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ORIGINAL PAPER

Monofunctionalized cyclodextrin polymers for the removal of organic pollutants from water

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Abstract Water is an important resource for domestic, industrial, agricultural and recreational purposes. The quality of water is however significantly deteriorating due to the accumulation of organic pollutants in aqueous systems. Conventional water treatment technologies fail to remove these contaminants to desirable levels. Recent studies have revealed that cyclodextrin nanoporous polymers are capable of absorbing pollutants from water to parts per billion levels. We have demonstrated that functionalised cyclodextrin polymers have enhanced absorption capacities for some organic pollutants. Here we report the synthesis of several insoluble monosubstituted cyclodextrin polymers or "nanosponges". We show that these polymers have improved abilities in the absorption of *p*-nitrophenol and pentachlorophenol from aqueous solutions.

Keywords Monofunctionalized cyclodextrins · Nanoporous polymers · Nanosponges · Organic pollutants · Water treatment

Introduction

Cyclodextrins (CDs) are biosynthetic cyclic oligomers consisting of anhydrous glucopyranosyl units linked together through α-1,4-glycosidic linkages. They are basically starch derivatives obtained through the enzymatic degradation of starch by glycosyl transferase of *Bacillus macerans* (Croft and Bartsch 1983). The three most common CDs are α-, β- and γ-CDs. They consist of six, seven and eight glucose units, respectively. Although CDs consisting of more glucose units are also known, their costs prohibit their use in practical applications. CDs have characteristic toroidal shapes that form well-defined cylindrical cone-shaped cavities (Fig. 1). Whilst their exteriors are hydrophilic, their interiors are hydrophobic.

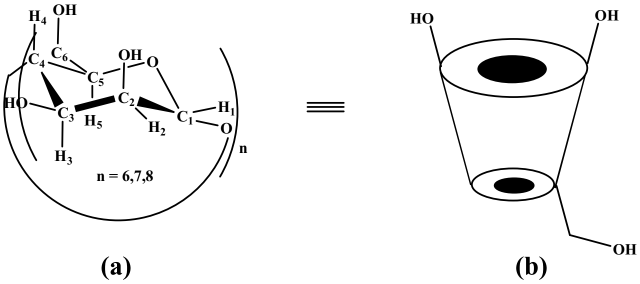

Fig. 1 Structure of the α-, β-, and γ-cyclodextrin (**a**) and illustration of their cylindrical shape (**b**)

The CD rings are about 8 Å deep and 5–10 Å in diameter, depending on the number of glucose units. CDs are also capable of interacting with a range of guest molecules within their cylindrical hydrophobic cavities (Bender and Komiyana 1978). These interactions are a basis for the inclusion of various organic species. The structures of the formed complexes are largely dependent on the sizes of the cavities of the CDs. However, the high solubility of cyclodextrins limits their application in the removal of organic pollutants from water. To make them insoluble, Li and Ma (1999) converted them into highly cross-linked polymers by polymerizing CDs with suitable bifunctional linkers.

Most modifications of CDs take place at the hydroxyl groups (OHs). There are basically three types of OHs present in the CD; two secondary OHs (at positions 2 and 3) and one

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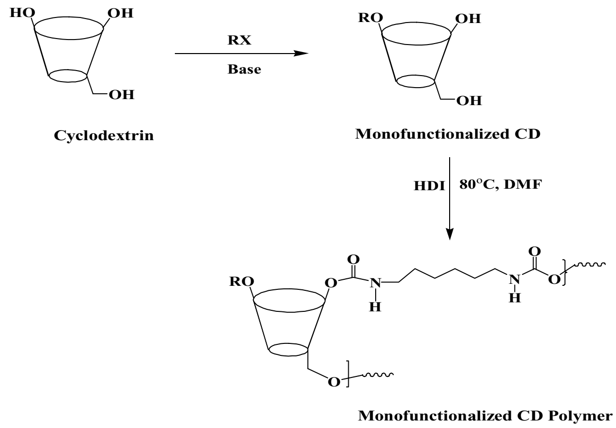

Scheme 1 Synthetic pathway for a monofunctionalized CD polymer with hexamethylene diisocyanate (HDI)

primary at position 6. Among these types of OHs, those attached to C-6 are the most basic and thus the most nucleophilic. Those at C-2 are most acidic and those at C-3 are the most inaccessible. According to Szejtli (1998a, b), an electrophilic reagent attacks at the most reactive OH-6. The OH-2 are the most susceptible to being deprotonated to form a nucleophilic oxyanion.

