Polymer-Immobilized Cyclodextrin Trapping of Model Organic Pollutants in Flowing Water Streams

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ABSTRACT: Epichlorohydrin-crosslinked β-cyclodextrin polymers (BCDPs) were prepared and characterized by Fourier transform infrared. Beads of the BCDPs were used to pack a column for trapping organic contaminants in flowing water (flow rate = 5–32 mL/min). The contaminants were naphthalene (a model for polyaromatic hydrocarbons), naproxen (a model for pollutants of pharmaceutical origin), and 2-naphthol (a model for pesticides with pH-dependent ionization states). The trapping efficiencies were determined with fluorescence spectroscopy as the analytical technique. The best trapping efficiencies were obtained for BCDPs with a nominal cyclodextrin/epichlorohydrin ratio of 1:29. Trapping was highly efficient for naphthalene (98%) and 2-naphthol (70%), but it was much less efficient for naproxen (18%). Possible causes for these differences were examined. The trapped organics could be flushed from the column with an ethanol wash. The recovery of the organics with this approach was very good (>95%). This simple column design, made of inexpensive and reusable materials, has potential applications in water remediation and water sampling. J Appl Polym Sci 90: 2103–2110, 2003

Key words: crosslinking; fluorescence; FT-IR, host-guest systems; inclusion chemistry

INTRODUCTION

Wastewater from industrial and municipal activities contains significant concentrations of inorganic and organic contaminants. Most of these substances are removed with a variety of bioreactor approaches (e.g., filters and activated sludge) during the secondary treatment of the wastewater.[1] As a result, effluent water discharged to the environment tends to be quite free of contaminants. However, secondary treatment has its limitations, and limited amounts of certain species do show up in discharged water. Two classes of compounds that are not fully removed in wastewater treatment plants are polycyclic aromatic hydrocarbons (PAHs)[1] and pharmaceutical materials.[2]

PAHs are very stable organic molecules that enter the environment in a variety of ways. In the atmosphere, they are generated both naturally (volcanoes and forest fires) and as a result of human activity (combustion processes).[3] The deposition of PAH in ground and surface water may result from airborne sources, municipal wastewater discharge, effluent from wood treatment plants, oil spills, and petroleum processing.[3] For example, PAHs containing two to five fused rings were detected in Taiwanese tap water.[4] Naphthalene (NAP) and fluorine were detected in the effluent from municipal wastewater plants in Karak, Jordan, and Montreal, Canada.[1,5] In these latter studies, it was found that the removal efficiencies of PAHs from wastewater were very poor.[1,5]

The U.S. Environmental Protection Agency has classified 17 PAHs as priority pollutants on the basis of their toxicity, high probability of human exposure, and reoccurrence at hazardous sites.[3,6] In particular, the carcinogenicity and bioaccumulation of some PAHs makes their presence in water a subject of significant concern. The elimination of PAHs from our water supplies is clearly a desirable goal.

Other compounds that have recently become of environmental concern are pharmaceuticals.[2,7–9] A special issue of *Toxicology Letters* has recently been devoted to this problem.[10] Pharmaceuticals are designed to elicit a biological response in living organisms. There is also ample evidence that pharmaceuticals do enter the environment. The massive amounts of therapeutic agents consumed make it highly likely that some fraction of these substances, or their metabolites, will enter the environment. For example, common over-the-counter drugs (paracetemol and aspirin) are sold in annual quantities that exceed 1000 tons in both the United Kingdom and Germany.[2] In Denmark, two human therapeutic categories alone [antibiotics and nonsteroidal anti-inflammatory drug (NSAID) analgesics] accounted for 66 tons of consumed drugs in 1995, whereas the veterinary application of growth promoters and antibiotics accounted for about 94 and 50 consumed tons, respectively, in the same year.[7] The

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total usage of veterinary antibiotics in the European Union in 1999 was on the order of 5000 tons,[11] whereas in the United States, the use of livestock antibiotics in 1985 was estimated to be at 8300 tons.[12]

