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ORIGINAL PAPER

Efficiency of a molecularly imprinted polymer for selective removal of phenols and phenoxyacids from contaminated waters

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Abstract The efficiency and the reuse of a bisphenol-A molecularly imprinted polymer (BPA-MIP) were evaluated for the selective removal of several phenolic compounds and phenoxyacid herbicides from environmental water samples. The proper sorption and selective recognition ability of the MIP were studied in aqueous solution by the batch equilibrium technique. Furthermore, removal of the analytes studied by the MIP was carried out from river, tap and ground waters, and different factors, such as the sample volume, the solution pH or the analyte concentration in the sample, were studied. Results obtained indicated a rapid sorption of analytes by the MIP, being the sorption dependent on the concentration of analyte in the solution. The MIP showed an excellent affinity toward phenolic compounds and phenoxyacid herbicides, and removal efficiencies of over 70 % were achieved in aqueous solution. Removal efficiency was not affected by the pH or by the water type, although it was affected by the volume of water especially for nitrophenols when amounts in solution were $\geq$1 mg. Removal efficiencies recorded by the MIP for the highest volume of water assayed were around 20 % higher than those obtained with traditional sorbents for chlorophenols and bisphenols, and similar removal efficiencies were obtained for phenoxyacid herbicides. The use of the MIP provided a selective, simple, reliable and viable solution for removing these compounds from water, and it could be re-used at least 20 times without losing any removal efficiency.

Keywords Molecularly imprinted polymers · Phenols · Phenoxyacids · Selective removal · Water treatment

Introduction

Many chemicals present in the environment may have adverse effects on aquatic life, wild animals and human beings. Among these chemicals, chlorinated phenols are an important class of pollutants because of their wide use in the production of wood preservers, pesticides and biocides. One of the most widely produced chlorophenols is 2,4-dichlorophenol (DCPL), which can cause respiratory failure, bone marrow atrophy, skin damage and even death in animals (Li et al. 2009a). Phenolic estrogen mimics, such as bisphenol-A and -F, can affect the endocrine system (Fromme et al. 2002). The toxic and carcinogenic nitrophenols are considered to be one of the most important class of organic contaminants (Sahiner et al. 2011). Finally, phenoxyacid herbicides are of proven toxicity to both humans and animals (Bus and Hammond 2007). These impacts may be cumulative, appearing even in subsequent generations, and are irreversible, endangering the sustainable survival of both humans and ecosystems.

Many of these compounds end up in the aquatic environment via sewage, atmospheric deposition, discharges of domestic and/or industrial effluents, or agricultural runoff. Several physical, chemical and biological methods, such as ozonation, UV radiation or sorption, have been developed to remove them from water (Zhang and Hu 2008). The implementation of techniques such as ozonation or UV

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radiation is only partially efficient, as waste stream may be generated and toxicologically relevant oxidation by-products may be formed during the treatment processes. Furthermore, the overall toxicity of treated water arising from a mixture of stable transformation products may increase the environmental and health impacts (Mompelat et al. 2009). However, physicochemical methods based on sorption are deemed more suitable processes for the removal of pollutants from water (Mohanty et al. 2006).

Activated carbon commercial or produced from natural waste products (Thuy et al. 2012), natural zeolites (Wang and Peng 2010) or clay minerals modified with cationic surfactants (Sanchez-Martin et al. 2006) are well-established sorbents for hydrophobic contaminants. They have often been used for water and wastewater treatment, although they are significantly affected by the presence of interfering substances, such as humic acid and natural organic matter. These substances can easily be sorbed by these sorbents, consuming most of its sorption capacity, and therefore, its removal efficiency could be compromised. In addition, all of these methods have relatively low selectivity. Recent research work has been focused toward alternative adsorbents, namely low-cost adsorbents (Zolgharnein et al. 2011). Hence, the search for low-cost and highly selective removal methods is still a priority. Hence, other alternatives have been investigated to determine their relative sorptive properties, such as a novel composite containing silver nanoparticles and colemanite ore waste to remove reactive dyes or a photocatalyst based on TiO_2 nanoparticles synthesized using a boron enrichment waste for photodegradation of atrazine from aqueous solution (Lütfi Yola et al. 2014a, b).

Molecular imprinting is a useful, simple and economical technique for the preparation of molecularly imprinted polymers (MIPs) as sorbents with a predetermined selectivity toward a given analyte or a group of structurally related species. MIPs can bind an analyte from a mixture of compounds, and this makes molecularly imprinted solid-phase extraction (MISPE) a very attractive technique for the removal of trace pollutants from water (Cacho et al. 2009; Carabias-Martínez et al. 2005; Feng et al. 2009). Krupadam et al. (2010) made a cost comparison of MIP and activated carbon showing that 1 g of MIP can purify 3,810 L of contaminated water with the cost of 1.2 USD, while 1 g of activated carbon can purify 190 L with the cost of 0.9 USD; that is, MIP could purify 3,556 L more than activated carbon with the same cost.