In this study, the reactivity of the hydroxyl groups was exploited by forming a series of 2- and 6-monosubstituted CDs. However, the significance of this modification is only realized once the solubility and absorption capability of the resulting polymers have been established. The process entails monofunctionalization of the hydroxyl groups of the parent CD compound followed by cross-linking with the appropriate bifunctional linker to give the desired nanoporous polymer (Scheme 1).

Experimental

Materials

Unless otherwise indicated, β-cyclodextrin and all the other reagents were obtained from commercial suppliers and utilized without further purification. All reactions were performed under nitrogen or argon using pre-dried and distilled solvents. *N*,*N*-Dimethylformamide (DMF) was dried over calcium hydride for 2 days and then distilled under reduced pressure over calcium sulphate before usage. TLC was performed on aluminium sheets precoated with a 0.25 mm layer of silica F_{254}. TLC eluant used for the cyclodextrin derivatives was $A = 5{:}4{:}3$ butanol/ethanol (95%)/water and $B = 4{:}1$ acetonitrile/water. TLC spots were visualized under a ultraviolet lamp (254 nm and/or 365 nm) or dipped in 5% H_2SO_4 in ethanol followed by heating on a hot plate.

Instrumentation

All NMR spectra were recorded at 300 MHz on a Varian Gemini 2000 spectrometer, unless stated otherwise. Proton and carbon chemical shifts are reported in parts per million (ppm) using the residual signal DMSO ($\delta = 2.49$ ppm for ^{1}H and 39.5 ppm for ^{13}C) or TMS ($\delta = 0$) as the internal reference. All the ultraviolet (UV) experiments were carried out using a Varian UV-Visible Cary 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 chromatograph and Saturn 2000 ion-trap mass spectrometer were used for quantification of the organic contaminant. The GC was equipped with a Chrompack CP Sil 8 CB, 30 m × 0.25 mm capillary column with an internal diameter of 0.25 μm. DSC analyses of the polymers were performed with a Mettler Toledo DSC 822^e analyzer. The samples were heated at a constant rate of 10°C/min in a DSC pan and the average mass of each sample was 15 mg. The TGA analyses were carried out on a Perkin Elmer instrument with a heating rate of 10°C/min in the temperature range 50–800°C in nitrogen gas.

Preparation of cyclodextrin derivatives

Mono-6-tosyl β-cyclodextrin (6-CDOTs) (2): This compound was prepared as previously synthesized (Zhong et al., 1998), with minor modifications. β-CD (2.86 g, 2.53 mmol) and *p*-toluene sulfonic anhydride (Ts_2O) (1.24 g, 3.80 mmol) in 62.5 mL of distilled water was stirred under inert atmosphere for 2 h at ambient temperature. A solution of NaOH (1.25 g in 12.5 mL of water) was then added. After 10 min, unreacted Ts_2O was removed by filtration through silica gel. pH of the filtrate was adjusted to 8 by the addition of ammonium chloride (3.36 g), affording **3** as a white precipitate that was collected after cooling overnight in the refrigerator before drying under vacuum. 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}H NMR/ppm, DMSO-$_{d6}$: 7.76 (d, H_{Ar}, 2H), 7.44 (d, H_{Ar}, 2H), 4.50 (s, OH-6, 5H), 4.20 (m, H-6), 4.33 (m, H-6), 3.76 (d, H-5), 3.29 (t, H-4), 5.71 (m, OH-3, 7H), 3.57 (t, H-3), 5.71 (m, OH-2, 7H), 3.21 (m, H-2), 4.65 (d, H-1, 7H), 2.42 (s, -CH_3, 3H); ^{13}C NMR/ppm, DMSO-$_{d6}$: 144, 132, 129, 127 (C_{Ar}), 101 (C-1), 79.3 (C-2), 61.6 (C-3), 81.0 (C-4), 72.3 (C-5), 68.6 (C-6), 21.0 (-CH_3); Yield = 2.25 g, 1.75 mmol, 69%; M.pt = 172–176°C; TLC: Eluant A, $R_f = 0.50$.

