '525.2' was adopted.²⁴ This method is used for the pre-concentration of a wide variety of semi-volatile organic compounds including polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in drinking water.

The SPE extraction was carried out as follows: cartridges were conditioned with deionized water (5 mL), methanol (5 mL) and deionized water (10 mL). A water sample (500 mL) was percolated through the cartridge at a flow rate of 5 mL min⁻¹. The cartridge was dried for 30 min under vacuum, and eluted with 2 mL of dichloromethane and 2 mL of ethyl acetate.

The pre-concentrated extracts were analyzed by gas chromatography-mass spectrometry (GC/MS) on an ion-trap Varian Saturn 2000 spectrometer (Varian Inc., Palo Alto, CA, USA). The GC was equipped with a Chrompack CP Sil 8 CB, 30 m × 0.25 mm i.d., 0.25 μm capillary column (Varian, Vorna Valley, South Africa). The GC conditions were 1 μL splitless injection at 300 °C using helium as a carrier gas at 1 mL min⁻¹ constant flow. The oven temperature settings were: 35 °C (held for 2 min) to 260 °C at 20 °C min⁻¹ then to 330 °C at 6 °C min⁻¹ (held for 1 min). Quantification of the spectral peaks was achieved using the MS data handling method of the mass spectrometer. The six most abundant specific ion peaks obtained from the chromatograms (SIM) were integrated and concentrations determined by comparing the peaks obtained from injected external reference samples using calibration curves. The use of single-component standards allowed us to identify pollutants by both retention time and specific daughter ions in the spectra (identification was also made on the six largest peaks, by comparison with reference spectra). We determined a limit of detection (LOD) of at least 10 ng L⁻¹ for the organic contaminants (taken at a point where the signal to noise level fell below 3:1), while the limit of quantification (LOQ) was taken to be 100 ng L⁻¹ (where the signal to noise level dropped below 11:1). While these limits were quite high, as an initial screening these limits would allow us to differentiate the polymers' capacities from the performance of granular activated carbon (GAC).

Laboratory scale column tests

In order to assess the absorption capability of the CD polymers and granular activated carbon (GAC), rapid small scale column tests (RSSCTs) were designed. The columns used empty SPE cartridges with a volume of 6 mL packed with homogenised powdery CD polymer or GAC (0.5 g equivalent).

Water samples were filtered through these modified cartridges in the same way as for the SPE set up, but using a flow rate of 10 mL min⁻¹. Samples filtered in this way were then subjected to the normal C18 SPE extraction for quantification by GC/MS. The tests were carried out in triplicate.

RESULTS AND DISCUSSION

Synthesis of cyclodextrin polymers

The synthesis of CD polymers has been reported in previous studies.⁸ Typically, α-, β- and γ-CD polymers were obtained by reacting a dimethylformamide (DMF) solution of the respective CD with the relevant linker (HMDI or TDI) (Fig. 3). The CDs were purchased from Wacker Chemie (Munich, Germany) and were used without further purification. The polymers were obtained in quantitative yields by removing the residual DMF.

Formation of the polymers was monitored by IR spectroscopy through the disappearance of the isocyanate peak at $\tilde{\nu} = 2273$. Similarly, successful incorporation of the linker was supported by the appearance of a peak corresponding to C=O at $\tilde{\nu} = 1600$. Other bands at $\tilde{\nu} = 2930$, $\tilde{\nu} = 1530$ and $\tilde{\nu} = 3460$ corresponding to C-H, NH(CO) and OH stretching were also observed in the polymer, allowing for further characterisation.