MIPs have been used in recent studies for the selective removal of single pollutants or groups of pollutants from complex water samples. For example, a MIP was used for the selective removal of single contaminants, such as 17β-estradiol at trace concentration (Koç et al. 2011; Le Noir et al. 2007), diclofenac from contaminated water (Dai et al. 2011), perfluorooctane sulfonate from aqueous solution (Yu et al. 2008), 2,4-dichlorophenol from contaminated water (Li et al. 2009b), 2,4-dichlorophenoxyacetic acid from water (Han et al. 2010) and nonylphenol from aqueous solution (Pan et al. 2013). MIPs also have been used for the selective removal of several contaminants of the same family, such as phenolic estrogens from different water sources (Lin et al. 2008), polycyclic aromatic hydrocarbons from contaminated water (Krupadam et al. 2010), endocrine-disrupting contaminants from aqueous effluents (Fernández-Álvarez et al. 2009), estrogenic compounds and water-soluble acid dyes from a water environment (Zhang and Hu 2008; Luo et al. 2011) and more recently, fluoroquinolone antibiotics from aqueous solution (Tan et al. 2013). Liu et al. (2014) have used a double-template MIP on the surface of carbon microspheres for the selective removal of benzothiophene and dibenzothiophene from gasoline. However, to our knowledge few works include compounds of different families as target compounds. Some of these studies used multi-template imprinted polymers for the selective removal (Dai et al. 2012), but works using only a template to remove compounds of different families as it is proposed here have not been reported. Furthermore, most of the reports included less than three compounds and the great majority included only one. Few works have included five compounds in the study, and works including eight compounds have not been found in the literature.

Some studies showing the use of MIPs in the determination of phenols and phenoxyacids in complex samples, such as urine, honey and river water, were previously published by us. They were focused in the solid-phase extraction analytical application (MISPE) (Herrero-Hernández et al. 2009, 2011), and more recently in the monitoring of the quality of environmental waters from a vineyard region in La Rioja (Spain) (Herrero-Hernández et al. 2013). Due to the high presence of BPA detected in these environmental waters, a new application of the MIPs was evaluated in the present work to explore whether these materials could be used to treat waters with high pollution levels (as can be waste waters of canned food factories) or high volumes of waters intended for human consumption with levels of pesticides higher than 0.1 $\mu g\ L^{-1}$.

Accordingly, and with a view to establishing a sound practice for the use of a MIP as sorbent in treating of polluted water, the objectives of this work were (1) to investigate the characteristics of the bisphenol-A imprinted polymer (BPA-MIP), including sorption properties, molecular recognition selectivity, and regeneration recognition selectivity, (2) to evaluate their efficiency as sorbent of different phenolic compounds and phenoxyacid herbicides in different experimental conditions and (3) to compare the MIP capacity as sorbent with the abilities of other materials, such as activated carbon or modified clays used usually as sorbents of organic contaminants.

Research described in this study was carried out during years 2012–2013 at the University of Salamanca and the Natural Resources and Agrobiology Institute of Salamanca (Spain).

Materials and methods

Chemicals

Phenolic compounds and phenoxyacid herbicides were obtained from Sigma-Aldrich (Steinheim, Germany) and were used without further purification. The compounds studied were as follows: bisphenol-A (BPA); bisphenol-F (BPF); 4-nitrophenol (NOPL); 3-methyl-4-nitrophenol (MeNOPL); 2,4-dichlorophenol (DCPL); 2,4,5-trichlorophenol (TCPL); 2,4-dichlorophenoxyacetic acid (2,4-D); 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). Stock solutions of each analyte were prepared in ultrapure water (UHQ) obtained from a Milli-Q water system (Millipore, Milford, MA, USA) at 1,000 μg mL^{-1}.

4-Vinyl pyridine (4-VP), ethylene glycol dimethacrylate (EDMA) and trimethylolpropane trimethacrylate (TRIM) were obtained from Sigma-Aldrich (Steinheim, Germany). 2,2′-Azobis (2-methylpropionitrile) (AIBN) was obtained from Acros Organics (Geel, Belgium).

HPLC grade methanol was supplied by Merck (Darmstadt, Germany) and used as received. Analysis grade toluene and acetic acid were provided by Scharlau (Barcelona, Spain). Octadecyltrimethylammonium bromide (ODTMA) for preparing modified clay mineral (Tidinit montmorillonite from Morocco) was supplied by Sigma-Aldrich (Steinheim, Germany), and activated carbon was supplied by Merck (Darmstadt, Germany).

Synthesis of the molecularly imprinted polymers

The procedure to obtain the polymers was as follows: the characterization (particle size, pore volume, surface area and scanning electron micrographs) and the study of the selectivity of the imprinted polymer BPA–MIP, were described previously by the authors (Herrero-Hernández et al. 2009, 2011). These characteristics are as follows: specific surface area, 62.25 m^2 g^{-1}; specific pore volume, 0.068 cm^3 g^{-1}; and average pore diameter, 4.06 nm. The polymer particles had a regular spherical morphology, independently of the cross-linker used, with an average particle diameter of about 0.8 μm.

A non-imprinted polymer (NIP) was also prepared for comparison with the MIP in the same way without the addition of a template to the polymerization mixture, and with EDMA as the sole cross-linker monomer. The physical characteristics of the NIP are similar to those of the BPA-MIP.