Mono-6-diaminoethyl β-cyclodextrin (6-CDOAm) (3): Compound **2** (1.01 g, 0.783 mmol) was dissolved in DMF (20 mL) and diaminoethane (0.317 g, 1.76 mmol) was added dropwise with stirring. The resulting solution was stirred for 8 h at 70°C under argon gas. The resulting solution was concentrated under reduced pressure by removal of DMF. Addition of acetone (100 mL) led to the precipitation of a yellow-brown compound, which was then filtered-off and dried under vacuum. Recrystallization from hot water yielded the title compound as a yellow brown solid in reasonably high yields. IR/KBr, cm^{-1}: 3328 (O–H, NH), 2924 (C–H), 1657 (C=O), 1022 (C–O); ^{1}H NMR, DMSO-$_{d6}$: 5.80–5.50 (m, OH-2, OH-3), 4.81 (s, H-1, 7H), 4.46 (s, br, OH-6, 6H), 3.72–3.45 (m, H-6, H-5, H-3), 3.42–3.20 (m, H-4, H-2), 2.07 (s, br); ^{13}C NMR, DMSO-$_{d6}$: 101 (C-1), 88.9 (C-4), 73.7 (C-5), 72.8 (C-3), 72.8 (C-4), 59.1 (C-6), 54.1 (NH-*C*), 48.2 (NH$_2$-*C*); Yield: 0.63 g, 0.528 mmol, 67%; M.pt = 192–195°C (dec); TLC: Eluant A, R$_f$: 0.58.

Mono-6-acetyl β-cyclodextrin (6-CDOAc) (4): β-CD (3.01 g, 2.64 mmol) was dissolved in DMF (50 mL) and acetyl chloride (0.19 mL, 2.64 mmol) was added dropwise. On dropwise addition of diisopropylamine (0.45 mL, 2.64 mmol) to the stirred reaction mixture, the colour changed immediately to yellow brown. This solution was stirred for 2 h at -30°C under a stream of argon gas. The mixture was then left to stand at room temperature (RT) for a further 14 h under a weak stream of argon. The solution was concentrated under reduced pressure to about 20 mL. Dichloromethane (200 mL) was added to the resulting white precipitate. The precipitate was filtered off, washed with CH_2Cl_2 and dried under vacuum to yield a white solid material. IR/KBr, cm^{-1}: 3384 (O–H, br), 2925 (C–H, sharp), 1651 (C=O), 1032 (C–O, sharp); ^{1}H NMR, DMSO-$_{d6}$: 5.71 (br, OH-2, 7H), 5.67 (br, OH-3, 7H), 4.81 (s, H-1, 7H), 4.46 (s, OH-6, 6H), 3.61–3.47 (m, H-3, H-5, H-6), 3.39–3.22 (m, H-4, H-2), 2.07 (s, CH$_3$, 3H); ^{13}C NMR, DMSO-$_{d6}$: 162 (C=O), 101 (C-1), 81.6 (C-4), 73.1 (C-3), 72.5 (C-2), 72.1 (C-5), 59.9 (C-6), 34.1 (-CH$_3$); Yield: 2.30 g, 1.95 mmol, 74%; M.pt = 160–164°C (dec); TLC: Eluant B, R_f:0.76.

Mono-2-methyl β-cyclodextrin (2-CDOMe) (5): β-CD (2.00 g, 1.76 mmol) was dissolved in DMF (20 mL) and NaH (0.317 g, 1.76 mmol) was added in one portion with stirring. The resulting milky reaction was left overnight at RT. Methyl iodide (0.16 mL, 0.375 g, 2.64 mmol, 1.5 molar equivalents) was added to this oxyanion. The reaction was stirred for a further 24 h at 70°C under argon. DMF was then concentrated under vacuum, followed by addition of acetone (100 mL) and suction filtration. After washing with acetone and drying, the desired CD derivative was obtained as a white solid material. IR/KBr, cm^{-1}: 3380 (O–H), 2919 (C–H), 1651 (C–C), 1406, 1157, 1032 (C–O), 937, 750–601; ^{1}H NMR, DMSO-$_{d6}$: 5.51 (d, OH-2, 6H), 5.44 (s, OH-3, 7H), 4.85 (s, H-1, 7H), 4.48 (s, OH-6, 7H), 3.76 (m, H-5, 7H), 3.63–3.56 (m, H-6, H-4, 14H), 3.40–3.26 (m, H-3, H-2, 21H), 1.23 (s, -CH$_3$, 3H); ^{13}C NMR, DMSO-$_{d6}$: 102 (C-1), 82.2 (C-4), 73.5 (C-3), 72.9 (C-5), 72.4 (C-2), 60.4 (C-6), 53.8 (-CH$_3$); Yield: 1.01 g, 0.870 mmol, 49%; M.pt = 205–207°C; TLC: Eluant A, R_f:0.38.