There has also been the direct observation of pharmaceuticals in the environment.[13–15] It has been reported that approximately 80% of the drugs administered at fish farms end up in the environment, and sediment collected under fish pens has been demonstrated to have drug concentrations sufficient to induce antibacterial activity.[16] Richardson and Bowden's[17] study predicted pharmaceutical concentrations to be at or above 0.1 μg/L in the River Lee in England. Pentobarbital, meprobamate, and phensuximide have been measured in an anaerobic ground water plume,[18] and the blood lipid regulator clofibric acid has been detected in tap water in Berlin and in surface waters at various Germans sites.[19–21] Antibiotics,[22,23] steroids,[24,25] and antineoplastic agents[26,27] have all been detected in river and potable water or wastewater. A stream water monitoring program of the U.S. Geological Survey detected veterinary and human antibiotics (e.g., erythromycin and sulfamethoxazole) in 30% of the samples tested, with maximum concentrations on the order of 1–2 μg/L.[15] Other prescription drugs (e.g., codeine and cimetidine) were detected in about 15% of streams at maximum concentrations on the order of 0.05–1 μg/L. The U.S. Geological Survey is currently engaged in similar studies of ground and drinking water in the United States,[28] highlighting the increasing concern over pharmaceutical contamination of the environment.

Although it is still open to some debate, the most likely sources of pharmaceuticals in the environment include agriculture, aquaculture (fish farms), and human therapeutic use.[7,29] Of particular concern in this context are substances that are hydrophilic or that are metabolized into hydrophilic forms. Such materials may readily escape fish farms, may enter ground or surface waters in field runoff, or may pass wastewater treatment plants and be discharged to receiving waters.

Although the mechanisms that introduce pharmaceuticals into the environment remain to be established, it is clear that such compounds can have a negative impact on biota. Ibuprofen shows activity as both an antifungal and an antibacterial agent (against gram-positive species).[30] Streptomycin inhibits the growth of blue-green algae.[31] Crustaceans show particular sensitivity to fish farm antibiotics, and this results in toxicity, reduced adult size, and reduced egg production in some species.[32,33] The limited data on fish show a minimal impact by ibuprofen,[34] but certain agricultural therapeutics, such as furazolidone and macrocyclic lactones, have a negative impact on mosquito larvae and dung degrading insects, respectively.[7,35–37] As in the case of PAHs, it is clearly desirable to eliminate pharmaceuticals and their metabolites from wastewater before discharge.

Current technologies for polishing water involve filtration through activated charcoal[38–40] or employ reverse osmosis.[41–43] Both methods suffer from limitations. Although activated charcoal is effective at adsorbing organic compounds, it is unable to reduce their aqueous concentrations into the parts-per-billion range and is not easily recycled.[44] Also, the adsorption of moisture from the air reduces the ability of charcoal to trap organic molecules. Reverse osmosis requires high pressure and is, therefore, energy-inefficient, and it does not remove all small molecules from water as the membranes are not perfectly semipermeable.[44]

Cyclodextrins (CDs) have also been proposed for use in trapping water-borne organic compounds. CDs are water-soluble, biodegradable, cyclic oligosaccharides that can act as the host component of host–guest complexes with organic molecules. The cavity of a CD provides a relatively hydrophobic space in which an organic guest can be sequestered in an aqueous medium. CDs are known to form moderately stable complexes with a wide range of organics,[45] including a number of important classes of pollutants such as PAHs, phthalic acid esters, and chlorinated biphenyls.[46–48] Furthermore, CDs complex a wide range of small-molecule drugs, including NSAIDs and steroids.[45,49–53]

Typically, the CD cavity binds the guest molecule in a 1:1 complex (N:CD) according to the following equilibrium process:

$$\mathrm{N} + \mathrm{CD} \rightleftharpoons (\mathrm{N} : \mathrm{CD}) \tag{1}$$

where N represents an organic guest. The strength of the complex can be described via the formation constant (K_f):