Sorption experiments

Sorption kinetics and isotherms of all analytes by MIP with the different cross-linkers (EDMA, TRIM or a mixture EDMA/TRIM) and by NIP were obtained using the batch equilibrium technique. Sorption kinetics was initially carried out to determine the time when equilibrium is reached. Triplicate samples (10 mg) of sorbents were equilibrated with 1 mL of UHQ water solution of each analyte studied at a concentration of 50 mg L^{-1}. The suspensions were shaken in a thermostated chamber at 20 °C for time periods of 5, 10, 15, 30 and 60 min and subsequently centrifuged at 3,000 rpm for 15 min. The supernatant was filtered through a GHP Acrodiscs 0.45 μm filter (Waters Corp.), and the equilibrium concentrations of analytes were then determined as indicated below. The amount of analyte sorbed by the polymers was considered to be the difference between the amount initially present in solution and that remaining after equilibration with the polymers.

For sorption isotherms, triplicate samples (10 mg) of sorbents were equilibrated during 15 min with 1 mL of UHQ water solution of each analyte studied at different concentrations between 5 and 200 mg L^{-1}.The sorption data for all the analytes were fitted to Freundlich and Langmuir sorption equations. The linearized form of the Freundlich equation is: $\log \mathrm{Qs} = \log K_{\mathrm{f}} + n\mathrm{f} \log \mathrm{Ce}$, where Qs (mg g^{-1}) is the amount of sorbed compound, Ce (mg L^{-1}) is the equilibrium concentration of compound in solution, and K_{f} (mg^{1-nf} g^{-1} L^{nf}) and nf are the Freundlich sorption coefficient and nonlinearity coefficient, respectively. The linearized form of the Langmuir equation is $\mathrm{Ce}/\mathrm{Qs} = \mathrm{Ce}/Q_{\max} + 1/Q_{\max}b$, where $Q_{\max}$ (mg g^{-1}) is a constant that indicates the sorbent’s maximum compound sorption capacity and b (L g^{-1}) is an index of sorption energy that determines the magnitude of the initial slope on the isotherm. Standard deviations were used to determine the variability in the sorption coefficient values among replicates.

Removal experiments

Removal experiments of the analytes studied by the MIP were carried out from different aqueous solutions in empty solid-phase extraction (SPE) cartridges. The cartridges were loaded with 25 mg of MIP and previously conditioned with 10 mL of methanol/acetic acid (9:1, v/v) and 10 mL of UHQ water, after aqueous samples were passed with a peristaltic pump at a flow of 2.5 mL min^{-1}. Different experimental conditions were evaluated, and the

MIP removal efficiency was calculated as $(C_0 - C_1)/C_0) \times 100$, where C_0 was the initial concentration of compounds in the spiked solution and C_1 was the concentration of compounds in the solution after loading (Lin et al. 2008).

Initially sample volume and analyte concentration were studied. UHQ water sample volumes of 5, 10, 25, 50 and 100 mL spiked with 1 mg of each compound (NOPL, MeNOPL, DCPL, TCPL, BPF, BPA, 2,4-D and 2,4,5-T) or UHQ water sample volumes of 5, 25, 50, 100 and 250 mL containing a smaller amount of each compound (0.5 µg) were initially passed through the cartridge loaded with MIP with a peristaltic pump.

The effect of pH on the removal of compounds from water was studied in 10 mL water samples spiked with 1 mg of NOPL, DCPL, BPA and 2,4-D (as representative of the compounds studied). The pH was adjusted in the 2–10 range by adding small amounts of hydrochloric acid or sodium hydroxide solution.

To study the influence of different water types on the removal efficiency of analytes by the MIP, volumes of 100 mL of groundwater collected from a 10-m-deep well in an agricultural region, tap water and water from the Tormes River in Salamanca (Spain) spiked with 1 mg or 0.5 µg of each compound were passed through a cartridge loaded with MIP (25 mg). These water samples were collected directly in 1-L glass bottles for spiking. Some water parameters measured in situ, for river water and groundwater, were: pH 7.17 and 6.33; conductivity 31.70 and 209 µS cm^{-1}; dissolved oxygen 9.41 and 3.25 mg L^{-1}; dissolved total solids 20.30 and 134 mg L^{-1} and NaCl content 15.05 and 98.1 mg L^{-1}, respectively. All the samples were filtered through 0.45-µm-pore-size cellulosic membrane filters (Osmonics®, Kent, WA, USA) and stored at 4 °C in the dark until extraction. Prior to spiking, all the water samples were analyzed using the analytical method proposed below to check for the presence of the analytes studied. No signals corresponding to target analytes were found, and so spiked water samples were used in the removal experiments.

Removal experiments with other sorbents

Removal experiments of analytes involving two different materials commonly used as sorbents of contaminants were also conducted as a complementary study to the use of MIP. Powdered activated carbon (Act C) and modified clay prepared by modifying the clay mineral montmorillonite (M) with the organic cation ODTMA as described by Sanchez-Martin et al. (2006) were used. The cartridges were loaded with 25 mg of each sorbent and conditioned only with 10 mL of UHQ water. Different volumes (10 and 100 mL) of UHQ water, groundwater, tap water and river water, spiked with 1 mg of each compound, were passed through cartridges loaded with Act C or ODTMA-M.

Regeneration of MIP and reuse

Regeneration of MIP was evaluated by passing 25 mL of groundwater, spiked with 5 µg of each analyte, through the cartridges loaded with 25 mg of MIP. The cartridges were then dried for 30 min under a vacuum of −15 mmHg and washed with 10 mL of methanol/acetic acid (9:1, v/v) and 10 mL of UHQ water for their regeneration. The regeneration capacity of the MIP was determined by the removal efficiency calculated in the same cartridges after reuse up to 20 times of the cartridges.

