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Highly selective detection of oil spill polycyclic aromatic hydrocarbons using molecularly imprinted polymers for marine ecosystems

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HIGHLIGHTS

- Polymer prepared with new crosslinker (*N*,*O*-bismethacryloyl ethnaolamine).
- Binding capacity of imprinted polymer for pyrene is 35 mg/g in seawater.
- Imprinted polymer showed high adsorption selectivity for PAHs in seawater.
- Highly useful reusable adsorbents for marine oil spill remediation.

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ABSTRACT

Im*plications due to oil spills on marine ecosystems have created a great interest toward developing more efficient and selective materials for oil spill toxins detection and remediation. This research paper highlights the application of highly efficient molecularly imprinted polymer (MIP) adsorbents based on a newly developed functional crosslinker (*N*,*O*-bismethacryloyl ethanolamine, NOBE) for detection of highly toxic polycyclic aromatic hydrocarbons (PAHs) in seawater. The binding capacity of MIP for oil spill toxin pyrene is 35 mg/g as compared to the value of 3.65 mg/g obtained using a non-imprinted polymer (NIP). The selectivity of all three high molecular weight PAHs (pyrene, chrysene and benzo[*a*]pyrene) on the NOBE-MIP shows an excellent selective binding with only 5.5% and 7% cross-reactivity for chrysene and benzo[*a*]pyrene, respectively. Not only is this particularly significant because the rebinding solvent is water, which is known to promote non-selective hydrophobic interactions; the binding remains comparable under salt-water conditions. These selective and high capacity adsorbents will find wide application in industrial and marine water monitoring/remediation.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) enter into the environment primarily by fossil fuel combustion, industrial stack emissions and solid waste incineration. Introduction of PAHs into the environment also occurs from accidental crude oil spills such as recently reported for the Deep Horizon tragedy which released 660 quadrillion gallons of crude oil in the Gulf of Mexico. Among crude oil toxins, PAHs represent the major danger due to the broad range of their carcinogenic, mutagenic and toxic effects; and are classified as priority pollutants by U.S. EPA [1]. Although the amount of oil which reaches the coast or remains in water gradually decreases over the time after an oil spill due to natural degradation processes (photolysis, oxidative and biological degradation, etc.), PAHs tend to persist [2]. For example, after more than 20 years since the Exxon Valdez spill, increased concentrations of polycyclic aromatic hydrocarbons (PAHs), and other highly toxic compounds are still found in the affected areas of Prince William Sound [3]. Furthermore, due to their hydrophobicity, they quickly accumulate in fish and other marine organisms, as well as rapidly sequester into the organic matrix of suspended sediments resulting in sediment contamination [4]. Because of environmental persistence and bio-accumulation through the food chain adversely affecting not only marine life but also human health [5], PAHs need to be targeted for routine monitoring and remediation from environmental waters.

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0304-3894/

Most adsorbents, such as activated carbon and polystyrene resins, are commonly used to remove organic contaminants and PAHs present in high levels from wastewaters and industrial effluents. However, removal of low concentration contaminants by non-selective adsorbents is difficult because of the complicated matrix of organic compounds (both natural and anthropogenic) that are present in significantly higher levels and dominate coverage of the adsorbent. Therefore an efficient and selective adsorbent is required to remove traces of soluble PAHs in water or seawater. An adsorbent that that has been developed for selective binding of a broad class of PAHs was reported using a tetrakis(*p*-carboxylphenyl)-porphyrin immobilized on polymeric ion-exchange resins, which sequestered PAHs from soil extracts [6]. In addition, carbon supports with mesoporous/nanoporous structure have been shown to selectively bind anthracene, naphthalene, and related PAHs via π–π interactions from a diesel mix [7]. However, most reports of PAH selective supports use molecularly imprinted polymers (MIPs) for extraction and analysis of PAHs from gas-phase, liquid and solid samples [8,9].

Molecular imprinting is a method for creating artificial receptors using a target molecule as a template for directing the assembly of monomeric units to form a pre-polymer complex (PPC) as shown in Fig. 1. The PPC is nearly always formed using non-covalent interactions such as hydrogen bonding or electrostatic interactions, which require organic solvents that will promote complexation and rebinding of the target molecule. The imprinted polymer is formed by copolymerization of the PPC with cross-linking monomers, followed by subsequent removal of the template which leaves binding cavities in the polymer that are complementary in shape to the template with a complementary array of complexing monomers lining the binding site cavity. A benefit of the highly cross-linked network MIP receptors is the ability to directly use them as molecularly specific adsorbents. Synthesis and applications of imprinted polymers under aqueous conditions are of tremendous interest for biological, environmental and nutrition related sciences. However, aqueous matrices are a challenge for MIPs, primarily because aqueous solutions tend to disrupt the non-covalent interactions involved in both the formation of the PPC and rebinding of the template. Furthermore, aqueous phases incorporating ions, e.g. seawater, present an even larger challenge due to the increased ionic strength that will disrupt electrostatic-based non-covalent interactions to a greater degree.

