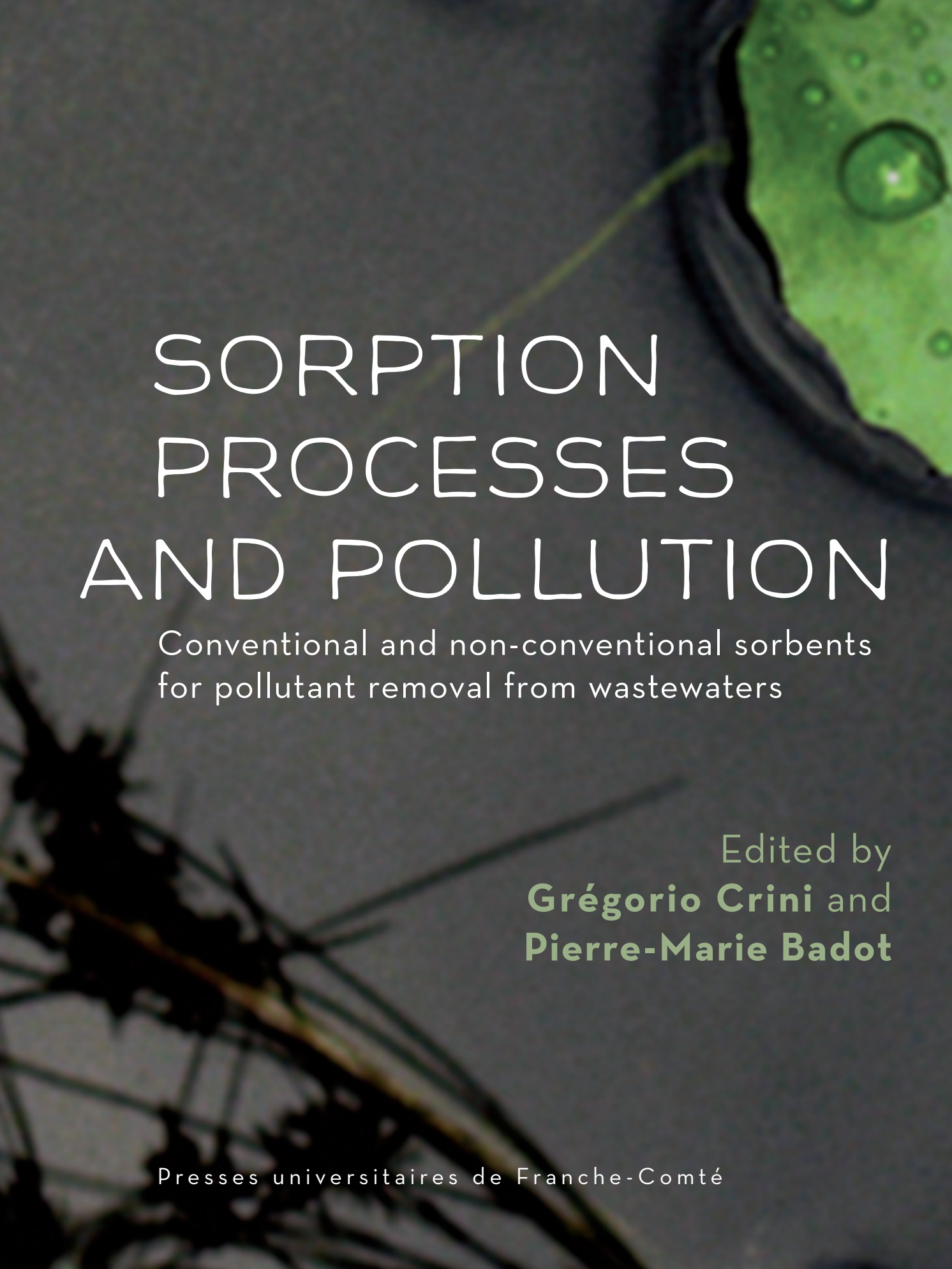

SORPTION PROCESSES AND POLLUTION

Conventional and non-conventional sorbents for pollutant removal from wastewaters

Edited by
Grégorio Crini and
Pierre-Marie Badot

Presses universitaires de Franche-Comté

This book shows a typical selection of the types of adsorbents studied and used in wastewater treatment, with emphasis on industrial effluents. The types of materials considered range from conventional sorbents such as carbons and silicas, to non-conventional solids such as sawdust and chitosan. Sorbents for specific applications (e.g. colour removal, metal extraction, fluoride removal) and new polymeric-based sorbents (calixarenes, molecularly imprinted polymers, cyclodextrins) are discussed in detail. For people who are new to the field, two special overview chapters, dealing with the principles and properties of adsorption processes, are provided at the beginning of the book. Also, the book provides a detailed review of sorption features.

Grégorio Crini, environmental polymerist, received his PhD in organic and macromolecular chemistry from the university of Lille in 1995. He joined the university of Franche-Comté at Besançon in 1997 where he was made research director in 2000. His current interests focus on the design of novel polymer networks and the environmental aspects of polysaccharide chemistry.