Properties of the cyclodextrin polymers

The air-dried polymers were generally formed as stable granular powders with grain sizes between 1 mm and 40 μm (typically 50% of the particles were larger than 300 μm, and 15% smaller than 75 μm). TDI polymers tended to have narrower particle sizes averaging 320 μm, compared to HMDI polymers with an average of 420 μm. BET surface area and pore volume measurements of the dried polymers were performed using a Tristar 3000 V6.05 automated gas adsorption analyzer (Micrometrics, Londonderry,

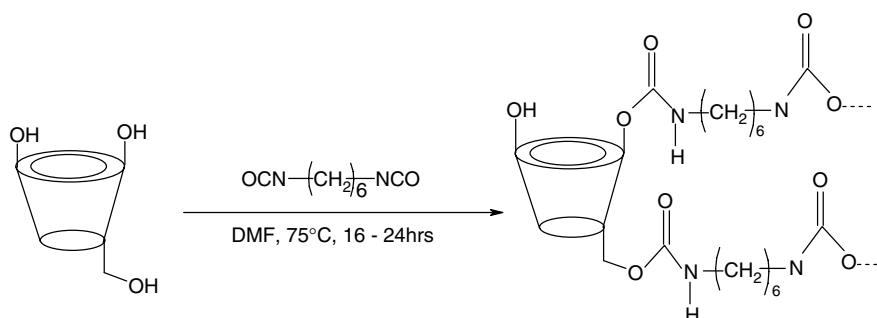


Figure 3. Synthetic pathway for the preparation of CD polymers.

NH, USA). The samples (0.2 g) were degassed for 5 h under a flow of N_2 prior to analysis. The surface area ranged between 1.7 and 3.5 $m^2 g^{-1}$, with pore volumes of 0.01 $cm^3 g^{-1}$.

Absorption studies on model water samples

The relatively non-polar cavity in comparison to the polar exterior enables CDs to form inclusion compounds with hydrophobic guest molecules in aqueous solution. The interaction between the CD and the organic guest is believed not to contain any covalent bonding interaction, and be driven mostly by the enthalpy increase of displacing water from the CD cavity to the bulk.^{19,20} A second important factor influencing binding is geometric and polar compatibility of the guest molecule with the cavity of the CD.^{21,22}

Functionalisation of the CD rims should in future allow us to modify the binding capacity of the polymers to allow for extraction of more polar pollutants, and hopefully allow us to tailor the material to future applications for removing both anions and cations. Currently anions are difficult to extract using CDs since their binding to either the negatively charged surface or the non-polar cavity is not favourable, but here again we are developing cationic surface modifications to improve this.

Apart from removing a variety of organic compounds to $ng L^{-1}$ levels, the polymers can be synthesized into various forms (e.g. powders, gels, films) thus providing ease of use.^{6,8}

A simple and convenient way of testing the absorption efficacy of the polymers was to use 'artificially polluted' water samples containing known amounts of organic contaminants. The pH of the water samples was measured in order to determine the pH for the extraction of the pollutants. Although the formation of CD complexes is known to be influenced by pH, our aim was to closely match conditions in

the "real" water samples from rivers and reservoirs where pH generally varied over the range pH = 5.8 to 7.8. The average pH of the test solutions was found to be pH = 6.5, hence no adjustment was made.

Table 1 shows the concentration of organic pollutant remaining after filtering a 20 $\mu g L^{-1}$ standard using α -, β -, γ -CD(HMDI) polymers and GAC. The results indicate that the α -, β -, γ -CD(HMDI) polymers absorbed 99% of the organic compounds from the water, but all the pollutants could still be detected after treatment with GAC (although at very low levels).

A detailed analyses of the results indicated that only naphthalene ($R_t = 9.3$ min) and 1,3-dichlorobenzene ($R_t = 7.8$ min) were detected after absorption with α -CDHDI and γ -CDHDI polymers, respectively. Tests are underway to model the fit of naphthalene molecules in the cavities of the α -CDHDI polymers to determine if the small cavity size could be the problem.

In a similar manner, a comparative study involving TDI-linked α -, β -, and γ -CD polymers and GAC was carried out, and the results are summarized in Table 2.