The goal of this study was to develop MIPs for the selective removal of PAHs from seawater, with potential applications toward monitoring and preventing the adverse effect of PAHs on the environment. Several studies have been published describing MIPs capable of metal ion uptake in seawater matrices [10–12], but few examples have been reported of MIPs imprinted with organic compounds that can be selectively rebound in seawater conditions. One example imprinted polyethersulfone particles formed using a phase inversion technique showing selectivity for the bisphenol-A template versus biphenyl and phenol in partially aqueous conditions with NaCl and $MgCl_2$ salts [13]. More recently, a naphthalene derivative has been imprinted using a more traditionally formulated polymer employing methacrylic acid (MAA) as the template interactive monomer and ethyleneglycol dimethacrylate (EGDMA) as the crosslinker. Competitive rebinding tests with an array of PAH compounds showed selective binding for the bicyclic template naphthalene and greater binding for the significantly larger tricyclic compound phenanthrene [14]. However, the PAHs of greatest concern are the more toxic and dangerous heavy PAHs such as benzo[*a*]pyrene (BAP), benz[*a*]anthracene, indeno[1,2,3-cd]pyrene, benzo[*e*]pyrene and chrysene (CHR); as well as pyrene (PYR) which intringuingly is neither mutagenic nor carcinogenic when isolated from other PAHs (Fig. 2). In a series of recent papers, Krupadam and coworkers developed MAA/EGDMA formulated MIPs imprinted with PAHs, such as benzo[*a*]pyrene or PAH mixtures, that exhibited molecular recognition for the PAH compounds in contaminated fresh-water samples [15–18]. Of current interest was to explore the binding behavior of PAH imprinted MIPs under saltwater conditions, with high capacity to facilitate oceanographic remediation and monitor PAH levels.

The binding capacity of MIPs is generally characterized by the number of binding sites per gram of material, where each binding site is postulated to arise from the template-monomer PPC. Therefore, maximizing the capacity is achieved by maximizing

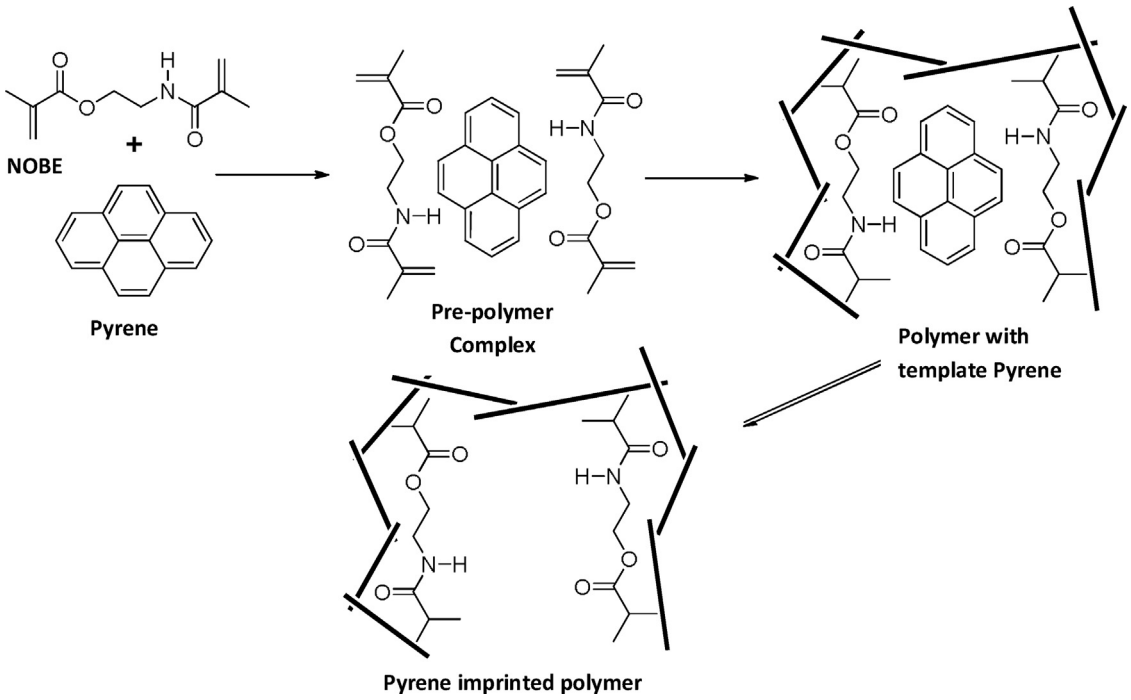

Fig. 1. Outline of the molecular imprinting process.