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Chapter 18

Molecularly imprinted polymers (mips) as selective sorbents for wastewater pollutants

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Introduction

Apart from the conventional processes used in industry for the removal of pollutants from wastewaters (flotation, degradation etc.), an adsorption/binding recent process is used from researchers to selectively recognize and adsorb/bind target molecules (pollutants) from effluents. It is of great interest to prepare/design materials, which only selectively remove carcinogenic pollutants from wastewaters, as ions, dyes and other typical and potential target molecules. The ability to selectively recognize a target molecule in a vast pool of similar molecules is essential to biological and chemical processes. This process is called molecular recognition and it is an event that occurs everywhere in nature. It occurs when two molecules are both geometrically and chemically complementary; that is, when they can both "fit together" spatially as well as bind to each other using non-covalent forces, including hydrogen bonds, electrostatic interactions, hydrophobic interactions and weak metal coordination (Chen et al., 2002). Examples of this process include the binding of an enzyme to a substrate, a drug to a biological target (Britschgi et al., 2003), antigen/antibody recognition in the immune system (Sundberg and Mariuzza, 2002), and the formation of messenger RNA from DNA templates (Hofstadler and Griffey, 2001). The molecular recognition is central to how biological systems work, especially at the cellular level. The observation of the various systems where processes of recognition occur (enzyme substrate complexes, antibody-antigen systems, DNA replication, membrane receptors, etc) has indicated a certain number of directions for the preparation of synthetic systems capable of molecular recognition. Molecular imprinting is not a new science. The earliest reports of imprinting go back to the early 1930s when a Soviet chemist M.V. Polyakov

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prepared a number of silica gels and observed that when prepared in the presence of a solvent additive the resulting silica demonstrated preferential binding capacity for that solvent (Polyakov, 1931). In 1949 a senior student of Linus Pauling, Frank Dickey, observed that after removal of the "patterning" dye the silica would rebind the same dye in preference to the others (Dickey, 1949). However, in 1972 a step change in molecular imprinting occurred when the group of Guenter Wulff reported that they had successfully prepared a molecularly imprinted organic polymer (Wulff and Sarhan, 1972). Wulff used what is now termed a "covalent approach" to prepare an organic molecularly imprinted polymer capable of discriminating between the enantiomers of glyceric acid. The classical methods of covalent imprinting involve readily reversible condensation reactions such as boronate ester (Sellegren and Andersson, 1990), ketal/acetal (Shea and Sasuki, 1991) and Schiff's base formation (Wulff, 2002) to prepare template-monomers. Subsequently, throughout the 1970s and 1980s, Wulff's group published extensively using this approach. The second major break through in organic polymer imprinting occurred in 1981 when Mosbach and Arshady reported that they had prepared an organic MIP using non-covalent interactions only (Arshady and Mosbach, 1981). This approach was termed the "non-covalent approach" as opposed to the covalent approach favored by Wulff, and it was this approach, with its simple, seemingly trivial methodology, that triggered the explosion in molecular imprinting that was to occur during the 1990s. Non-covalent imprinting uses the typical forces of attraction between molecules such as hydrogen bonds, ion-pairs, dipole-dipole interactions and van der Waals forces to generate adducts of template and functional monomers in solution. Unlike those used in covalent methods of imprinting, these adducts are unstable and dynamically rearrange on a time scale relevant to the imprinting process. To this day the non-covalent versus covalent debate continues with both sides being championed. However, it is generally accepted that there are pros and cons to both approaches. So, in 1995 Whitcombe reported an intermediate approach that combine the advantages of both approaches (Whitcombe et al., 1995). This approach relies on covalent interaction during the polymerization stage but non-covalent interactions during rebinding. Importantly, in order to improve subsequent non-covalent binding geometry, Whitcombe's approach incorporated a sacrificial spacer group that was designed to be lost during template removal. The non-covalent approach however is still by far the most widely used approach in MIP synthesis. Several of its drawbacks can be overcome by the use of stoichiometrically associating monomer-template systems (Sellegren, 1994). This has resulted in a range of receptors exhibiting high capacity and effective recognition properties in aqueous media. The simplicity of use, the relatively low cost and the broad range of possible guest molecules (small organic molecules, ions but also biological macro-molecules) have since led to the important development of this technique, as illustrated by the increasing numbers of publications over recent years. Nowadays, MIPs are highly cross-linked polymeric phases with predetermined selectivity for a single molecule or a group of structurally related molecules (template) (Vlatakis et al., 1993), employed in separation processes of environmental pollutants (chromatography, solid-phase extraction, membrane separations, adsorption), artificial antibodies and sensors recognition elements (Haupt and Mosbach, 2000; Wulff, 2002). This chapter aims to report: (i) the synthesis of MIPs, (ii) the use of the main reagents in MIPs synthesis (cross-linkers, initiators, solvents/porogens, monomers), and (iii) mainly all the typical (dyes, ions) and potential (drugs, pesticides, insecticides, phenols) environmental pollutants resulted in environmental ways.