$$K_f = \frac{[(\mathrm{N} : \mathrm{CD})]}{[\mathrm{N}][\mathrm{CD}]} \tag{2}$$

Because they are water-soluble, simple CDs cannot be used for separations. However, some recent work has investigated the use of polymer-immobilized cyclodextrins (CDPs) to trap organic pollutants. For example, phthalic acid esters were found to be strongly adsorbed by columns of epichlorohydrin-crosslinked β-cyclodextrin polymers (BCDPs), as were several phenols.[47,54] The adsorption capacity was comparable to that of activated charcoal. Thin films of nanoporous CD polymers have also been examined.[44] They were found to be effective at trapping 4-nitropenhol and the model pollutants toluene and trichloroethylene. Again, the adsorption properties compare well with those of charcoal and molecular sieves. One advantage of both types of CD systems is that the trapped or-

ganic compound can be recovered by the flushing of the solid material with an alcohol. The pollutant material can then be analyzed or discarded, and the CDP can be reused.

An additional advantage of the CDP strategy is the size tunability of the trapping sites. Underivatized CDs are available in three different size cavities. The cavity dimensions (wider cavity opening and cavity length) are 0.57 and 0.79 nm for α-CD, 0.78 and 0.79 nm for β-CD (BCD), and 0.95 and 0.79 nm for γ-CD.[45] Therefore, within the constraints of these sizes, a CDP can be synthesized with size-tuned sites, tailor-made to selectively trap pollutants in a particular size range.

The goal of this contribution is to assess if it is possible to extend the usefulness of the BCDP approach to other classes of pollutants. In particular, we are interested in PAHs and pharmaceutical materials. This selection is not to imply that PAHs and pharmaceuticals are comparable contaminants. Clearly, they behave as pollutants in rather different fashions. Nonetheless, these designations do represent pollutants of current concern. As such, we have carried out a study with BCD crosslinked with epichlorohydrin and used this material to trap a model PAH (NAP) and a model NSAID drug [naproxen (NAX)]. We have also used 2-naphthol (NAO) as a model for pesticides that are subject to acid–base equilibria in natural waters and as a comparison with earlier work.[54,55] All three model pollutants are NAPs and, as such, are readily analyzed by fluorescence spectroscopy.

EXPERIMENTAL

Materials

NAP (Fluka; 99%), NAX (Fluka; 98%), epichlorohydrin (Aldrich; 99%), and sodium hydroxide (BDH AnalR) were used as received. Naphthol (NAO; Fluka; 99%) was recrystallized twice from water. BCD (Aldrich) was vacuum-dried at 60°C for 24 h. Poly(epichlorohydrin) (Aldrich; weight-average molecular weight = 700,000) was ground into small (ca. 1 mm diameter) particles before use. Ethanol and other solvents were of the highest quality commercially available and were used as received. The water was conductivity-grade (V 2.04, MilliQ Academic). Ultraviolet–visible absorption spectra were recorded with a PerkinElmer Lambda 40 spectrometer, Fourier transform infrared (FTIR) spectra were recorded with a PerkinElmer Spectrum One instrument, and fluorescence spectra were measured with a PerkinElmer LS50B luminescence spectrometer (typical bandpass $\sim$ 2 nm). pH was measured with a VWR model 8000 pH meter calibrated with standard buffers.

Preparation and characterization of the BCDP

The BCDP was prepared with a modification of Sugiura's procedure.[56] Under our optimized conditions, we proceeded as follows. A known mass of BCD was dissolved in a stirred (500 rpm) aqueous solution of 20% NaOH at 60°C. Once the BCD dissolved, epichlorohydrin was added dropwise to the stirred solution. The molar ratio of BCD to the crosslinking agent was 1:29 (this corresponds to polymer **7** of Crini et al.[54]). Once epichlorohydrin was added, the solution was kept at 60°C and stirred. After about 2 h, the viscosity of the solution increased, and a yellow-white gel formed. At this point, water was added to quench the reaction, and the reaction mixture was vacuum-filtered to collect the solid material. The solid polymer was washed with ethanol and vacuum-dried at 60°C for 24 h. The resulting product was a yellow-white solid consisting of small, brittle particles. The material was ground in a mortar and pestle to yield particles about 1.0 mm in diameter, which were used in subsequent experiments.

Several batches of BCDPs were prepared with alcohols (propylene glycol and 1-octanol) as additives. This was an attempt to obtain a polymer with rapid water swelling properties.[57] The synthesis was essentially as previously described but with a CD/alcohol/epichlorohydrin molar ratio of 1:1:29.