Analytical determination of phenols and phenoxyacid herbicides

The compounds were determined by HPLC–MS–ESI operated in negative mode on a Waters (Milford, MA, USA) system with a Waters Micromass ZQ quadrupole mass spectrometer with an ESI interface. The analytical column used was a Waters Symmetry C18 column (75 × 4.6 mm i.d., 3.5 µm) used at ambient temperature, and the mobile phase was methanol (solvent A)—water 0.1 % formic acid (solvent B). The elution gradient was as follows: the mobile phase started with 58 % of methanol, which was raised to 60 % in 4 min and to 90 % in 2 min. The percentage was then increased to 100 % in 4 min with an isocratic period of 2 min and returned to initial conditions in 2 min, with an equilibration time of 5 min. The flow rate was 0.3 mL min^{-1} and the volume injected was 20 µL. The MS parameters were as follows: capillary voltage, 3.1 kV; cone voltage 20 V, source temperature, 120 °C; desolvation temperature was set at 300 °C; the desolvation gas flow and the cone gas flow were set at 400 and 60 L h^{-1}, respectively. Calibration was performed from 0.05 to 2.0 mg L^{-1} and the limit of detection (LOD) and limit of quantification (LOQ) were lower than 0.015 and 0.034 µg mL^{-1}, respectively.

Results and discussion

Sorption experiments: influence of the cross-linker

Different sorption experiments were conducted to study the influence of the cross-linker in this process not evaluated in our previous works. Sorption kinetics of analytes by the MIPs prepared with EDMA, TRIM or mixtures (1:1) of both as cross-linker and by the NIP prepared with EDMA were determined to establish the sorbent/analyte equilibrium time before studying the sorption isotherms. Figure 1

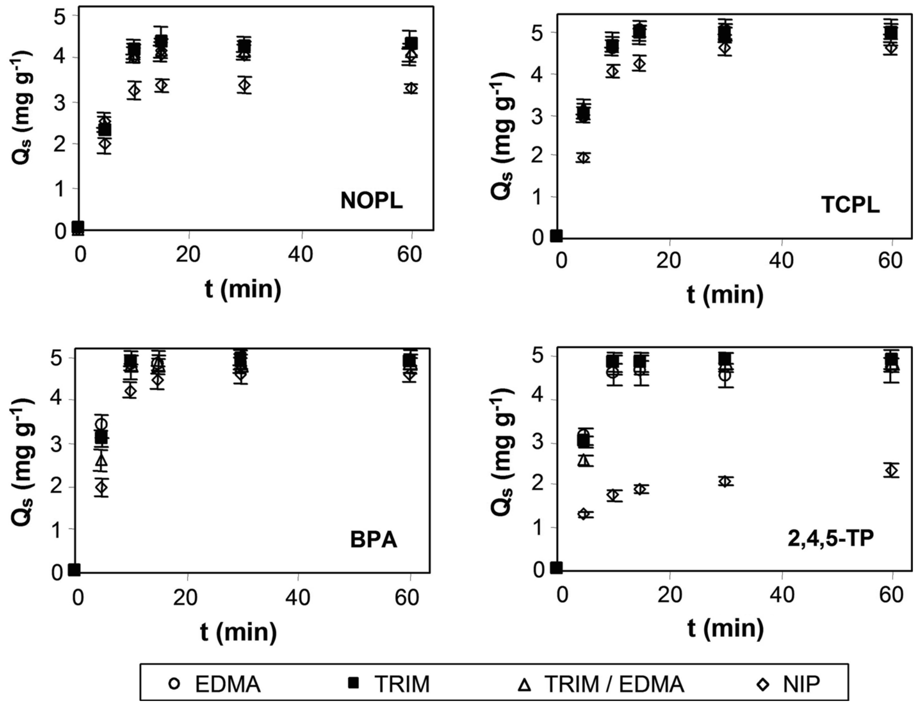

Fig. 1 Sorption kinetics of 4-nitro-phenol (NOPL), 2,4,5-trichlorophenol (TCPL), bisphenol-A (BPA) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) by a MIP with different cross-linkers and a NIP in aqueous solution. Sorbent: 10 mg; volume: 1 mL; temperature: 20 °C

includes kinetics corresponding to NOPL, TCPL, BPA and 2,4,5-T representative of phenols and phenoxyacid herbicides studied. Similar sorption kinetics were obtained for the other compounds belonging to the same groups, that is, MeNOPL, DCPL, BPF and 2,4-D, respectively. MIPs have affinity toward phenols and phenoxyacid herbicides in UHQ water. The sorption kinetics could be divided into two phases. In the first phase, the sorption rate was higher and the contact time to sorb more than 80 % was lower than 15 min. In the subsequent phase, sorption rate was slower and sorption equilibrium was reached (Fig. 1). Sorption kinetics by MIPs were similar independently of the cross-linker used as it is indicated by the maximum amounts sorbed. In the case of NIP, sorption was slightly lower for the compounds studied, but this decrease was only significant for the phenoxyacid herbicides with sorbed amounts 2–3 times lower than those for MIPs.