Mono-2-benzoyl β-cyclodextrin (2-CDOBz) (6): β-CD (2.00 g, 1.76 mmol) was dissolved in DMF (20 mL) and NaH (0.317 g, 1.76 mmol) was added in one portion with stirring. The reaction was left stirring overnight at RT. Benzoyl chloride (0.20 mL, 0.25 g, 1.76 mmol) was then added to the resulting clear solution. The reaction was stirred for a further 24 h at room temperature under nitrogen gas. After the addition of acetone (100 mL), filtration and drying, white granules of the title compound were obtained at a yield of 58%. IR/KBr, cm^{-1}: 3382 (O–H), 2926 (C–H), 1660 (C=O), 1554, 1403, 1308, 1232, 1016 (C–O); ^{1}H NMR, DMSO-$_{d6}$: 7.56 (d, H-8, 2H), 7.22 (d, H$_{Ar}$, 2H), 7.40–7.44 (m, H$_{Ar}$), 5.56–5.80 (m, OH-2, OH-3), 4.81 (s, H-1, 7H), 4.30 (d, OH-6, 7H), 3.41–3.72 (m, H-6, H-5, H-3), 3.37–3.21 (m, H-4, H-2, overlap with H_2O); ^{13}C NMR, DMSO-$_{d6}$: 157 (C=O), 144, 132, 129, 127 (C$_{Ar}$), 101 (C-1), 81.5 (C-4), 72.4 (C-5), 73.1 (C-3), 72.0 (C-2), 59.9 (C-6); Yield: 1.27 g, 1.02 mmol, 58%; M.pt = 188–190°C (dec); TLC: Eluant A, R_f:0.68.

General procedure for preparation of polymers

A monofunctionalized CD (3, 4, 5 and 6) was reacted with a DMF solution of hexamethylene diisocyanate (HDI) and toluene-2,4-diisocyanates (TDI) in a 1:8 molar ratio. The solution was heated at 70°C for 16–24 h under inert conditions. Filtration and washing of the resulting material with copious amounts of acetone to remove residual DMF led to the isolation of solid granules. These were then dried overnight under high vacuum to generate the target polymers in quantitative yields (90–100%).

Results and discussion

Synthesis and characterization of monofunctionalized CDs

Cyclodextrin monotosylates are generally important precursors for a variety of modified CDs. This is because nucleophiles can attack the electrophilic carbon (C-6) to produce the corresponding monofunctionalized derivatives. The monotosylation at the primary side was accomplished (69% yield) by treatment of the β-cyclodextrin with *p*-toluene sulfonic anhydride in an alkaline solution. According to Zhong et al. (1998), this reaction is accompanied by the formation of an inclusion complex between the Ts_2O and the CD moiety before the addition of NaOH solution. The anhydride method was adopted in this study because it is less complicated and affords the target compound at superior yields.

The structure of the mono-6-tosyl β-cyclodextrin was confirmed by IR and NMR spectroscopy. The ^{1}H NMR spectrum of the monotosylate precursor showed, in the aromatic region, the characteristic pattern of a tosyl system. The 6-hydroxyl substitution was also confirmed by the reduction in the integration (4.45 ppm) of the peak due to the OH-6 protons. The carbon linked to the tosyl group appeared downfield (68.6 ppm) relative to the neighbouring C-5 (72.3 ppm) (Breslow 1982). The structure was further confirmed by the emergence of the aromatic peaks at 144, 132, 129 and 127 ppm. Furthermore, the IR spectra showed the S=O asymmetric and symmetric stretches at 1295 and 1157 cm^{-1}, respectively.

Treatment of compound **2** with diaminoethane in DMF at elevated temperatures (70°C) led to the formation of the CD derivative **3**. Recrystallization in hot water afforded this compound in good homogeneity and in satisfactory yields. In this reaction, the tosyl group is displaced through nucleophilic substitution by the diaminoethyl group. The disappearance of the tosyl group in the aromatic region of both the ^1H and ^{13}C NMR spectra provided evidence for successful CD amination.

The acetylation method was adopted with minor adjustments from a previous procedure (Sutyagin et al. 2000). The reaction involved the reaction of a DMF solution of β-CD with acetyl chloride (as an acetylating reagent) in the presence of a hydrochloric acid acceptor (diisopropylamine). The reaction was performed at very low temperatures (− 30°C). Yet again, it was easily concluded from the spectroscopic techniques that the acetyl group was successfully incorporated onto the CD backbone. The emergence of a sharp peak (1651 cm^{-1}) and a small signal 162 ppm in the respective IR and ^{13}C NMR spectra of the target compound were identified as the carbonyl group. In addition, there was a new carbon peak at 34.1 ppm which was assigned to methyl carbon of the acetyl group.