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Preparation of MIPs

The preparation of MIPs starts by positioning the functional monomers around a template molecule. The monomers interact with sites on the template via interactions that can be reversible covalent or non-covalent (hydrogen, ionic, van der Waals, π-π interactions, etc.). Then, they are polymerized and cross-linked around the template in order to fix their position and to "freeze" the geometry of the pores in the network. The template molecule is then extracted, leaving a polymer with functional sites capable of molecular recognition. The first step is the contact between the functionalised monomers and the template molecule which leads to the formation of a complex. Its structure and stability will then determine the behaviour of the future MIP. The interactions involved must be sufficiently strong to remain intact during the polymerisation stage but sufficiently labile to enable template extraction and re-insertion of guest molecules in the later stages. These interactions must therefore occur rapidly and be reversible. It is crucial to optimise the choice of the different components of the system at this point. Different types of strategies can be distinguished depending on whether the bonding between template and host is covalent or not: (i) covalent interactions, (ii) non-covalent interactions, (iii) double approach: covalent plus non-covalent. The second step is the polymerisation step of the monomers around the complex formed in the first step (Piletsky et al., 2002). Owing to its ease of use, radical polymerisation is the most frequent. The crucial question is to determine how to carry out this polymerisation/cross-linking step with minimum disturbance of the complex already in place. Choices must be made, for instance in radical polymerization, the radicals can be generated at 60°C (AIBN as initiator) or 45°C (ABDV as initiator) which could cause heat destabilisation of the complex, or at 4°C with low-temperature photochemical radical production (AIBN, 360 nm). Comparative studies on recognition specificity have shown that the photochemical approach gives the most specific materials (O'Shannessy et al., 1989). Another, crucial point of the preparation of MIPs is the extraction step. The proportion of extraction of the template molecules interacting with the MIP via easily hydrolysable covalent bonds or non-covalent linkages is estimated to be about 90%. The remaining molecules are trapped in highly cross-linked zones. This problem is exacerbated with macromolecules where steric hindrance lowers the efficiency of extraction. In addition, the synthesis of MIPs requires large quantities of guest molecule (50 to 500 μmoles per gram of polymer). So, when pure template molecule is difficult or expensive to obtain, reaching quantitative template extraction yields can be primordial. Extraction conditions must then be optimised to obtain yields of over 99% (Müller et al., 1993). The extraction step uses an appropriate solvent. It often proves to be long and the actual process involved is dependent on the system in question. So, automation of the washing steps for industrial applications still remains problematic. Extraction of the template leaves a three-dimensional material in which the cavity shapes and functional group locations are complementary to the guest molecule. Solvent plays an important role in the formation of the porous structure of MIPs, which are a subset of a larger class known as macroporous polymers. The morphological properties of porosity and surface area are determined by the type of solvent, referred to as "porogen", used in the polymerization. Many solvents were tested in literature for the preparation of MIPs, presenting their main differentiation in the phase. The main organic solvents used are DMSO, DMF, acetonitrile, toluene, chloroform, while deionized water is also used as solvent (Spivak and Shea, 1997). Moreover, it is notable

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to be reported that a prepared MIP is composed typically of a 70% to 98% of its final mass from cross-linker. Numerous cross-linkers have been tested for the preparation of a rigid MIP, as DVB, EGDMA, EBA and TRIM. The groups of Wulff (Wullf and Vietmeir, 1989) and Spivak (Sibrian-Vasquez and Spitak, 2004) have systematically studied the effect of cross-linkers on the recognition properties of MIPs. After the preparation of MIPs, a full characterization is necessary to examine the morphological and functionalized properties of the prepared materials. The common techniques of MIPs characterization is spectroscopy (NMR, FT-IR), swelling tests, BET analysis (Sellergren and Shea, 1993). Summarizing, essentially two strategies for molecular imprinting have been established based on whether the template is associated with interactive monomers using covalent bonds or non-covalent interactions. Of the two strategies, the non-covalent approach has been used more extensively for three reasons:

(i) non-covalent methodology is easier because it does not require synthetic steps toward the prepolymer complex; interactions between monomers and template are easily obtained when all components are mixed in solution;

(ii) removal of the template is generally much easier, and usually it is accomplished by continuous extraction;

(iii) a greater variety of functionality can be introduced into the MIP binding site using noncovalent methods.

Selectivity

Prior to its use in experiments, a MIP is usually evaluated to check its recognition properties for a target. Chromatographic evaluation and equilibrium batch rebinding experiments are the methods most commonly used to investigate the selectivity of the imprinted materials (Andersson and Nicholls, 1997). Chromatographic evaluation allows measurement of capacity factors (k') and imprinting factors (IF) of MIPs (Mayes et al., 1994). These values are obtained from the retention time of the template molecule on a chromatographic column packed with the MIP and a second column packed with the NIP. If the MIP is imprinted, then the analyte should be retained more strongly on the MIP than on the NIP because of the selective interactions. In some studies (Caro et al., 2003; Chapuis et al., 2004), the selectivity of the MIP was also probed using compounds structurally related to the template. If the MIP retains these compounds almost as well or better than the template, this indicates that the MIP shows cross-reactivity (Caro et al., 2003). For equilibrium batch rebinding experiments, a known mass of template in solution is added to a vial containing a fixed mass of polymer. Once the system has come to equilibrium, the concentration of free template in solution is measured and the mass of template adsorbed to the MIP calculated (Bruggemann et al., 2004). Some of these experiments are based on radio-ligand binding, which is a very highly sensitive method to study the population of binding sites with the strongest binding characteristics (Shea and Sasaki, 1991). Typically, the sample is incubated with the radioligand for several hours and a centrifugation step is used to sediment the polymer particles. The radioactivity in the supernatant is then measured.