The crosslinked polymer BCDP is a well-known material. To confirm that we had successfully prepared it, we simply measured the IR spectrum (KBr pellet) of the polymer, which we compared to the literature spectra of BCDP, BCD, and epichlorohydrin.[58] The IR spectrum of our material (Fig. 1) did not resemble that of either BCD or epichlorohydrin. However, it matched the literature spectrum of BCDP exactly (3400 cm^{-1}, O—H stretch; 3000 cm^{-1}, C—H stretch; and 1040 cm^{-1}, C—O—C stretch). Therefore, we concluded that our synthesis successfully yielded BCDP.

In the reaction batches with alcohols, the basic IR spectrum of BCDP was preserved, but additional bands due to the additives could be detected. For example, in the 1-octanol batch, the IR spectrum of the product contained bands that could be associated with the alcohol (C—H stretch at 2940 cm^{-1}, CH_2 and CH_3 bends near 1500 cm^{-1}, and long-chain band at 700 cm^{-1}). This suggests that some amount of alcohol was trapped in the polymer matrix during the synthesis.

NAP derivatives and their analysis

NAP solutions were prepared from 150 μM aqueous stock solutions. This, in turn, we prepared by weighing the appropriate mass of NAP into a 1-L flask, diluting it with water, and stirring it overnight. We prepared stock solutions of NAX (100 μM) by weighing the appropriate amount of NAX into a 1-L flask and diluting it with an aqueous solution adjusted to pH 7 (NaOH–HCl). Stock solutions of 100 μM NAO were prepared in a similar fashion. The pH was not

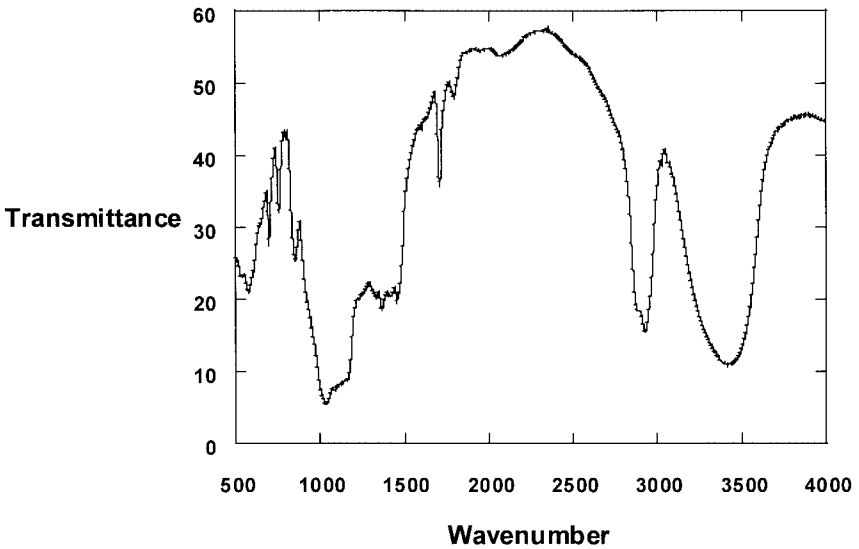

Figure 1 FTIR (KBr pellet) spectrum of epichlorohydrin-crosslinked BCDP powder. The ratio of CD to epichlorohydrin was 1:29.

controlled in this case, but the pH of a 0.1 m*M* NAO aqueous solution (the concentration used in our tests) was 6.0.

The analytical concentrations of the various NAP derivatives were obtained with steady-state fluorescence measurements. In each case, calibration curves of the fluorescence intensity versus the concentration were prepared in either water or ethanol. The following excitation/emission conditions were used: NAP, λ_{ex} = 280 nm and λ_{em} = 337 nm; NAO, λ_{ex} = 310 nm and λ_{em} = 355 nm; and NAX, λ_{ex} = 280 nm and λ_{em} = 355 nm.