The feature of the acidity of the C-2 hydroxyl groups was exploited by deprotonating them with sodium hydride (NaH), a strong base, under anhydrous conditions. Thus, addition of benzoyl chloride to the oxyanion formed produced the corresponding ester (6) in a yield of 63%. The aromatic signals in the region 7.56–7.40 ppm (doublet) and a multiplet at 7.20 ppm (representing all the other aromatic protons of the ring) were observed. Successive appearance of the carbons at four different regions in the ^{13}C NMR spectrum accounted for all the carbon peaks including the quaternary carbon (157, 127, 129, 132 and 144 ppm), confirmed successful incorporation of the benzoyl group. The benzoyl group was successfully built-in to the backbone of the CD in the 2-position. A carbonyl (C=O) peak was observed in the IR and ^{13}C NMR spectra at 1660 cm^{-1} and 157 ppm, respectively.

Finally, mono-methylation of the β-CD was achieved by the addition of methyl iodide to the nucleophilic oxyanion. The methyl ether **5** was produced at reasonably high yields (49%) under non-optimized conditions. The ^{13}C NMR spectrum shows an additional peak at $\delta = 53.8$ ppm assigned to the methyl group carbon.

Synthesis and characterization of monofunctionalized CD polymers

Nanoporous polymers were then prepared from the monofunctionalized CDs. All the nanosponges were found to be insoluble in water and it was therefore impossible to do the characterization of these compounds with the NMR instrument at our disposal. NMR characterization can only be achieved by solid-state NMR spectroscopy. Characterization in this study was however performed by IR spectroscopy. The diisocyanate peak at 2270 cm^{-1} was reduced significantly as the reaction was progressing. On average this peak disappeared completely after 22 h. The appearance of bands at about 3370 cm^{-1} (N–H), 1600 cm^{-1} (C=O) and 1530 cm^{-1} (C–O) also confirmed the successful synthesis of the derived nanosponges. The synthesis and characterization of all the other HDI- and TDI-linked derivatives were carried out using a similar approach.

Thermal analysis

The thermal behaviour of all the monofunctionalized CD polymers was observed to be generally the same. Differences could only be found in the water loss, onset temperatures and mass loss at given temperatures. Thermoanalytical profiles of these compounds are divided into four different regions, which suggest a four-step process. These steps are interpreted as follows: The first step, which occurred from ambient temperature to 250°C, can be interpreted as loss of water. The second (300°C) and third (410–500°C) weight loss steps account for most of the weight loss and are associated with the formation of a residue of the CD polymer. The fourth step, which occurred at temperatures over 500°C, symbolizes a relatively slow degradation nature of the polymer residue.

Generally, all the DSC curves of the polymers show two endothermic peaks; one at 95°C corresponding to the boiling point of water and the other small endotherm appeared at around 250°C corresponding to the melting point of the polymers. Degradation of the polymers occurred at temperatures above 300°C. The TGA and DSC results reveal that the monofunctionalized CD polymers have similar thermal stabilities with their unsubstituted counterparts.

Absorption studies

UV-Visible spectroscopy results

An investigation of the absorption capability of these polymers was accomplished by modelling contamination experiments. The phenolic compounds were chosen for this study as model pollutants because they have been found to be ubiquitous environmental pollutants particularly in aqueous systems (Macalady 1998; Dubroca et al. 2005). *p*-Nitrophenol

Table 1 Results obtained after treating 10 mg/L PNP water samples with monofunctionalized HDI- and TDI-linked β-CD polymers

Polymer	Conc. after abs. (C)/mg/L	Abs. efficiency $\frac{C_o - C}{C_o} \times 100\%$
CDHDI	4.20	58
2-CDOBz/HDI	3.10	69
6-CDOAc/HDI	3.52	65
2-CDOMe/HDI	5.00	50
6-CDOAm/HDI	4.21	58
CDTDI	4.30	57
2-CDOBz/TDI	2.95	70
6-CDOAc/TDI	4.77	52
2-CDOMe/TDI	4.90	51
6-CDOAm/TDI	4.73	53