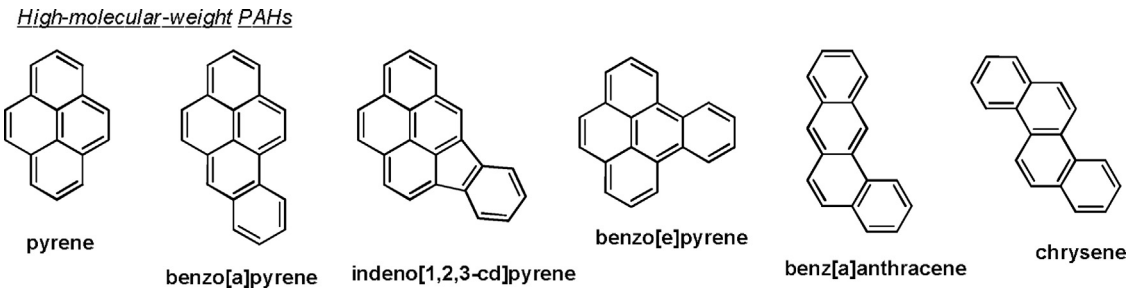

Fig. 2. Highly toxic or mutagenic PAH compounds of interest, and pyrene.

the amount of template that is loaded into the MIP during the imprinting process. However, MIPs formed with the commonly used formulation MAA/EGDMA often lose binding and selective properties above 10 mol% template loading; in this case at mole ratios higher than 1/10 for moles of pyrene/moles of all monomers (MAA + EGDMA). Recently, a simpler approach to MIP formation has been developed that utilizes a single crosslinking monomer, *N*,*O*-bismethacryloyl ethanolamine (NOBE), which eliminates variables that must be empirically optimized such as choice of functional monomer and crosslinker, the ratio of functional monomer/crosslinker, and the ratio of functional monomer/template which normally complicate MIP design. This relatively new approach is referred to as OMNiMIPs (a pseudo-acronym for "one monomer molecularly imprinted polymers"), and has been shown to form MIPs that often exhibit higher affinity and better selectivity than traditionally formulated MAA/EGDMA imprinted polymers [19–21]. More importantly, significantly higher binding capacities can be obtained for OMNiMIPs when the template loading is increased up to 25% template loading or more, without losing selective binding of target molecules.

2. Experimental

2.1. Preparation of molecularly imprinted polymers

The following procedure was used for imprinted polymers employing the cross-linkers-NOBE and EGDMA. In a 13 × 100 mm test tube, (0.016 g, 1 mmol) of pyrene was dissolved in 2 mL of acetonitrile. To this solution was added NOBE (0.63 g, 40 mmol) and AIBN (0.020 g, 0.12 mmol). For comparision to traditionally formulated imprinted polymer, another polymer was imprinted using formulation above, substituting EGDMA (0.53 g, 40 mmol) as crosslinking monomer and adding MAA (MAA (0.029 g, 4 mmol) as the functional monomer. The solution was purged by bubbling nitrogen gas into the mixture for 5 min and then capped and sealed with Teflon tape and parafilm. The polymer precursors in test tubes were sonicated for 5 min before initiating the polymerization reaction. The samples were inserted into a photochemical turntable reactor, which was immersed in a constant temperature bath. A standard laboratory UV light source (medium pressure 450 W mercury are lamp) jacketed in a borosilicate double-walled immersion well was placed at the center of the turntable. The polymerization was initiated photochemically at 20 °C and then temperature was maintained by both the cooling jacket surrounding the lamp and the constant temperature bath holding the entire apparatus. The polymerization was allowed to proceed for 6 h. After completion of polymerization, the monolith formed in each sample was crushed separately and each solid polymer was washed repeatedly with acetonitrile (five washings) and chloroform (five washings) at 35 °C to remove the template. The polymer particles were finally dried in vacuum. The non-imprinted reference polymers were synthesized under identical conditions except for omission of the template.