Batch experiments

Batch experiments involving BCDP and the model pollutant NAP were performed to establish whether there was a lag time for the adsorption of NAP by the polymer. In these rate experiments, 2.0 g of the polymer was weighed into a 500-mL volumetric flask, and an aqueous solution of 10 μM NAP was added. The sample was stirred, and aliquots were collected at various time intervals. The fluorescence intensity of NAP ($\lambda_{monitor}$ = 337 nm) was recorded for each collected aliquot and converted into the NAP concentration on the basis of a calibration curve. Similar experiments were carried out with NAX and NAO.

Flow experiments

We performed several experiments with flowing water samples to evaluate the potential for BCDP trapping of the model pollutants under these conditions. BCDP particles (10 g) were hydrated in MilliQ water for 1.5 h and then used to pack a 150-mL glass column fitted with a stopcock. A feed of model effluent water (deionized water containing a model pollutant) was led through poly(vinyl chloride) tubing from a 20-L Nalgene carboy into the BCDP column. The total volume of the test solution used in each case was 5 L, and it was gravity-fed into the column. The flow rate was controlled by the manual adjustment of the stopcock at the bottom of the column. The fluorescence intensity of the collected fractions was recorded and converted into the concentration via a calibration curve.

RESULTS AND DISCUSSION

Figure 2 shows the results of batch experiments in which various BCDP preparations were exposed to a solution of 10 μM NAP for various lengths of time at 22°C. For simple BCDP, it is clear that close to 60% of all the NAP present was trapped by the polymer in the first 30 s of exposure. By 30 min, this increased to 80% trapping. The extent of trapping at 60 min (80.1% of NAP, data not shown) was no greater than that at 30 min. The experiment was repeated at 50°C, and the results were unchanged. These data clearly show that there is no significant barrier to NAP uptake by BCDP.

Figure 2 also shows similar plots of the NAP intensity as a function of the exposure time for BCDP prepared in the presence of propylene glycol, 1-pentanol, or 1-octanol. As for simple BCDP, there was a vary rapid initial trapping period during which a large portion of the available NAP was taken up by the polymer. After this period was over (ca. 30 s), the uptake essentially ceased. In contrast to the case of simple BCDP, the batches of polymer prepared in the presence of alcohols took up a much smaller total amount of NAP. Therefore, the total uptake by the

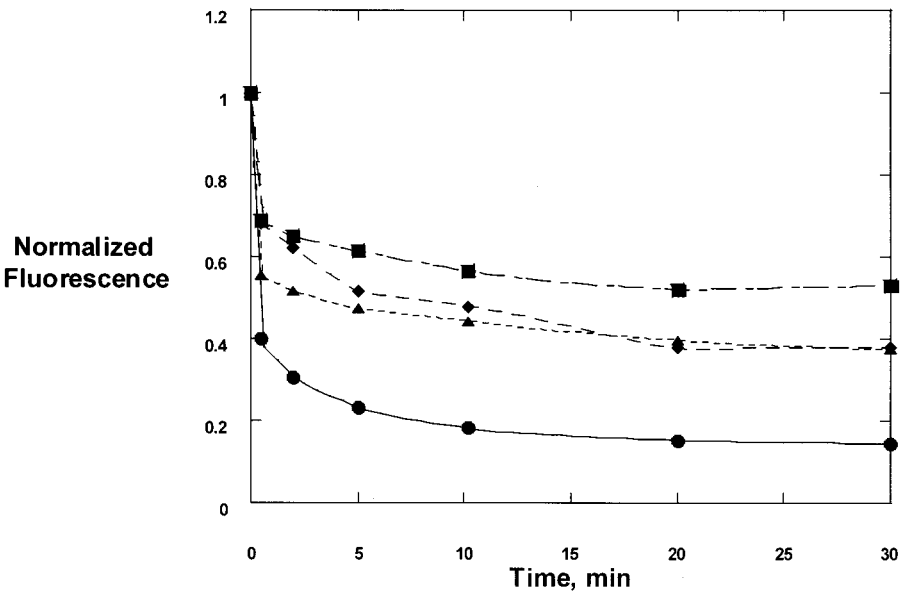

Figure 2 Normalized fluorescence intensities of a 10-μM NAP solution exposed to different BCDP preparations at 22°C: (●) BCDP, (▲) BCDP prepared with octanol, (♦) BCDP prepared with pentanol, and (■) BCDP prepared with propylene glycol.