Sorption isotherms of analytes by $\mathrm{MIP_{EDMA}}$, $\mathrm{MIP_{TRIM}}$ and $\mathrm{NIP_{EDMA}}$ were obtained. Figure 2 includes only those corresponding to phenols MeNOPL, DCPL and BPF, and phenoxyacid herbicide 2,4-D, as similar sorption isotherms were obtained for the compounds belonging to the same groups, that is, NOPL, TCPL, BPA and 2,4,5-T, respectively. All the isotherms were characterized by a high initial solute sorption by the sorbents, and sorption decreased as compound concentration increased. They were classified as L-type according to the Giles classification (Giles et al. 1960).

Many models have been successfully used to describe experimental data on sorption isotherms, with Freundlich and Langmuir models being widely used. The isotherms obtained in this work fitted these models, and the sorption parameters of analytes were calculated for the different sorbents (Table 1). In general, the sorption of most of the compounds was better described by the Langmuir equation ($r \geq 0.946$) than by the Freundlich equation ($r \geq 0.934$). The Langmuir constants $Q_{\max}$ and b for the MIP sorbents were always higher than those for the NIP sorbent possibly due to stronger interactions between phenols and phenoxyacid herbicides and the functional groups of the MIPs where template was bonded before being removed. These interactions are not present in the case of NIP, where they could only be established between compounds and the polymeric matrix.

The Freundlich equation is suitable for heterogeneous surfaces and has been applied in the sorption of perfluorooctane sulfonate by the non-covalently prepared MIPs (Yu et al. 2008). In this study, the experimental data also fitted the Freundlich equation quite closely, which can be explained by adsorption site heterogeneity, electrostatic attraction and other sorbent–sorbate interactions. This is consistent with the interaction mechanism explained by the authors in a previous work for a propazine-MIP (Carabias-Martínez et al. 2006). Compounds can interact in a specific way with the MIP or by non-specific hydrophilic interactions (hydrogen bridges) with the polymeric matrix.

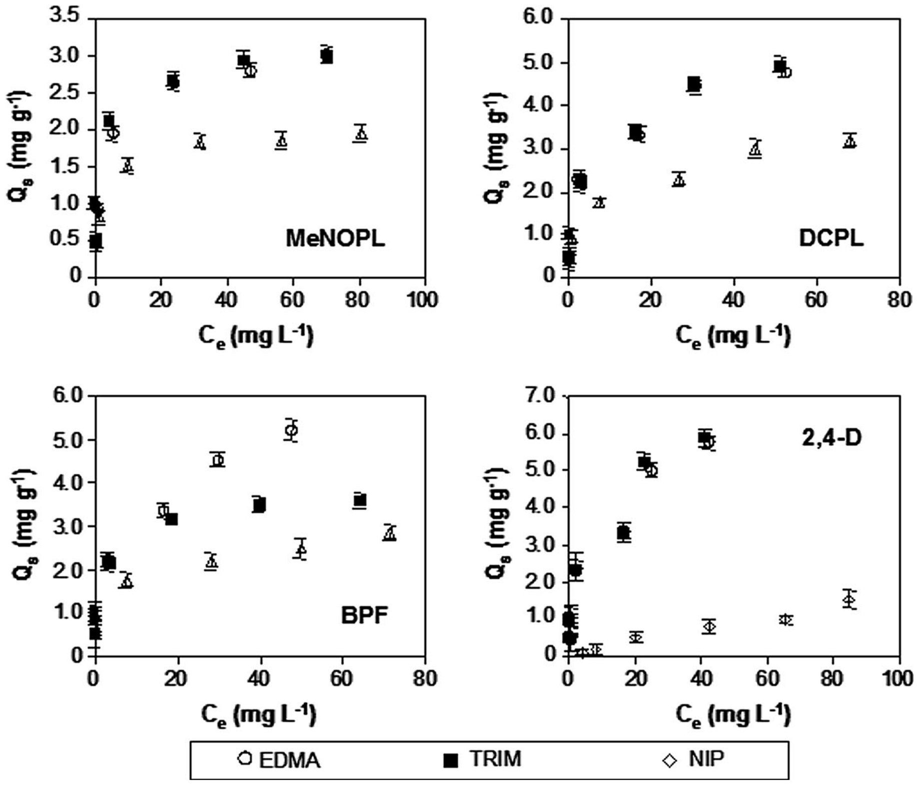

Fig. 2 Sorption isotherms of 3-methyl-4-nitro-phenol (MeNOPL), 2,4-dichlorophenol (DCPL), bisphenol-F (BPF) and 2,4-dichlorophenoxyacetic acid (2,4-D) by a MIP with different cross-linkers and a NIP in aqueous solution. Sorbent: 10 mg; volume: 1 mL; time: 15 min.; temperature: 20 °C

Significative differences were not observed between the sorption parameters obtained when different cross-linkers were used to obtain the imprinted polymer. For this reason, studies carried out later were conducted only with the polymer obtained with EDMA as cross-linker.

Influence of pH, concentration, volume and type of water on the MIP removal efficiency

The pH of water plays an important role in the extent of sorption. pH values can be significantly different according to the type of contaminated water, and this could influence the properties of the MIP surface and also the speciation of the target compounds. The influence of water pH on the MIP's removal efficiency was investigated in the 2–10 pH range and results showed that water pH did not affect removal efficiency significantly in the range studied (data not shown). Only a slight decrease was observed in the removal efficiency values of the chloro- and nitrophenols at a pH of 2. Li et al. (2009b) found similar results for DCPL.