2.2. Job's plots for PPC stoichiometry

During imprinting, the template molecule form pre-polymer complex (PPC) with functional monomers and the stoichiometry of PPC was determined by Job's plots. The combined concentration of functional monomer NOBE and template pyrene were kept at constant molarity, but the relative molar fractions of NOBE and the template pyrene was varied in a compensatory manner. The shift in fluorescence intensity (F.I. counts $1/s \times 10^5$) in the presence of NOBE and f_M is the mole fraction of template pyrene used to determine PPC concentration. Different values of FI counts were used to plot the complex concentration versus the molar fractions of pyrene at concentrations above the necessary threshold value to establish Job's plot.

2.3. Equilibrium binding analysis

The binding properties of the polymers were evaluated by equilibrium binding analysis. In a series of disposable scintillation vials, 10 mg of NOBE-MIP was suspended in 5 mL of pyrene solutions concentrations ranging from 1 ppm through 25 ppm. The mixture was agitated at room temperature for 3 h and then samples were centrifuged at 15 000 rpm for 5 min. The remaining pyrene was quantified using spectrofluorometer. The optimum contact time (i.e. 3 h) was determined by measuring residual pyrene concentration in solution at different contact times. The percentage uptake was calculated using calibration curves obtained from external standards. Three repeated measurements were performed for every sample, and the mean of the concentration was recorded.

2.4. Fluorescent intensity measurements

Fluorescence intensity measurements were performed on a Quanta Master Model C-60/2000 spectrofluorometer from Photon Technology International (Lawrenceville, NJ, USA). The instrument includes a light source (75-W xenon compact arc lamp), a model 101M monochromator and a model 814 detector samples were recorded using a fixed excitation wavelength (260 nm), and the intensities of fluorescence emission 390 nm were used for quantification.

3. Results and discussion

The first step in the molecular imprinting process is the formation of a solution phase complex between the template and the functional monomer, referred to as the PPC in the introduction. To establish the existence of the PPC, fluorescence spectrophotometric response from titration of the template, pyrene, with increasing concentrations of the functional monomers and crosslinkers was monitored. For the OMNiMIP, the monomer NOBE acts as both the functional monomer and the crosslinker; therefore, a single titration study was carried out on pyrene with increasing amounts of

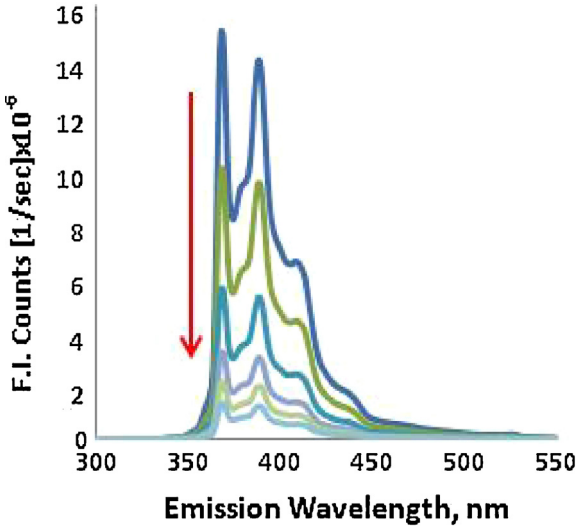

Fig. 3. Cascade fluorescence spectra from the titration of pyrene (1 mL of 0.1 ug/L) with increasing amounts of NOBE (0.5, 1, 2, 3, 4, 5 mL of 0.1 ug/L) in acetonitrile.

NOBE, and the results shown in the cascade spectra in Fig. 3. The decrease in the peaks at 360 nm and 390 nm as the concentration of NOBE increases is indicative that there is a complex forming between the NOBE monomer and pyrene. The complex was further characterized by Job's plot analysis, which showed a 2:1 stoichiometry for the NOBE monomer to pyrene (Fig. 4).