BCDP–alcohol systems was only about 50%, whereas that of the simple BCDP was about 80%. A probable explanation for this observation invokes the well-known fact that linear alcohols bind to the BCD cavity.[48,59] If CD cavities include alcohols when the polymerization takes place, many of the potential binding sites for NAP will be blocked, and the trapping of this guest by the polymer will be rendered inefficient. This result also indicates the requirement of CD trapping sites for a polymer to be an effective material for removing organics from water (as discussed later).

Batch experiments showing a BCDP uptake of NAX and NAO as a function of time were also performed. For NAX, the initial uptake after 30 s amounted to only 10% of the total NAX, and even after 30 min, only about 34% of the available NAX was bound to the polymer. That is, the rate and efficiency of NAX uptake by BCDP in batch experiments were much lower than those observed for NAP. The total NAX uptake increased gradually to 45% by 60 min. For NAO, the overall uptake was moderately efficient (ca. 60% over 30 min), but again there was a slow component, the uptake being only 35% after 10 min. Therefore, there seems to be a clear difference between the test compounds in terms of the rapidity and efficiency of uptake. The nonpolar NAP was better trapped by BCDP than either the polar NAO or the ionized NAX.

A series of flow experiments with NAP as a model pollutant were carried out as previously described. Three different test concentrations of NAP were used: 6.0, 12, and 19 μM. Figure 3 shows fluorescence spectra of 6.0 μM NAP for the influent as well as the spectrum of the 4th liter of the effluent collected from the BCDP column. The tiny amount of NAP coming out of the column could be judged by the fluorescence intensity of NAP at 4 L in comparison with the intensity of the broad peak near 315 nm. The latter was the Raman scattering of water.

The fluorescence intensities observed in these flow experiments could be converted into NAP concentrations with a calibration curve. The concentrations could, in turn, be converted into trapping efficiencies with the following simple relationship:

$$\% \text{ Trapping} = \frac{C_I - C_E}{C_I} \times 100\% \qquad (3)$$

where C_I is the concentration of the pollutant in the influent and C_E is the concentration in the effluent. The flow rate was 15 mL/min in these experiments. This value is much higher than that used in earlier studies and, therefore, better mimics actual flow situations.

Figure 4 shows the percentage of trapping of NAP as a function of the effluent volume (L). Nearly all the NAP in each liter of the influent was trapped by the polymer, the trapping efficiency being about 90% in each case. There was no drop-off in the trapping efficiency over the 5-L volume collected. The overall trapping percentage (i.e., calculated on the basis of the total NAP input and the total NAP output of the column) was also very high at 95% (Table I). Changing the flow rate through the column within the range of 5–32 mL/min had no impact on the trapping efficiency of the BCDP column. Clearly, the column was highly effective at trapping NAP from a flowing water stream.