With a view to designing a water treatment procedure that would provide suitable removal efficiency, the effect of the water volume to be treated was studied (Fig. 3). It is known that conventional sorbents such as activated carbons record a gradual decrease in removal efficiency as the loading volume increases, as there is no binding selectivity to the pollutants treated. An increase in the volume of the sample treated has certain limitations because the loading capacity of the sorbent might be surpassed or a breakthrough phenomenon may occur for highly polar pollutants.

The influence of treated water volume on removal efficiency was studied under two different conditions: water containing 1 mg or 0.5 µg of each compound studied. Figure 3a shows the results for UHQ water volumes ranging between 10 and 100 mL containing 1 mg of each pollutant. Different behaviors were observed for the different groups of compounds, with a significant effect of the volume treated, with as much as a fourfold reduction in the removal efficiency for a volume of 100 mL being observed for nitrophenols (NOPL and MeNOPL). This behavior could be explained by the presence of the nitro group in position *para,* with the consequent steric impediments, facilitating the access of all the other compounds. For chlorophenols (DCPL and TCPL) and bisphenols (BPF and BPA), a small effect of the volume of water was observed, and removal efficiencies were around 80 %, even for the maximum volume, due to more effective binding mechanisms. For phenoxyacid herbicides (2,4-D and 2,4,5-T), an intermediate behavior was observed, and decreases in the removal efficiencies were less than 30 % for the maximum volume, remaining at around 60 %.

These kinds of compounds are usually present in water at lower concentrations, especially herbicides such as

Table 1 Sorption coefficients of phenols and phenoxyacids by the imprinted (MIP) and non-imprinted (NIP) polymers determined by Langmuir equation (Q_{max} and b) and Freundlich equation (K_f and n_f) and correlation coefficients (r^2) of sorption models

Compound/sorbent	Langmuir isotherm			Freundlich isotherm		
	Q_{max} ± SD[a]	b ± SD	r^2	K_f ± SD	n_f ± SD	r^2
4-Nitro-phenol (NOPL)						
MIP_{EGDMA}	2.18 ± 0.05	0.41 ± 0.01	0.997	0.86 ± 0.01	0.24 ± 0.00	0.976
MIP_{TRIM}	2.24 ± 0.06	0.92 ± 0.01	0.995	1.07 ± 0.01	0.20 ± 0.01	0.927
NIP_{EGDMA}	1.36 ± 0.08	0.26 ± 0.01	0.995	0.59 ± 0.02	0.19 ± 0.01	0.873
3-Methyl, 4-nitro-phenol (MeNOPL)						
MIP_{EGDMA}	2.87 ± 0.04	1.14 ± 0.01	0.997	1.22 ± 0.00	0.23 ± 0.00	0.979
MIP_{TRIM}	3.03 ± 0.05	0.99 ± 0.02	0.953	1.80 ± 0.03	0.13 ± 0.01	0.949
NIP_{EGDMA}	1.93 ± 0.06	0.51 ± 0.01	0.995	0.71 ± 0.03	0.26 ± 0.02	0.957
2,4-Dichlorophenol (DCPL)						
MIP_{EGDMA}	3.37 ± 0.03	1.14 ± 0.01	0.991	1.23 ± 0.04	0.37 ± 0.01	0.968
MIP_{TRIM}	4.23 ± 0.06	0.64 ± 0.01	0.991	1.22 ± 0.03	0.38 ± 0.01	0.959
NIP_{EGDMA}	2.71 ± 0.06	0.46 ± 0.02	0.993	0.79 ± 0.05	0.34 ± 0.01	0.946
2,4,5-Trichlorophenol (TCPL)						
MIP_{EGDMA}	4.90 ± 0.04	0.85 ± 0.01	0.934	2.26 ± 0.05	0.27 ± 0.01	0.927
MIP_{TRIM}	5.49 ± 0.03	0.83 ± 0.01	0.961	2.08 ± 0.04	0.33 ± 0.02	0.947
NIP_{EGDMA}	2.94 ± 0.04	0.44 ± 0.01	0.926	1.59 ± 0.02	0.09 ± 0.01	0.924
Bisphenol-F (BPF)						
MIP_{EGDMA}	4.31 ± 0.05	1.77 ± 0.01	0.991	1.62 ± 0.02	0.29 ± 0.00	0.993
MIP_{TRIM}	3.67 ± 0.03	0.41 ± 0.01	0.996	1.77 ± 0.05	0.28 ± 0.02	0.964
NIP_{EGDMA}	2.76 ± 0.05	0.21 ± 0.02	0.904	1.11 ± 0.03	0.11 ± 0.02	0.977
Bisphenol-A (BPA)						
MIP_{EGDMA}	3.81 ± 0.04	0.46 ± 0.01	0.978	0.80 ± 0.03	0.56 ± 0.02	0.971
MIP_{TRIM}	5.74 ± 0.02	0.33 ± 0.01	0.896	1.7 ± 0.4	0.7 ± 0.3	0.941
NIP_{EGDMA}	3.36 ± 0.06	0.13 ± 0.01	0.981	0.29 ± 0.02	0.33 ± 0.01	0.906
2,4-Dichlorophenoxyacetic acid (2,4-D)						
MIP_{EGDMA}	4.87 ± 0.05	0.65 ± 0.01	0.967	1.21 ± 0.06	0.42 ± 0.02	0.933
MIP_{TRIM}	4.95 ± 0.04	0.55 ± 0.01	0.911	1.75 ± 0.04	0.51 ± 0.03	0.946
NIP_{EGDMA}	2.38 ± 0.07	0.01 ± 0.01	0.997	0.04 ± 0.03	0.02 ± 0.01	0.989
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)						
MIP_{EGDMA}	4.15 ± 0.06	0.59 ± 0.02	0.973	1.30 ± 0.03	0.72 ± 0.02	0.921
MIP_{TRIM}	4.09 ± 0.04	0.56 ± 0.02	0.907	1.58 ± 0.03	0.71 ± 0.02	0.938
NIP_{EGDMA}	2.06 ± 0.05	0.06 ± 0.01	0.987	0.09 ± 0.02	0.22 ± 0.01	0.960