Having established the nature of the pre-polymer complex, the amount of solvent (referred to as porogen) was analyzed for its affect on uptake capacity of the MIP. For this investigation, two formulations were polymerized; one with a v/v ratio of the monomers/porogen (acetonitrile) equal to 1.5 and the other with a ratio of 3.0. Evalution of binding was carried out at saturation levels of pyrene in a solvent mixture of acetonitrile and water (1:99 v/v), to obtain maximum pyrene uptake under saturation conditions. The results from this study indicated that a 40% higher uptake of pyrene is evident for the NOBE-molecularly imprinted polymer (N-MIP), and 25% increase in pyrene uptake for the

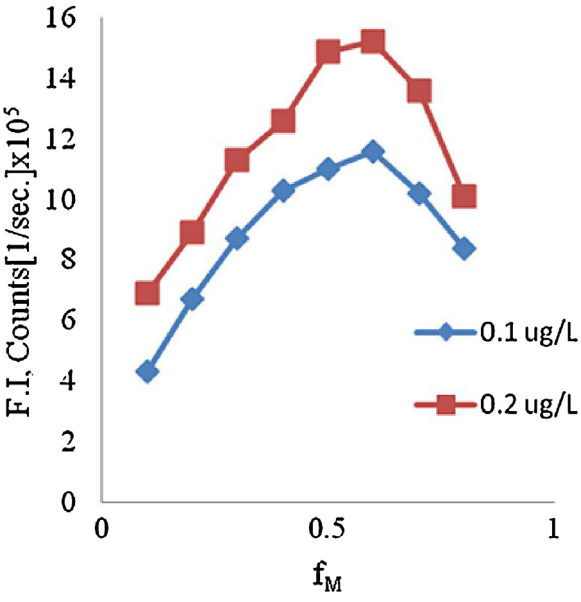

Fig. 4. Job's plot for the complexation of NOBE to pyrene. The parameter f_M is the ratio of functional monomer NOBE and template pyrene (of different mole fractions) in the pre-polymer complex.

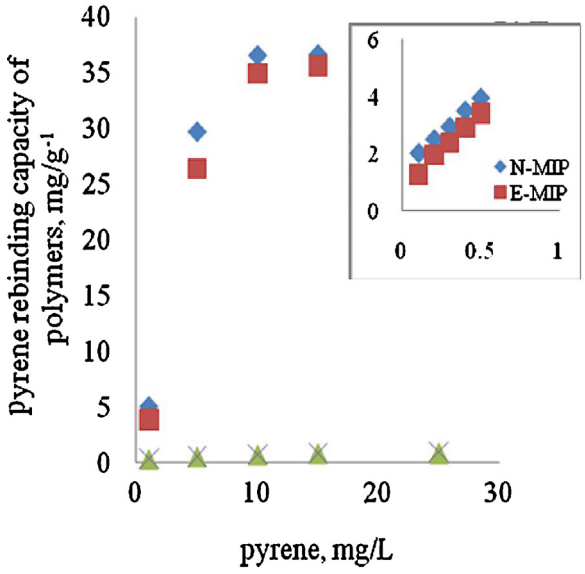

Fig. 5. Binding isotherms for uptake of pyrene by imprinted and non-imprinted polymers formulated with a monomers/porogen ratio of 3.

EGDMA/MAA-molecularly imprinted polymer (E-MIP) when a larger volume of porogen is used. Thus, the higher porogen volume was chosen for further binding and selectivity experiments comparing the N-MIP to the E-MIP. The isotherms in Fig. 5 show that the saturation value of both MIPs is approximately 35 mg/g; but below saturation levels the N-MIP shows higher uptake versus the E-MIP (inset). However, selectivity studies shown in Fig. 6 indicate for the E-MIP that the increase in uptake is mainly due to non-specific binding, whereas the N-MIP maintains excellent selectivity as well as a high uptake capacity.

The molecular imprinting effect creates specific molecular recognition binding sites by forming a cavity with good shape complimentarity and a strategically placed balance of hydrophobic/hydrophilic interactions on the cavity surface that are complimentary to the original target [22]. Therefore, in addition to uptake capacity of MIPs, selectivity is an important test for molecular recogntion by these materials. The selectivity studies were carried out comparing pyrene rebinding to the binding values of the pyrene analogs benzo[*a*]pyrene and chrysene, which have greater