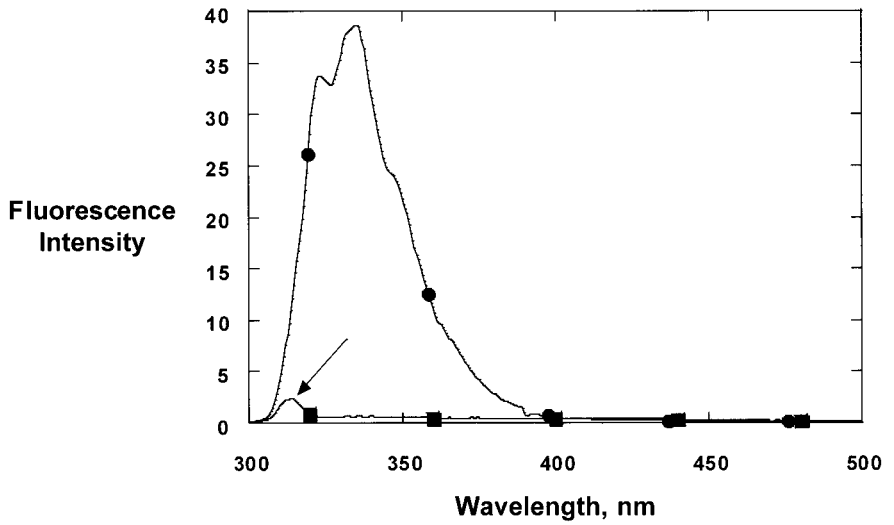

Figure 3 Fluorescence spectra of (●) a 6 μM NAP influent and (■) a 4th liter of the effluent from the BCDP column. The arrow indicates the Raman band of water. The flow rate was 15 mL/min.

One of the potential advantages of using BCDP to polish wastewater is the fact that the trapped pollutants should be recoverable. It is well known that alcohols cause the displacement of organic guests from CD cavities in aqueous solutions.[48,53,59] This suggests that washing the polymer column with a simple alcohol such as methanol or ethanol may be an effective means of regenerating the column for reuse and for collecting the trapped organics. In test recovery experiments, a BCDP column was exposed to a total of 3820 μg of NAP by a flow of 5 L of an aqueous solution of NAP over the column at 15 mL/min. About 95%, or 3630 μg, of this total was trapped by the column. The column was flushed with a total volume of 450 mL of ethanol, and the NAP fluorescence of the collected ethanol was recorded. The collected ethanol contained 3060 μg of NAP, and this means that 84% of the trapped pollutant was recovered. We found that the same batch of polymer could be used at least four times, while high recovery efficiencies were maintained, with the ethanol wash approach. Certainly, the number of trap-and-release cycles is not limited to four, but only four cycles were tested.

Flow experiments were also conducted with NAO as the model pollutant. In unbuffered aqueous solutions of NAO, the pH was about 6.0. Under these

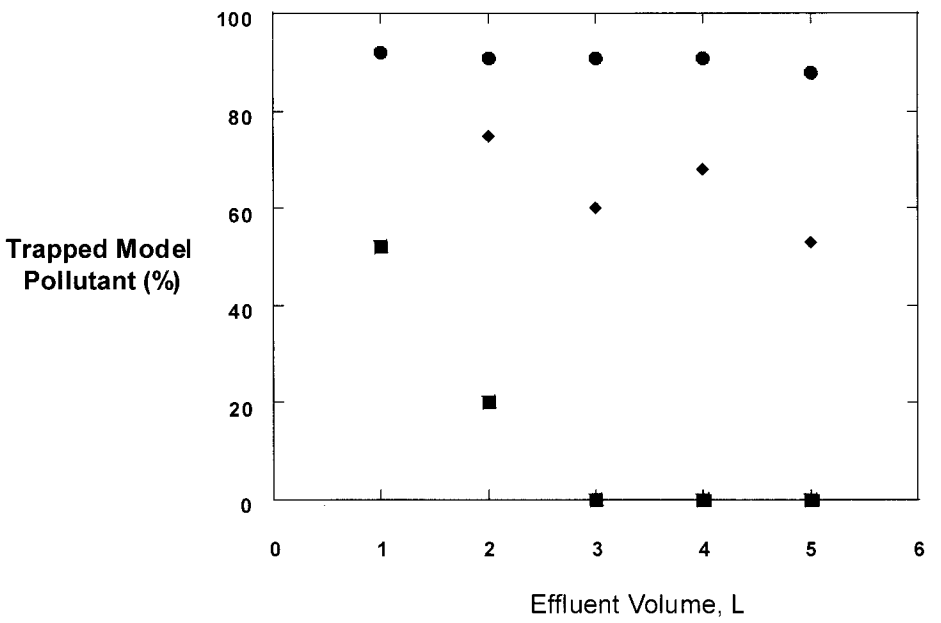

Figure 4 Trapping as a function of the effluent volume: (●) NAP, (♦) NAO, and (■) NAX. The trapping is expressed as the percentage of the influent concentration (C_I).