As observed with α -CD(HMDI) polymer, naphthalene and 1,3-dichlorobenzene were the only pollutants detected after percolation through the α -, and the γ -CD(TDI) polymers, respectively, while most of the pollutants were still detectable after the GAC treatment.

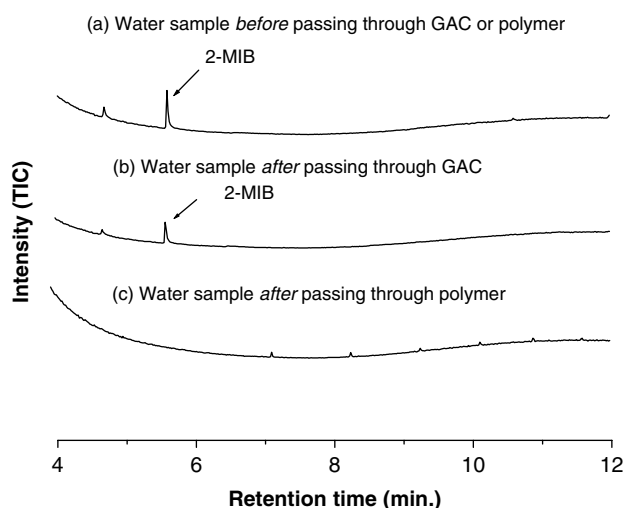
The results in Tables 1 and 2 indicate that both the HDI- and TDI-linked α -, β -, and γ -CD polymers were effective in the removal of the organic contaminants from a 20 $\mu g L^{-1}$ water sample. However, the compounds could still be detected after treatment of the same water sample with GAC. This generally indicates that GAC is less effective at such low levels of concentrations.

Table 1. Amounts of organic contaminant remaining after treatment of 20 $\mu g L^{-1}$ contaminated water samples using HMDI-linked CD polymers and GAC

Organic contaminant	Absorbing material used:			
	α -CDHDI	β -CDHDI	γ -CDHDI	GAC
	Remaining pollutant concentration			
Phenol	–	–	–	<100 $ng L^{-1}$
2-Chlorophenol	–	–	–	<100 $ng L^{-1}$
1,3-Dichlorobenzene	–	–	<100 $ng L^{-1}$	<100 $ng L^{-1}$
2-Nitrophenol	–	–	–	<100 $ng L^{-1}$
2,4-Dimethylphenol	–	–	–	<100 $ng L^{-1}$
Naphthalene	<100 $ng L^{-1}$	–	–	<100 $ng L^{-1}$
4-Chloroaniline	–	–	–	<100 $ng L^{-1}$
2,4,6-Trichlorophenol	–	–	–	<100 $ng L^{-1}$
2,4,5-Trichlorophenol	–	–	–	<100 $ng L^{-1}$
2,4-Dichlorophenol	–	–	–	<100 $ng L^{-1}$
Pentachlorophenol	–	–	–	<100 $ng L^{-1}$
- Could not be detected (less than 10 $ng L^{-1}$)				
<100 $ng L^{-1}$ – concentration too low to quantify accurately (below LOQ)				

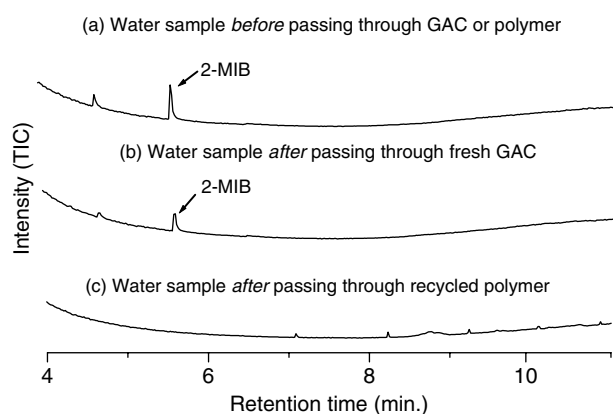
Table 2. Amounts of organic contaminant remaining after treatment of 20 µg L⁻¹ contaminated water samples using TDI-linked CD polymers and GAC