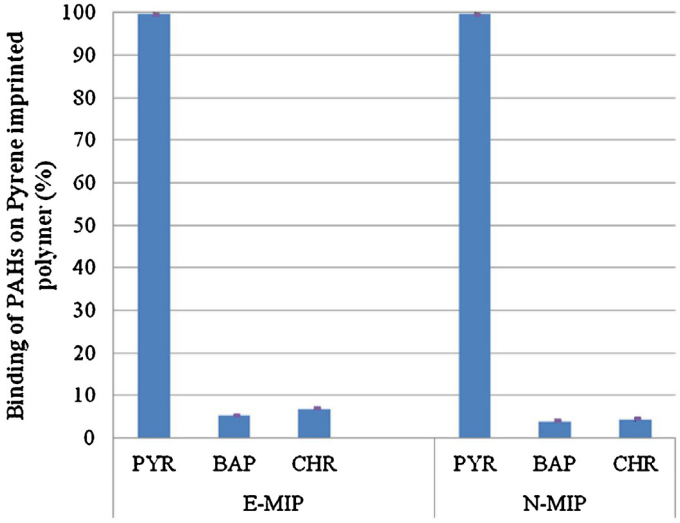

Fig. 6. Selectivity of pyrene MIPs for pyrene versus benzo[*a*]pyrene (BAP) and chrysene (CHR) from binding studies in deionized water.

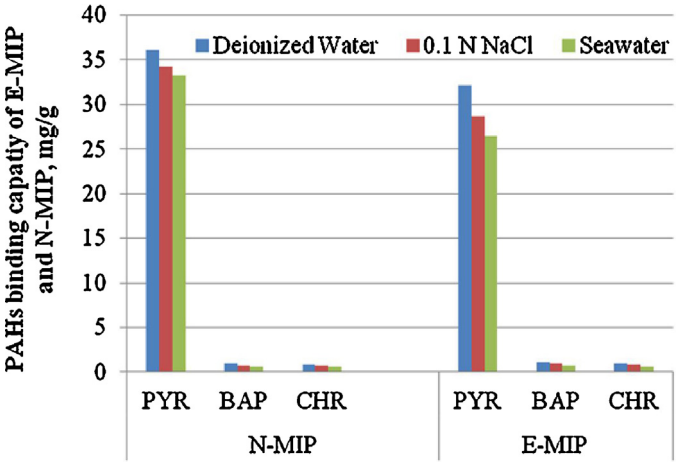

Fig. 7. Selective binding of pyrene by the N-MIP and E-MIP under different ionic strength matrices. A 5 mL solution containing pyrene, BAP, and CHR, at a 0.1 μg/L concentration level, was incubated with N-MIP or E-MIP under the optimized working conditions for pyrene, and residual concentration of each PAH was determined based on fluorescence peak height. The binding capacity of pyrene imprinted N-MIP and E-MIP for BAP and CHR are 1.8 and 2.3 mg/g and 3.4 and 4.7, respectively, in deionized water. A similar trend was observed in 0.1 N NaCl and seawater. N-MIP, pyrene imprinted polymer with NOBE as the cross-linking monomer; E-MIP, pyrene imprinted polymer with EGDMA as the cross-linking monomer; PYR, pyrene; BAP, benzo[*a*]pyrene; CHR, chrysene.

toxicity compared to other PAHs. The selectivity of all three compounds on the N-MIP and E-MIP is shown in Fig. 6 with the uptake of the different PAHs normalized to pyrene adsorption taken to be 100%, and the relative binding reported for the other analogs. The figure shows excellent selectivity by the N-MIP with only 5% and 7% cross-reactivity for chrysene and benzo[*a*]pyrene, respectively, indicating that pyrene is bound specifically in the selective cavities (Fig. 6). This is particularly significant because the rebinding solvent is water, which is known to promote non-selective hydrophobic interactions outside of the binding site. These non-selective interactions were problematic for the E-MIP, which showed greater than 50% uptake for the other two pyrene analogs, limiting the utility of the E-MIP for uptake of target compounds in component mixtures.

The ability of the MIPs to selectively rebind pyrene in distilled water encouraged further studies to test rebinding in a salt water or sea water type matrix, which better mimics oil spill conditions. Thus, two additional binding studies were carried out in artificial sea water made in the laboratory [23], and in sodium chloride solution with the same molarity as the total sum of the artificial sea water salts. The latter sodium chloride solution was chosen in order to determine whether effects of adding salts were merely due to ionic strength, or if any effects seen were dependent on salt identity.

The findings in Fig. 7 reveal that binding of pyrene to the N-MIP is unaffected by a simple sodium chloride solution; however, the artificial sea water solutin with a mixture of different salts shows a decrease in binding capacity while still maintaining high molecular selectivity. The highly selective binding of a single N-MIP in varying aqueous environments could be extremely important for comprehensive application to environmental and industrial detection and recovery of PAHs. In comparison of pyrene uptake, the N-MIP shows approximately 50% higher capacity versus the E-MIP for pyrene; furthermore, the E-MIP exhibits a slight increase in the uptake of pyrene (not seen by the N-MIP) in the solutions containing salts that cannot be selective in nature and may be due to non-specific hydrophobic effects. There is a very significant improvement in selectivity by the N-MIP versus the E-MIP as shown in Fig. 7. The origin of this improvement may be due to the greater amount of functional monomer available in N-MIP for interacting with pyrene. For N-MIP, the NOBE cross-linker incorporates amide

Table 1
Changes in pyrene uptake as the template loading is increased from 4 mol% to 25 mol% on the N-MIP and E-MIP*.