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MIPs as sorbents for wastewater pollutants

Treatment of wastewaters is an important point of the current research, given the numerous pollutants existing in waterways. Some of these (dyes, ions) were originated directly from industries (dyeing industries/mills, tanneries), but other were resulted in the environment from indirect ways (pesticides, herbicides, insecticides, phenols, biofluids, pharmaceuticals/drugs). In all occasions, the final result is the same: the environmental pollution. Nowadays, conventional and non-conventional techniques were reported in literature (Crini, 2006), suggesting different separation processes, but maintaining the same target, which is the removal of the hazardous/carcinogenic molecules (pollutants) from all the possible environmental sources. In this section of review, it was realized an attempt to gather the reported published works dealing with the remove of various pollutants with MIPs. These pollutants were classified according to the target molecule removed/bound from MIPs. So, it was determined the behavior of MIPs to remove selectively (i) dyes, (ii) ions, (iii) herbicides, (iv) phenols, and (v) pharmaceuticals/drugs from real water samples (river, lake, soils or other). In each case, a comparative table is presented giving the main preparation reagents (cross-linker, monomer), the target molecule removed, and, if it was possible, some selective or sorption parameters of the study. Given that the majority of target molecules were analyzed with SPE or HPLC techniques, the authors give the "recovery" parameter as the crucial factor of MIP's evaluation and in few papers both the sorption capacity (**Tables 1-5**).

Dyes

A limited number of researchers studied the removal of dyes through molecular imprinting. Kyzas et al. (2009) was succeeded in preparing two types of MIPs, the one for the removal of reactive dye molecules and the other for basic ones. MIPs were prepared in both aqueous (water as solvent) and organic media (DMF/DMSO as solvents), presenting ability to remove/bind reactive and basic dye molecules, respectively. The monomers used were MAA for basic-dye, MIP and AAM for the reactive-dye MIP. Experiments were carried out both in real dyeing effluents and in simulated samples. The removal percentage of basic dye target was reached 75%, while the respective for reactive one was 70%. However, the crucial key-point of that study was the high selectivity parameters resulted and the capability of binding/removing selectively the dyes from industrial effluent (high distribution coefficients approaching 1 L g^{-1} and separation factor about 70) (Kyzas et al., 2009). Furthermore, another study was reported in literature dealing with the removal of a basic dye (Malachite Green, MG). In that study, Yan et al. (2007) presented only results from real dyeing samples with selective binding properties. The preparation of MIPs was realized using MAA as monomer, EGDMA and AIBN as cross-linker and initiator, respectively. The selectivity results showed distribution coefficients approximately equal to 0.4 L g^{-1}, while the sorption capacity was ranged about 1 μmol g^{-1}. Li et al. (2008) studied the removal of the aforementioned dye, using from fish-water samples. The synthesis of MIP was carried out with MAA, EGDMA and AIBN as monomer, cross-linker and initiator, respectively. The rebinding data showed 0.52 μmol g^{-1} capacity. Furthermore, MIPs were studied from Li et al. (2007) as sorbents for removing and degrading the methyl orange dye. These limited researches have been realized with dye as template molecules applying either in real or in simulated samples of wastewaters. All the above data were presented in **Table 1**.

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Table 1
Adsorption capacities by MIPs for different dyes.

Target Dye	MIP's Preparation Monomer/Cross-linker/Initiator	Adsorption Capacity (Q)	Reference
Malachite Green (MG)	MAA/EGDMA/AIBN	1 µmol g^{-1}	Yan et al., 2007
Malachite Green (MG)	MAA/EGDMA/AIBN	0.5 µmol g^{-1}	Li et al., 2008
Methyl Orange (MO)	MAA/EGDMA/AIBN	0.7 µmol g^{-1}	Li et al., 2007
Remazol Red 3BS (RR)	AAM/MBA/KPS	12 mg g^{-1}	Kyzas et al., 2009
Remacryl Red TGL (BR)	MAA/EGDMA/AIBN	18 mg g^{-1}	Kyzas et al., 2009

Ions

Contrary to the dye template molecules, a great number of recent published works is occurred with ion templates. Metal ions can also serve as templates for cross-linked polymers via imprinting. One of the first ionic template effects in the synthesis of chelating polymers was reported by Nishide et al. (1977) in the mid-1970s. Cross-linking bonds of linear chain polymers (poly(4-VP)) were realized with a bifunctional agent (dibromoalkane, DBM) in the presence of metal ions. Takagi and coworkers (Yu et al., 1992; Tsukaghoshi et al., 1993) introduced the concept of surface-imprinting polymers. The specific solids were prepared by emulsion polymerization involving a functional host-monomer (phosphoric acid derivatives), an emulsion stabilizer, a cross-linking agent and a metal cation template, which was selectively complexed by the metal-binding groups at the aqueous-organic interface to form recognition sites. The template cation was removed by acidic stripping to yield microspheres with a metal ion-templated surface. A third approach was based on the copolymerization of isolated/non-isolated monomers/ion complexes with the cross-linking agent (Kuchen and Schram, 1988; Chen et al., 1997). In the preparation of ion-MIPs by this approach, suitable ligand groups were brought in contact with metal ions to form a complex that was then covered with a cross-linked polymer. After removal of the template (metal ion), the uptake of metal ions is strongly enhanced and also more selective in many cases. The selectivity arises mainly because of the following factors:

i) the specificity of interaction of ligand with the metal ion;
ii) the coordination geometry and the coordination number of metal ion;
iii) the charge of the metal ion and;
iv) to a large extent on the size of the metal ion.