[a] SD, standard deviation of three replicates

phenoxy acids, with a maximum permitted level in waters for human consumption of 0.1 μg L^{-1} (CEC-Council of the European Communities 1998). Hence, a different study was carried out with different volumes of water (ranging between 5 and 250 mL) spiked with a lower amount of each compound (0.5 μg). Results obtained (Fig. 3b) indicated that the removal efficiency of the MIP was less influenced and remained approximately constant and independent of the volume of water treated. Moreover, removal efficiencies were slightly higher than that in the case of water with a higher concentration. This is probably because the binding sites of the MIP were not saturated, and there were free binding sites even for compounds with less affinity toward the MIP, such as nitrophenols.

The feasibility of applying a MIP for removing phenols and phenoxyacid herbicides from polluted natural waters was evaluated for waters with different origins (groundwater, tap water, river water and UHQ water) spiked with 1 mg of each compound. Figure 4 shows the removal efficiencies obtained for each type of water. Small differences in the removal efficiency values for the different types of water were observed, but no general trends could be established. For nitrophenols, the best removal efficiencies were obtained for groundwater,

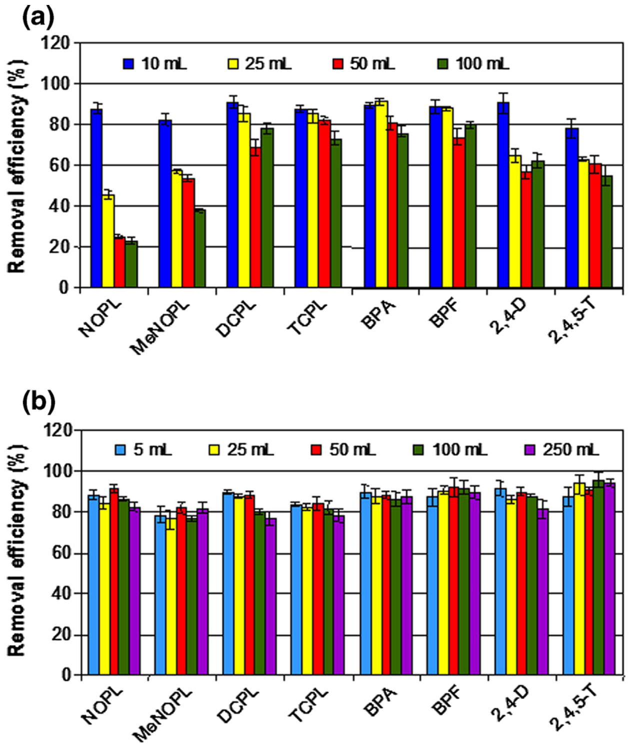

Fig. 3 Influence of water sample volume and contaminant concentration on the removal efficiency of the MIP. **a** 10, 25, 50 and 100 mL of water spiked with 1 mg of each compound and **b** 5, 25, 50, 100 and 250 mL of water spiked with 0.5 µg of each compound. Sorbent: 25 mg

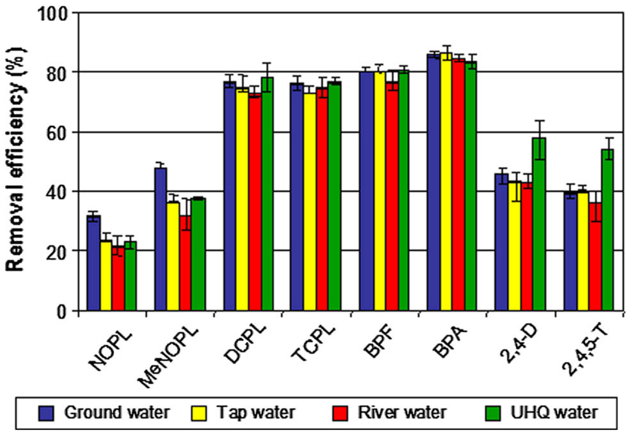

Fig. 4 Removal efficiency of the MIP for the contaminants in different water samples (groundwater, tap water, river water and UHQ water). Volume of water treated: 100 mL spiked with 1 mg of each compound. Sorbent: 25 mg