	4%	25%
N-MIP	28.9	48.3
N-NIP	1.7	2.5
E-MIP	35.4	23.1
E-NIP	3.6	4.9

* Pyrene uptake (mg/g) was measured in deionized water for all MIPs. N-MIP, pyrene imprinted polymer with NOBE as the cross-linking monomer and N-NIP is the control polymer prepared without template (pyrene); E-MIP, pyrene imprinted polymer with EGDMA as the cross-linking monomer and E-NIP is the control polymer prepared without template (pyrene).

group for hydrogen bonding to the templates, providing essentially 100% of interactive functional groups. The E-MIP use mixture of EGDMA and MAA, there is always a limit on the amount of interactive functional monomer that can be used. This is a consequence of the minimum level of cross-linking needed in MIPs to maintain the structural properties of the template binding site. The N-MIP exhibits high selectivity in the salt and sea-water solutions comparable to that found in deionized water, effectively recovering the imprinted compound without interference of related molecules in all three aqueous conditions. Looking at Fig. 7, the binding of pyrene $97 \pm 2\%$ ($n = 3$) onto its own MIP it can be seen that the rebinding process of pyrene was not significantly affected by the presence of the other PAHs. The binding capacity of pyrene imprinted N-MIP and E-MIP for BAP and CHR are 1.8 and 2.3 mg/g and 3.4 and 4.7, respectively, in deionized water. The similar trend was observed in 0.1 N NaCl and seawater. This data showed that the N-MIP was selectively binding pyrene more compared with the E-MIP,while BAP and CHR were less bound on N-MIP. The selectivity by E-MIP was relatively poor compared to the N-MIP, and showed approximately 50% uptake of other PAHs (BAP and CHR) compared to the imprint compound pyrene from the aqueous solutions. Unfortunately, this high uptake of related PAH compounds would interfere detrimentally with any recovery and sensing efforts of the target imprint compound (pyrene in this case).

Changes in the uptake capacity of the imprinted polymers was investigated by increasing the template loading from the previously employed 4 mol% to 25 mol% pyrene in both N-MIP and E-MIP formulations. The concentration of the template (pyrene) is reported as mol% in polymer formulations. The unit mol% is the relative amount of each of the monomers and template; to get the desired moles of each one divided by the total moles of all components. The effects on the capacity for total pyrene uptake for imprinted polymers are shown in Table 1. The data for the N-MIP shows nearly an 70% increase in the capacity of the N-MIP as a result of the increased template loading from 4 mol% to 25 mol%. In contrast, the E-MIP actually decreased its capacity by approximately 35%; this decreasing effect has been reported previously in the literature for polymers formulated with EGDMA and MAA monomers [24,25]. Selectivity factors of different PAHs on pyrene imprinted polymers (both 4 mol% to 25 mol% template loading) were determined as the ratio of imprinting factors (uptake on MIP/uptake on NIP) for pyrene over each PAH. These values were normalized by dividing all selectivity values by the lowest selectivity factor in each row of the table (i.e for each imprinted polymer in that row), and the results shown in Table 2. Virtually all of the selectivity of the E-MIP is lost when the template loading is increased to 25 mol%; but the N-MIP selectivity remains nearly the same as the previous polymer with 4 mol% template loading in addition to its signficant increase in PAH uptake. For the N-MIP, binding for the template pyrene is approximately 20 fold more selective than the other PAH analogs for both low and high template loadings. Thus increased template loading in the N-MIP increases the binding capacity without adverse effects

Table 2
Normalized selectivity factors for PAHs on both N-MIPs and E-MIPs with two different template loadings*.

Template Loading (mol%)	Type of Polymer**	Analytes		
		Pyrene	Benzo[*a*]pyrene	Chrysene
4	N-MIP	20	1	1
	E-MIP	20	2	1
25	N-MIP	20	1.6	1
	E-MIP	1.4	1.2	1

* Samples analyzed in deionized water.
** N-MIP = polymer formulated with NOBE; E-MIP = polymer formulated EGDMA/MAA.

on selectivity. The improved molecular recognition properties of NOBE have been discussed in the literature [26,27] and stems from the increased cross-linking that keeps the fidelity of the imprinted sites through better rigidity of the imprinted polymer.