Kuchen and Schram (1988) prepared macroporous resins (specific surface area ~400 m^2 g^{-1}) by radical polymerization of copper(II) methacrylate complexes with water, pyridine and 4-vinyl pyridine (4-VP), with ethylene glycoldimethacrylate (EGDMA) as cross-linking agent in presence of benzene/methanol as porogen and AIBN as initiator. The selectivity coefficients of Cu-MIPs and NH^{4+} ion blind MIPs for copper with respect to Zn, Cd and Pb were established. Copper(II)-imprinted beads were prepared with a dispersion polymerization technique by dissolving 0.2 g of polyvinylalcohol in 60 mL of distilled water. Previously synthesized copper(II)-n-methacrylamidohistadinedihydrate complex was dissolved in ethanol, mixed with EGDMA in toluene and AIBN, and transferred to the dispersion mixture. After polymerization, the poly (EGDMA-MAH/Cu(II) beads were separated, washed with methanol and water and the Cu(II)-imprint ion

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was leached with EDTA. The effect of imprinting was clearly shown by comparing the adsorption of Cu, Zn, Ni and Co with Cu-imprinted and non-imprinted microbeads (Say et al., 2004). Cu-MIPs were prepared with EGDMA, AIBN, PVA showing 48 mg g^{-1} capacity and 5329 distribution coefficient. Tsukaghoshi et al. (1993) prepared imprinted microspheres using seeded emulsion polymerization of DVB, styrene, butyl acrylate and methacrylic acid (MAA). The imprinted structure was introduced on the carboxylated microsphere by surface imprinting, in which the carboxyl groups were reorganized through complexation with metal ions on the surface and then fixed in their specific orientation by cross-linking polymerization. The imprinted effects were verified on Cu(II)-, Ni(II)-, and Co(II)-imprinted microspheres. Novel zinc ion-imprinted resins were prepared by surface-template polymerization with water-in-oil emulsion using dioleylphosphoric acid (DOLPA). Yoshida et al. (1996) have clearly demonstrated that gamma irradiation of MIPs after they were obtained by surface template polymerization resulted in more rigid polymer matrices and also allowed the functional monomer to attach firmly to the matrices. The irradiated, imprinted resin exhibits a tremendously high selectivity for Zn over Cu ions. The improved selectivity of Zn over Cu using MIP prepared by surface template polymerization using the same bifunctional monomer (DOLPA/DVB) was clearly shown (Uezu et al., 1997). Monomer-type functional surfactants [2-(p-vinyl benzylamino)-alkanoic acid and N,N-dialkyl derivatives] have been used as both a ligand and an emulsifier for the preparation of surface-template resins (Koide et al., 1998). The surfactants were adsorbed at the toluene-water interface and emulsified DVB-styrene in a Cu^{2+} or Zn^{2+} solution. Emulsion polymerization using a $K_2S_2O_8$ initiator (80°C) or by irradiation with gamma-rays gave particles of 200-800 nm in diameter. Both resins showed an imprinting effect for Cu or Zn, respectively. Chen et al. (1997) synthesized 4-vinyl benzyl-substituted 1,4,7-triazacyclononane (TACN) ligand by treating 1 or 3 moles of 4-vinyl benzyl chloride with TACN, and formed complexes with zinc. The copolymerization of Zn^{2+} complexes with the cross-linking agent DVB (80%) and the use of AIBN as initiator provided highly crosslinked macroporous polymers. However, attempts to prepare a Cu IIP or a blank polymer were unsuccessful. The overall order of metal-ion selectivity for Zn^{2+} as the imprint ion MIPs is $Mn^{2+} < Ni^{2+} < Zn^{2+} < Co^{2+} <<< Cu^{2+}$, which somewhat, but not exactly, follows the Irving-Williams order of stability. Chen et al. (1997) have postulated that Zn^{2+} imprinting (the ionic radius of Zn^{2+} and Cu^{2+} being comparable) accounts for the selectivity for the Cu^{2+} ion over the Fe^{3+} ion, because usually the Fe^{3+} ion can readily compete for any polymer-pendant ligand site because of its favorable charge-to-radius ratio. Yoshida et al. (1996) showed that incorporating aromatic rings and a suitable straight alkyl chain in the functional monomer (organophosphorus compound) provided high binding affinity to Zn, the target metal ion. Uezu et al. (1999) prepared Zn(II)-imprinted microspheres by surface-template polymerization with water-in-oil-in-water emulsions. Dioleylphosphoric acid, which has two long alkyl chains in the hydrophobic moiety, and DVB were employed as functional host and crosslinking agent, respectively. The metal-imprinted beads exhibit a high selectivity towards target Zn ions over Cu ions. Subsequently, Uezu et al. (2001) succeeded in enhancing the imprinting and selectivity of the Zn-MIP by systematically studying the optimum polymerization conditions. A novel metal-MIP was prepared by the same group (Yoshida et al., 1999) via a surface molecular imprinting technique. Trimethylopropane trimethacrylate (TRIM), zinc ions and 1,2-dodecandiol-o,o'-diphenylphosphonic acid (DDDPA)