Table 2 Results obtained after treating 100 μg/L PCP water samples with monofunctionalized HDI- and TDI-linked β-CD polymers

Polymer	Conc. after abs. (C)/mg/L	Abs. efficiency $\frac{C_o - C}{C_o} \times 100\%$
CDHDI	ND	>99
2-CDOBz/HDI	ND	>99
6-CDOAc/HDI	20	80
2-CDOMe/HDI	28	78
6-CDOAm/HDI	10	90
CDTDI	ND	>99
2-CDOBZ/TDI	5	95
6-CDOAc/TDI	ND	>99
2-CDOMe/TDI	22	78
6-CDOAm/TDI	30	70

(PNP) is highly soluble in water and can be easily monitored by UV-Visible spectroscopy. The absorbances of the PNP water samples were measured before and after treatment of standard solutions with the CD polymers. Typically, 300 mg of the monofunctionalized polymer was weighed and placed in 250 mL Erlenmeyer flask. To the flask, 200 mL of the PNP standard sample (10 mg/L) was carefully added and sealed with a rubber stopper. The flask and its content were stirred for 30 min with a mechanical stirrer at a constant rate and thereafter filtered using Whatman-5 ashless filter paper.

While the polymers were in solution, it was also observed that they gradually assumed the yellow colour of the organic compound. The absorbance of the filtrate was then measured. Finally, the calibration curve obtained was used to determine the residual pollutant concentration of each sample from which the amount of the pollutant absorbed by the polymer was determined.

As shown in Table 1, the highest absorption efficiencies of the PNP samples observed are 70 and 69% and these are associated with 2-CDOBz/HDI and 2-CDOBz/TDI polymers, respectively. The amount of pollutant removed by these polymers seems to be higher than that removed by the unfunctionalized polymers (58 and 57%, respectively). The methylated polymers (2-CDOMe/HDI and 2-CDOMe/TDI) have the lowest efficiencies (50 and 51%, respectively). The average absorption efficiencies of all the HDI-linked polymers (60%) and TDI-linked polymers (57%) were determined to be similar to those of the unfunctionalzed polymers.

GC/MS analysis

Samples of much lower concentrations were prepared by spiking deionized water with known concentrations (100 μg/L) of the organic pollutant (pentachlorophenol). Before any analysis of trace compounds could be carried out, pre-concentration of the samples was performed by solid-phase extraction. The pre-concentration Method 525.2 of the Environmental Protection Agency (EPA), which is used for the determination of a wide variety of semi-volatile organics including PAHs, pesticides and PCBs in drinking water, was used. The pre-concentration procedure consists of the following four steps: washing/conditioning, sample loading, washing and finally elution. Quantification of extracted sample was carried out using GC/MS. Our GC/MS demonstrated very low detection limit (up to 10 ng/L), which make it particularly suitable for this study.

A summary of the absorption efficiencies of different monofunctionalized polymers on a 100 μg/L pentachlorophenol (PCP) sample is outlined in Table 2. These nanosponges demonstrate high absorption efficiencies ranging between 70 and 100%. These values are favourably comparable to the absorption efficiencies of the unfunctionalized CD polymers. This suggests that the introduction of the various functional groups to the backbone of the polymer did not alter their absorption capabilities. While 6-CDOAm/TDI has the lowest absorption efficiency (70%), the average absorption percentage of the HDI-linked polymers is 90% and that of the TDI-linked polymers is 89%.

Another important observation is that the 2-substituted polymers are generally better in absorption of both organic pollutants investigated compared to the 6-substituted polymers.

An inferior absorption efficiency was observed for PNP at high concentration (i.e. mg/L levels). This confirms earlier studies, that the CD polymers are only effective at low concentrations (i.e. μg/L levels). At such high concentrations it is likely that the polymers easily get saturated and lose their effectiveness. The performance of the polymers can however be improved by performing recycling experiments.

Conclusion

A wide variety of insoluble monofunctionalized CD polymers were successfully prepared in quantitative yields using straightforward procedures. The polymers were characterized mainly by infra-red spectroscopy due to the insoluble nature of the nanoporous polymers. These nanosponges are extremely effective when lower concentrations of water samples spiked with known organic contaminants were used. As evidenced by the TGA and DSC studies, these polymers are stable over a wide range of temperature (100–400°C). It would be recommended that further work be carried out for the other types of cyclodextrins (α- and γ-CDs) in order to fill the growing need for the development of modified CD polymers. Solid-state NMR techniques are required for full characterization of these insoluble polymeric compounds.

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