While excellent selectivity and uptake was found for pyrene imprinted N-MIPs, the decisive test of the imprinting effect is whether the selective binding performance can be reversed by imprinting one of the other PAH analogs. Thus, BAP was imprinted using both the N-MIP and E-MIP formulations, and the selectivity shown in Fig. 8. The size of the template in addition to hydrogen bonding and hydrophobic interactions is the primarily responsible for selectivity. The MIP prepared with BAP template selectively recognizes BAP while the MIP prepared with PYR selectively binds the template PYR even in the presence of BAP and CHR. The cross-selectivity experiments demonstrated that the NOBE cross-linking monomer could be responsible for formation of strong forces in the binding site of N-MIP. Again, the best selectivity is found for the N-MIP showing only 12% and 6% cross-reactivity for chrysene and pyrene, respectively. Cross reactivity on the E-MIP was 57% and 28% for chrysene and pyrene, respectively, which is only slightly better than the pyrene imprinted E-MIPs reported earlier (*vida infra*). For removal of BAP from seawater for environmental remediation applications, studies shown in Table 3 show that uptake of BAP on the N-MIP stays much the same as the values previously found in deionized water; while there is nearly a 50% change in uptake with the E-MIP. The nature of the increase for E-MIP is unclear but may be due again to hydrophobic effects. However, the static value for

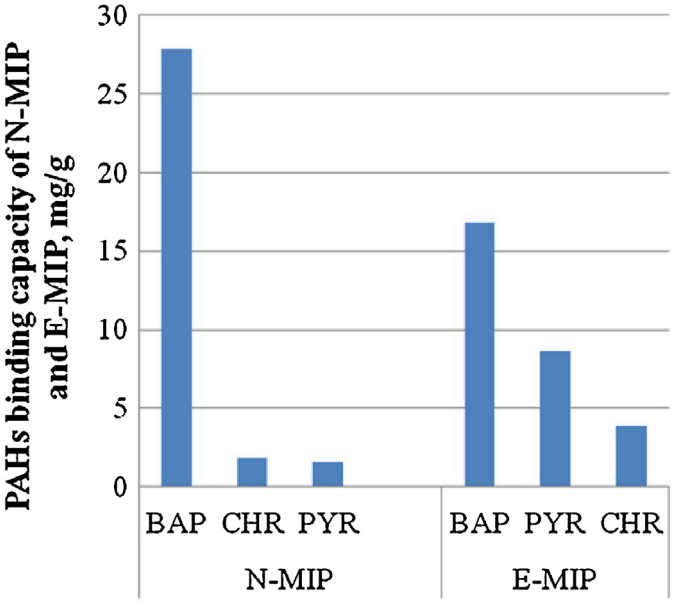

Fig. 8. Selectivityof benzo[*a*]pyrene (BAP) MIPs for BAP versus pyrene (PYR) and chrysene (CHR) in seawater.

Table 3
Comparison of BAP uptake on N-MIP versus the E-MIP in both deionized water and artificial sea water.

	Uptake of BAP in deionized water (mg/g)	Uptake of BAP in sea water (mg/g)
N-MIP	26.9	25.4
E-MIP	14.5	21.3

* Benzo[*a*]pyrene uptake (mg/g) was measured in deionized and artificial sea water. The template benzo[*a*]pyrnee loading is 4% mol in both the imprinted polymers. N-MIP and E-MIP are benzo[a]pyrene imprinted polymer with NOBE and EGDMA are the cross-linking monomers, respectively.

the N-MIP again supports the fact that binding applications can be carried out in saline water and in drinking water effectively with the same material.

4. Conclusion

Most studies on molecularly imprinted polymers in the literature focus on binding in organic solutions with a small number of reports on binding in aqueous systems, and even fewer that examine binding in salt water solutions. One reason for the few reports of MIPs in aqueous systems is that the non-covalent interactions that are employed for rebinding generally are disrupted by water and aqueous salts. In the example provided here, MIPs made with NOBE provided selective binding in an array of aqueous environments while maintaining high selectivity and good uptake capacity. This allows general application by the environmental community, whereas other MIP materials are usually developed for optimized binding in one solvent. As a result, these materials should find ubiquitous use for environmental and industrial PAH detection and recovery.

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