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were used as a matrix-forming monomer, imprinting molecule and functional monomer, respectively. The template effect of the TRIM-based polymer was enhanced by the high rigidity of the polymer matrix compared to that of the imprinted polymer with divinyl benzene as matrix. In addition, the adsorption equilibrium constant was evaluated on the basis of Langmuir analysis of the adsorption data. Novel molecular imprints for Al was prepared via a non-covalent imprinting technique, using the Al(III)-Morin chelate as the template. Based on the fluorimetric properties of the chelate, it was possible to design a selective optical flow-through sensor for Al^{3+}. The affinity of the polymer-binding sites was higher for Al^{3+} than for other divalent and trivalent ions (Be^{2+}, Ca^{2+}, Mg^{2+}, Eu^{3+}, Zn^{2+} and Fe^{3+}), suggesting that the nature of the metal ion, its ionic radius and metal-Morin stoichiometry play important roles in ionic recognition. Panasyuk et al. (1998) studied the features of combining a chemically modified electrode with an artificial receptor system prepared by imprinting and electropolymerized (Ni-(protoporphyrin IX) dimethyl ester in the presence of nitrobenzene. The responses of the modified glassy carbon electrode towards template molecules were analyzed by cycling over the nitrobenzene reduction wave, which shows higher selectivity for imprinted polymer. Ca^{2+}- and Mg^{2+}-ion-selective sorbents were prepared by ion imprinting using *N,N'*-dimethyl-(*N,N'*-bis4-vinyl phenyl)-3-oxapentane diamide; then used as the ion-complexing monomer. The resulting polymers were analyzed for their ability to extract calcium ions from methanolic water. The polymers prepared against Ca^{2+} and Mg^{2+} ions were found to bind Ca^{2+} ions with 6 and 1.7 times lower K_{diss} values, respectively, when compared with reference polymers prepared in the absence of metal ions. In addition, the number of binding sites for Ca^{2+} ions, determined for the respective polymer preparation, fitted well with theoretical values calculated from the stoichiometry of the complexation of the ionophore by Ca^{2+} and Mg^{2+} ions, respectively. **Table 2** provides a comparison of the sorption capacities of MIPs synthesized by various researchers over the years. The range of metal ions imprinted in organic polymers now includes uranium (as UO_2^{2+}) (Gladis and Rao, 2004), erbium (Kala et al., 2004), dysprosium (Biju et al., 2003), gadolinium (Vigneau et al., 2003), cadmium (Liu et al., 2004), and lead (Guney et al., 2002), among others.

Table 2
Adsorption capacities by MIPs for different metal ions.

Target Pollutant	MIP's Preparation Monomer/Cross-linker/Initiator	Adsorption Capacity (Q in mg g^{-1})	Reference
Cu(II)	DVB/EGDMA/AIBN	0.26	Koide et al., 1998
Zn(II)	DVB/EGDMA/AIBN	0.22	Koide et al., 1998
Zn(II)	DVB-DOLPA/EGDMA/AIBN	0.87	Uezu et al., 1997
Ni(II)	DVB/EGDMA/AIBN	0.17	Tsukaghoshi et al., 1993
Cu(II)	PVA/EGDMA/AIBN	48	Say et al., 2003
Cu(II)	DVB/EGDMA/AIBN	0.40	Tsukaghoshi et al., 1993
Co(II)	DVB/EGDMA/AIBN	0.34	Tsukaghoshi et al., 1993
Cu(II)	MAA/EGDMA/AIBN	3.28	Kuchen and Schram, 1988
Pd(II)	4-VP/EGDMA/AIBN	21.5	Daniel et al., 2003
Cd(II)	4-VP/EGDMA/AIBN	11.8	Liu et al., 2004
U(VI)	4-VP/EGDMA/AIBN	30.1	Gladis and Rao, 2003
Dy(III)	4-VP/EGDMA/AIBN	40.15	Biju et al., 2003

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Herbicides

A considerable part of potential environmental pollutants, which should be removed from MIPs is triazines. In the last years, several studies have focused on extracting triazines from river water (Turiel et al., 2001; Pap et al., 2002; Chapuis et al., 2003). A recent paper describing an environmental application was published by Ferrer et al. (2000). In this study, an MIP prepared using terbutylazine as the template molecule showed cross-reactivity; subsequently, the MIP was used to enrich six chlorotriazines from groundwater and sediment samples. After a cleanup step with 2 mL of dichloromethane, the matrix components that were retained non-specifically on the MIP were removed, and the recovery of all six chlorotriazines was higher than 80% (except for propazine, 53% of which was recovered) after percolating 100 mL of water sample. Chapius et al. (2003) and Pap et al. (2002) followed the same synthetic procedure described by Ferrer et al. (2000) to prepare an MIP, also imprinted with terbutylazine, so, when the polymers were obtained and applied to MIPs, they also showed cross-reactivity. Chapuis et al. (2003) used different triazines to determine the selective bahaviour of MIPs prepared (deethylterbutylazine, deethylatrazine, chlorotriazine, thiotriazine, deisopropylatrazine, hydroxytherbutylazine), while Pap et al. (2002) tried to observe the difference between the porogens used (acetonitrile, ethylacetate, dichlomethane, toluene). In contrast, Turiel et al. (2001) prepared a MIP using propazine as template and acetonitrile or toluene as porogen. The polymerization was thermal instead of UV-initiated (as had been the case for the polymer prepared by Ferrer et al. (2000)). However, the MIP synthesized by Turiel et al. (2001) also showed cross-reactivity, which enabled the MIP to extract a mixture of triazines with recoveries higher than 70% in all instances. The key-point for these SPE techniques was the recovery presented. In the aforementioned papers the range of the recoveries was 80-90%. Futhermore, carcinogenic pollutants, such as cyanide, have been bound with imprinting (Say et al., 2004). The synthesis of MIPs was realized with EGDMA, AIBN, nickel(II)-methacryloylhistidine dihydrate complex monomer and KCN. The sorption capacity was approximately 5.5 mg g^{-1}, while the desorption reached 95%. Benzo[a]pyrene was also removed by MIPs (Lai et al., 2004) using different portions of monomers (4-VP, TFMAA, MAA) in DCM and ACN. The capacity for each pair of monomer-template was about 10 μg g^{-1}. Phenoxy-acid herbicides have also been used as templates to prepare MIPs in the last few years (Baggiani et al., 2001). For their synthesis, the herbicide 2,4,5-trichlorophenoxyacetic acid was used as template, 4-VP as monomer and EGDMA as cross-linker in water/methanol solvent. Cyanide and benzo[a]pyrene seem more difficult to imprint than most other analytes because cyanide is an ion and a specific metal-complexing polymer has to be prepared, and benzo[a] pyrene is a polycyclic aromatic hydrocarbon (PAH) without any functional group. Nevertheless, both MIPs were successfully applied to the extraction of their respective templates from wastewater and surface water. Zhu et al. (2002) prepared an MIP using the herbicide methysulfuron-methyl (MSM) as a template, TFMAA as a functional monomer, DVB as a cross-linker, and dichloromethane as a porogen, which allowed 1000 mL of tap-water and river-water samples to be extracted. As this MIP also showed cross-reactivity, this feature was exploited to extract a mixture of sulfonylurea herbicides with recoveries not lower than 96%. In some studies (Caro et al., 2004), it was observed that an MIP imprinted with 1-naphthalene sulfonic acid (1-NS), which showed cross-reactivity, allowed the template molecule and a mixture of eight naphthalene sulfonates (NSs) with