Organic contaminant in water sample	Absorbing material used:			
	α-CDTDI	β-CDTDI	γ-CDTDI	GAC
	Remaining pollutant concentration			
Phenol	-	-	-	<100 ng L ⁻¹
2-Chlorophenol	-	-	-	<100 ng L ⁻¹
1,3-Dichlorobenzene	-	-	<100 ng L ⁻¹	<100 ng L ⁻¹
2-Nitrophenol	-	-	-	-
2,4-Dimethylphenol	-	-	-	<100 ng L ⁻¹
Naphthalene	<100 ng L ⁻¹	-	-	<100 ng L ⁻¹
4-Chloroaniline	-	-	-	<100 ng L ⁻¹
2,4,6-Trichlorophenol	-	-	-	-
2,4,5-Trichlorophenol	-	-	-	<100 ng L ⁻¹
2,4-Dichlorophenol	-	-	-	<100 ng L ⁻¹
Pentachlorophenol	-	-	-	<100 ng L ⁻¹
- Could not be detected (<10 ng L ⁻¹)				

**Figure 4.** Chromatograms showing (a) 20 ng L⁻¹ water sample (b) treated with 500 mg GAC and (c) treated with 50 mg β-CD(HMDI) polymer.

Analysis of 2-MIB

The β-CD polymers consistently performed the best in the standard tests and were used for the remaining investigations. A 20 ng L⁻¹ spiked water sample of 2-MIB (prepared from a 200 µg L⁻¹ standard provided by Rand Water Laboratories, Glenvista, South Africa) was distinctly identified in our system (either by comparison with library spectra, retention time, or using the $m/z = 95$ peak). Multiple injections of the extracts of this sample gave reproducible results and all chromatograms of the 2-MIB samples could be confidently reported in the same scale of the total ion count. Treatment of water samples spiked with 2-MIB (20 ng L⁻¹, 500 mL) with one tenth the amount of polyurethanes (50 mg) showed that the polymers absorbed 99% of the pollutant (Figs 4 and 5) compared to GAC (500 mg). This is significant since the GAC is currently used by local water treatment plants for removing 2-MIB and other odour-causing chemicals. The 2-MIB concentration decreased by

**Figure 5.** Chromatograms showing (a) 100 ng L⁻¹ water sample; (b) after absorption with GAC; and (c) after absorption with a recycled β-CD(TDI) polymer.

about 75% when filtering through GAC, but it was still clearly detectable in all samples.

Comparing the performance of a recycled polymer with fresh GAC

One of the unique features of the nanosponge polymers is that they can be recycled by washing with ethanol (*ca.* 50 mL for the 500 mg columns), followed by rinsing with deionized water and drying with air or nitrogen.

Remarkably the polymers do not lose their ability to remove pollutants. Figure 5 shows chromatographs of samples treated with fresh GAC (b) and a recycled β-CD(TDI) polymer (c). The results obtained demonstrate that the recycled CD polymers are still more effective at removing 2-MIB at the ng L⁻¹ level than fresh GAC.

Apart from the GC/MS analyses of the 2-MIB samples the absence of the musty smell in the treated samples confirmed the effectiveness of the polymers. The musty odour was, however, detected on the used polymers after drying, indicating that the polymers were more effective when wet.