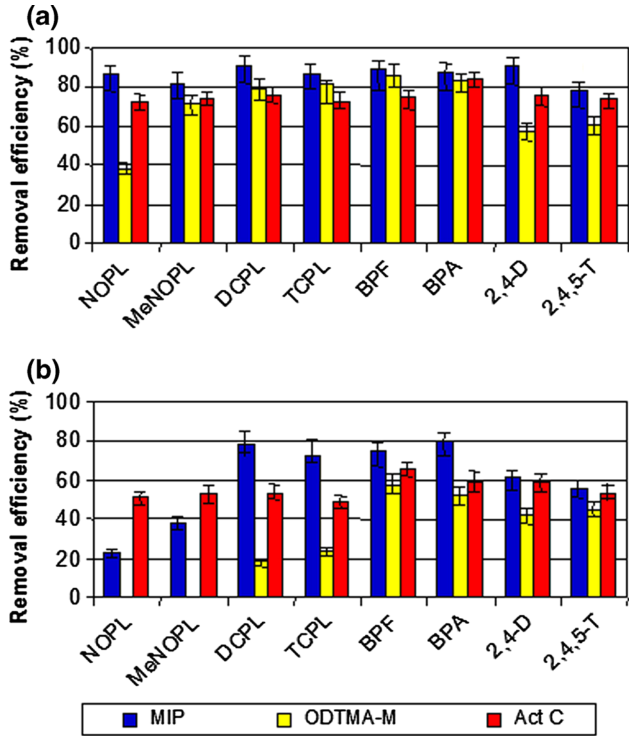

Fig. 5 Removal efficiency of different sorbents (MIP, ODTMA-M and Act C) for the contaminants in river water samples. Volume of water treated: 10 mL spiked with 100 mg L^{-1} of each compound (**a**) and 100 mL spiked with 10 mg L^{-1} of each compound (**b**). Sorbent: 25 mg

while UHQ water recorded the highest efficiencies in the case of phenoxyacid herbicides. In both cases, the differences observed were lower than 20 %. In the case of chlorophenols and bisphenols, the efficiencies were similar (≈80 %) for all waters. When this study was performed with waters spiked with a lower amount of each compound (0.5 µg of each), no significant differences were observed in the removal efficiencies of any compound (data not shown).

Removal efficiency of MIP and other sorbents

The capacity of the MIP as sorbent was compared with other widely used and effective sorbents, such as ActC or ODTMA-M, for the treatment of phenols and phenoxyacid herbicides in polluted river water. For a sample volume of 10 mL (Fig. 5a), the results indicated a removal efficiency of MIP in the range 80–90 % in general for all analytes; it was higher than that obtained with ActC (range 72–85 %) or with ODTMA-M, (range 38–85 %) for some of the compounds studied.

When the volume of water treated was 100 mL (Fig. 5b), the removal efficiencies recorded by the MIP decreased (range 22–85 %) although they were up to 20 % higher than those obtained with ActC for chlorophenols and bisphenols. Removal efficiencies of ActC and ODTMA-M were in the ranges 50–65 and 0–58 %, respectively, and only removal efficiency of ActC was higher than that of MIP for nitrophenols compounds.

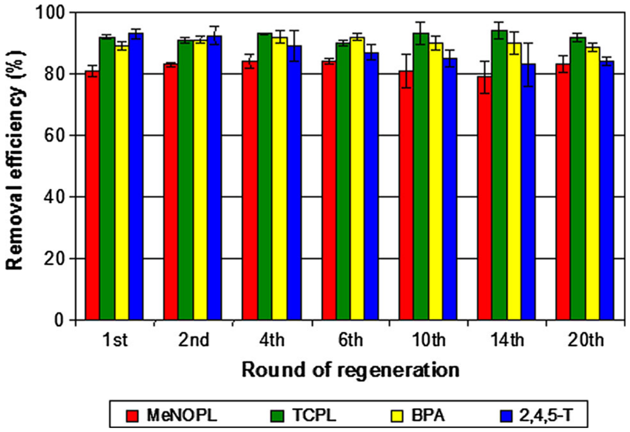

Fig. 6 Removal efficiency of the MIP for the contaminants in groundwater after different cycles of regeneration. Volume of water treated each cycle: 25 mL of ground water spiked with 5 µg of each compound. Sorbent: 25 mg

Evaluation of MIP reuse and regeneration for removal

Considering the way in which MIPs work, compounds retained can be extracted and binding sites freed up for a new sorption. Accordingly, MIPs could be reused several times in removal experiments. This reuse is a key factor for improving the cost of contaminated water treatment processes. The stability and potential regeneration of the MIP was evaluated. As shown in Fig. 6, the MIP can be regenerated and reused repeatedly at least twenty times without a significant decrease in the removal efficiency for any one of the compounds. The demonstrated reusability of the MIP over several sorption/desorption cycles is an advantage with regard to the single use of ActC, which is difficult to regenerate and tends to saturate at lower loads. Therefore, the use of MIPs to remove pollutants from water clearly has the potential to reduce the cost of contaminated water treatment.

Conclusion

This study revealed the potential of MIPs for the removal of certain phenols and phenoxyacid herbicides from different types of water. It is interesting to note that a group of six phenolic compounds and two phenoxyacid herbicides were sorbed by a single imprinted polymer, which is more desirable for polluted water treatment. The sorption of these compounds was very rapid, and sorption equilibrium was achieved within 15 min. Another advantage of this kind of sorbents is that the removal efficiency was practically independent of the pH and the nature of the polluted water. In comparison, the MIP has higher removal efficiency than the same amount of a conventional sorbent, such as activated carbon or modified clays, especially when the amount of water treated was increased. MIP sorbents have an excellent regeneration performance and can be reused at least twenty times without any appreciable loss of sorption capacity. The MIP provided a reliable and effective solution for removing these kinds of pollutants from water.

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