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different functional groups (hydroxyl (–OH), amino ($–NH_2$) or nitro ($–NO_2$)) to be extracted with good recoveries from 500 ml of river water. Good recoveries were also obtained when another MIP synthesized with ibuprofen as template molecule, was applied to the selective extraction of a mixture of non-steroidal anti-inflammatory drugs (NSAIDs) from 1000 ml of river water. In the last few years, some attempts have been made to apply the molecular imprinting procedures to the extraction of environmental pollutants from soil samples, whose extract was obtained after an appropriate soil treatment (e.g., Soxhlet- and microwave-assisted extraction) and passed through the MIP. In some of these studies (Ferrer et al., 2000; Turiel et al., 2001), the target compound was also extracted from water samples, but, in the studies published by Chapius et al. (2004) and Dong et al. (2004), a MIP was developed to extract triazines and monosulfuron from soil samples, respectively. Chapius et al. developed an extraction method in which the selectivity of the MIP prepared using ametryn as the template was compared with an immunosorbent (IS) based on anti-triazine polyclonal antibodies immobilised on silica.

Table 3
Recovery capacity by MIPs for different herbicides.

Target Pollutant	MIP's Preparation Monomer/Cross-linker/Initiator	Recovery Capacity (in %)	Reference
Terbutylazine	DCM/EGDMA/AIBN	~80	Ferrer et al., 2000
Triazines	DCM/EGDMA/AIBN	~80	Dong et al., 2004
Triazines	DCM/EGDMA/AIBN	~75	Chapius et al., 2004
Triazines	DCM/EGDMA/AIBN	~90	Sambe et al., 2007
Triazines	DCM/EGDMA/AIBN	~85	Koeber et al., 2001
Propazine	DCM/EGDMA/AIBN	~90	Turiel et al., 2001
Terbutylazine	DCM/EGDMA/AIBN	~85	Pap et al., 2002
Terbutylazine	DCM/EGDMA/AIBN	~80	Chapius et al., 2003
Simazine	MAA/EGDMA/ABDV	79	Mhaka et al., 2009
Atrazine	MAA/EGDMA/ABDV	98	Mhaka et al., 2009
Propazine	MAA/EGDMA/ABDV	86	Mhaka et al., 2009
DIA-D5	MAA/EGDMA/AIBN	85	Amalric et al., 2008
DIA	MAA/EGDMA/AIBN	88	Amalric et al., 2008
DEA-D6	MAA/EGDMA/AIBN	97	Amalric et al., 2008
DEA	MAA/EGDMA/AIBN	98	Amalric et al., 2008
Atrazine-D5	MAA/EGDMA/AIBN	94	Amalric et al., 2008
Atrazine	MAA/EGDMA/AIBN	90	Amalric et al., 2008
Terbultylazine-D5	MAA/EGDMA/AIBN	92	Amalric et al., 2008
Isoproturon	MAA/EGDMA/AIBN	93	Amalric et al., 2008
Isoproturon-D6	MAA/EGDMA/AIBN	90	Amalric et al., 2008
Simazine	MAA/EGDMA/AIBN	98	Amalric et al., 2008
MSM	TFMAA/DVB/AIBN	>96	Zhu et al., 2002
Benzo[a]pyrene	DCM-ACN/EGDMA/AIBN	~90 (10 µg g^{-1})	Lai et al., 2004
2,4,5-trichlorophenoxyacetic acid	4-VP/EGDMA/AIBN	~90	Baggiani et al., 2001
Cyanide	PVA/EGDMA/AIBN	~90 (5.5 mg g^{-1})	Say et al., 2004