TABLE I
Comparison of K_f Values for Complexes of BCD and NAPs with the Efficiencies of Trapping of NAPs by BCDP

Model pollutant	K_f (M^{-L})	Trapping efficiency[a] (%)
6.0μM NAP	730[b]	95
5.0μM NAX	475,[c]620[d]	18
5.0μM NAO	699[e]	70

[a] For 5-L total flow volume.
[b] Ref. [60] and references therein.
[c] Ref. [53], pH 7.4.
[d] Ref. [61], pH 9.
[e] Ref. [59], pH 6.4.

conditions, NAO (ground-state pK_a = 9.5[59]) was essentially not ionized. The detection wavelength for NAO fluorescence was 355 nm, a wavelength at which the fluorescence was due almost exclusively to the protonated form of the molecule. Furthermore, under these conditions, K_f for the 1:1 NAO/CD complex was very similar to that for the 1:1 NAP/CD complex (Table I.) One might, therefore, expect NAO to behave in a similar fashion to NAP with respect to trapping by BCDP. In fact, this is the case, with the trapping efficiency of BCDP for NAO also being quite high, or 70% (Table I). In recovery tests using ethanol to flush NAO off the BCDP column, 100% of the NAO was recovered. This level of trapping for NAO is quite comparable to that found by Crini et al.[54] (75% at a flow rate of 1.5 mL/min). Clearly, non-ionized PAHs, even relatively polar PAHs, were effectively removed from flowing water streams by BCDP.

There seems to be a weak correlation between the binding constants (K_f) and the trapping efficiencies observed for the three model pollutants tested in this study (Table I). The pharmaceutical NAX bonded most weakly to BCD in aqueous solutions and was also trapped most weakly by BCDP. The weak interaction of NAX and BCDP was probably a result of the ionized state of the drug. In comparison with the non-ionized NAP and NAO, the anionic NAX was strongly hydrated. To be trapped by the polymer binding sites, NAX had to lose its water of hydration. This was also true of NAP and NAO, but the energy cost was higher for NAX, and this made binding less favorable.

If ionization resulted in only minimal trapping, one can ask why any NAX was trapped. The sorption of PAHs by BCDP could conceivably occur via trapping of the aromatic by the CD cavity, at sites existing within the crosslinked epichlorohydrin network, or at a combination of both locations. To establish the relative importance of CD versus epichlorohydrin sites, we prepared a column packed with poly(epichlorohydrin), a crosslinked polymer without CD sites. In flow experiments with this column (flow rate = 15 mL/min) with NAP as the analyte, we observed that the total trapping after 60 min of flow was only 30%. The crosslinked polymer network had some ability to sorb PAHs, but it was limited compared with that of BCDP. However, physical adsorption to the epichlorohydrin could easily account for the 18% trapping observed with the ionized species NAX (as discussed previously).

The results of this study show that BCDPs are powerful sorbing agents for PAHs based on the NAP moiety and suggest a role for BCDPs in water remediation. Our data extend the range of application of BCDPs to include U.S. Environmental Protection Agency priority pollutants. They also show that one cannot use BCDPs to effectively trap ionized species. This may ultimately limit the BCDP strategy for the remediation of flowing waters, in which pH conditions are such that pollutant species are ionized. This has particular implications for the remediation of pesticides. However, many important pharmaceutical materials are hydrophobic, and the BCDP approach should be useful for these species.

The BCDP approach has several advantages. BCDPs are cheap and reusable, and CDs are biodegradable. The trapping efficiency is high for several classes of pollutants, and the recovery of trapped materials is also efficient. This latter point is important as it implies that BCDP columns can be used to collect organic pollutants from water for subsequent analysis; that is, the column can be used as a sampling device. This feature, coupled with the potential for remediation already noted, makes BCDPs attractive tools for water treatment.

This study has been restricted to model waters devoid of particulate matter. This is in part because this contribution is intended as a proof of concept of the usefulness of BCDPs for a range of pollutant categories. Furthermore, we envision BCDPs being used as resins for polishing and/or sampling at the end of thorough municipal wastewater remediation processes. Such remediated waters are quite clean, and these model systems mimic them. Work currently underway in our laboratory is assessing the potential of BCDPs to remove other pharmaceuticals and endocrine modifiers from flowing water, and we are expanding our tests to samples containing particulates.

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