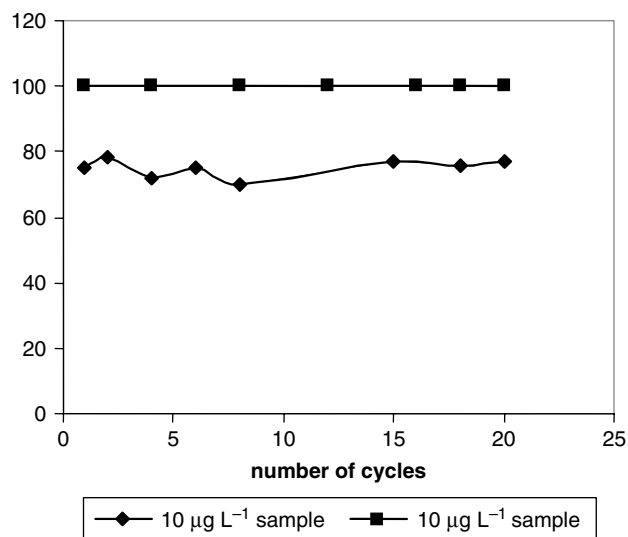


Figure 6. The amount of organic pollutant removed after treating 500 mL of a spiked water sample with β -CD(HMDI) polymer.

Absorption studies on environmental water samples

The polymers were also tested on *raw water* samples obtained from the Rietvlei Dam, to verify if there is any competitive absorption of pollutants. Naphthalene, 2,4-dichlorophenol and pentachlorophenol were monitored for this initial study. Again we concentrated on the β -CD(HMDI) and (TDI) polymers because of the better performance observed in the previous investigation. The levels of these pollutants were only around 10 to 20 ng L⁻¹, but again the initially detected naphthalene ($R_t = 9.3$ min), 2,4-dichlorophenol ($R_t = 11.0$ min) and pentachlorophenol ($R_t = 12.9$ min) could no longer be detected after treatment with the CD polymers. This indicates that the polymers effectively remove selected organic pollutants, even in the presence of other contaminants.

Recycleability studies of the CD polymers

Studies on the recycleability or regeneration of the CD polymers were performed using the β -CD(HMDI) polymers. The objective here was to find out how effective the polymers would be at removing the organic contaminants from water after a number of cycles of use.

Studies were performed by flushing 500 mL of a 10 mg L⁻¹ pentachlorophenol solution through a RSSCT column packed with 500 mg of the polymer. The recycleability was also investigated under much lower concentrations typically found in polluted water (i.e. using a 10 µg L⁻¹ standard water sample). Experiments were performed to the twentieth cycle for both concentrations, and Fig. 6 shows that the polymers maintained their efficiency even after 20 cycles. The polymers were recycled by soaking with 10 mL of ethanol for 30 min, followed by flushing with more ethanol (10 mL) and then drying before performing the next experiment. A fresh sample of spiked water was used after each cycle. As part of

a longer-term study the polymers are being tested using other pollutants such as *p*-nitrophenol and 1,1,1-trichloroethylene. Again the polymers remain effective up to a sufficiently high number of cycles (25 cycles). This ongoing investigation is also looking at the biodegradation of the polymers to determine if the use of toxic starting materials such as diisocyanates has any detrimental environmental impact, especially if discarded. Initial results are promising, indicating minimal environmental concerns for the disposal of the spent polymers once they have been cleaned of trapped pollutant.

CONCLUSIONS

The work reported herein demonstrates the absorption capacity of CD polymers at quenching organic pollutants over a wide concentration range (from 10 mg L⁻¹ to 10 ng L⁻¹). Comparative studies using activated carbon reveal that the polymers supersede GAC at removing the organic pollutants at very low concentration levels. A further advantage of the CD polyurethanes is that they can be recycled a number of times without losing their efficiency, which is not easily done with GAC. The results also show that the CD polymers have a tremendous potential in quenching taste and odour-causing compounds from drinking water, and further studies in this regard are ongoing. Experiments involving testing the performance of these polymers using larger volumes of water on a much broader range of pollutants are also in progress.

ACKNOWLEDGEMENTS

The authors wish to thank the University of Johannesburg, the National Research Foundation (NRF), and the Water Research Commission (WRC) for funding this work. Donations and assistance from Rand Water are also gratefully acknowledged.

The paper was presented in part at the 10th Green Chemistry and Engineering Conference, Washington, 2006.

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