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Phenols

Another class of environmental pollutants are phenols. In literature, different forms of phenols have been isolated/removed via molecular imprinting. However, the main forms are nitrophenols (mono-substituted 4-NP), and chlorophenols (monosubstituted 4-CP, PCP, and polysubstituted 2,4-DCP). Masque et al. (2000) realized the application of a non-covalently imprinted MIP to selectively isolate 4-nitrophenol (4-NP) from a mixture of phenolic compounds in river-water samples. In this example, the MIP showed very good selectivity for 4-NP but the recovery of this compound decreased after the clean-up step (36%). In order to increase the recovery of this analyte, another MIP was prepared following a semi-covalent approach (Caro et al., 2002). In this study, although the recovery of 4-NP was increased (50%), only slight amounts of other phenolic compounds were retained on the MIP. In view of the good results obtained in these particular studies, another MIP design to selectively extract 4-chlorophenol (4-CP) from river water (Caro et al., 2003) was prepared following the same protocol described by Masque et al. (2000). In this study, a strong cross-reactivity was observed for all the 4-chlorosubstituted compounds and 4-NP present in the sample after the clean-up step (Masque et al., 2000), and the other chlorophenols or nitrophenols were removed selectively during this step,. Surprisingly, this cross-reactivity was not observed for any of the 4-NP MIPs described previously, even though 4-NP and 4-CP are structurally very similar. Watabe et al. (2004) prepared an MIP for selective enrichment of bisphenol A (BPA) from water samples (lake and river water). In a similar fashion, San Vicente et al. (2004) prepared a MIP selective for BPA. The conditions used to prepare the MIP had been optimized previously (Navarro-Villoslada et al., 2004), when an experimental design and a multivariate analysis were used for screening and optimizing the polymerization parameters to enhance the selectivity of the MIP and the affinity towards the template. Feng et al. (2009) have realized the isolation of different forms of phenols (4-NP, 4-CP, 1,4-DCP, 2,4,6-TCP, PCP) preparing molecularly imprinted polymers with EGDMA, MAA. The analysis of the polluted river samples was realized with HPLC. The majority of the aforementioned target molecules is given in **Table 4**.

Table 4
Recovery capacity by MIPs for different phenols.

Target Pollutant	MIP's Preparation Monomer/Cross-linker/Initiator	Recovery Capacity (in %)	Reference
4-NP	MAA/EGDMA/AIBN	~36	Masque et al., 2000
4-NP	MAA/EGDMA/AIBN	~50	Caro et al., 2002
4-CP	MAA/EGDMA/AIBN	~65	Caro et al., 2003
BP-A	4-VP/EGDMA/AIBN	~70	Watabe et al., 2004
BP-A	4-VP/EGDMA/AIBN	~75	San Vicente et al., 2004
BP-A	4-VP/EGDMA/AIBN	~78	Navarro-Villoslada et al., 2004
2,4,6,-TCP	MAA/EGDMA/AIBN	~95	Feng et al., 2009
4-CP	MAA/EGDMA/AIBN	~88	Feng et al., 2009
PCP	MAA/EGDMA/AIBN	~90	Feng et al., 2009
2,4,-DCP	MAA/EGDMA/AIBN	~87	Feng et al., 2009
HQ	4-VP/EGDMA/AIBN	~75	Lin et al., 2008
4-NP	MAA/EGDMA/AIBN	~78	Lin et al., 2008
BP-C	4-VP/EGDMA/AIBN	~85	Lin et al., 2008
BP-Z	4-VP/EGDMA/AIBN	~85	Lin et al., 2008
DES	4-VP/EGDMA/AIBN	~80	Lin et al., 2008

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Pharmaceuticals/drugs

MIPs is the most widely studied application so far for the extraction of compounds from pharmaceuticals/drugs, (Hu et al., 2005; Chassaing et al., 2004; Martin et al., 2004; Moller et al., 2004; Caro et al., 2004; Xie et al., 2003; Dirion et al., 2002; Brambilla et al., 2001; Crescenzi et al., 2001; Muldoon and Stanker, 1997; Andersson and Nicholls, 1997). Several analytes such as diphenyl phosphate (Moller et al., 2004), naproxen (Caro et al., 2004), and amobarbital (Hu et al., 2005) have been isolated from urine samples. Sameridine (Andersson and Nicholls, 1997) and quercitin (Xie et al., 2003) have been isolated from plasma. Other drugs such as propranolol and enrofloxacine (Martin et al., 2004) and alfuzosin (Chapius et al., 2006) have been extracted from several matrices (urine, plasma, bile, and animal tissue). When these analytes have to be extracted from a biofluid, this extract could be applied directly to the MIP after a filtration step. Nevertheless, in nearly all these studies, the biofluid was diluted with an organic solvent to minimize the aqueous content of the sample and to precipitate some proteins. There were only a few studies in which the sample was applied directly to the MIP (Chassaing et al., 2004; Caro et al., 2004; Hu et al., 2005; Xie et al., 2003). These were enabled because binding of the target analyte on the MIP was complete in aqueous samples, although synthesis of the polymer was carried out in an organic solvent, as usual. Furthermore, many researchers have tried to remove pharmaceuticals substances from real samples with MIPs using the same monomer and cross-linker reagents (MAA/EGDMA). In this way, hyoscyamine (Theodoridis et al., 2003), dopamine (Suedee et al., 2006), mycophenolic acid (Yin et al., 2006), atropine (Nakamura et al, 2005), verapamil (Moller et al., 2004), and caffeine (Theodorodis et al., 2004) have been removed from real environmental samples presenting high percentages of recovery (~98%), and adequate capacity (~3-7 mg g^{-1}) (**Table 5**).

Table 5
Recovery capacity by MIPs for different pharmaceuticals and drugs.

Target Pollutant	MIP's Preparation Monomer/Cross-linker/Initiator	Recovery (in %)	Reference
Diphenyl phosphate	MAA/EGDMA	~85	Moller et al., 2004
Naproxen	4-VP/EGDMA	~80	Caro et al., 2004
Amobarbital	MAA/EGDMA	~84	Hu et al., 2005
Sameridine	MAA/EGDMA	~90	Andersson and Nicholls, 1997
Quercitin	MAA/EGDMA	~92	Xie et al., 2003
Hyoscyamine	MAA/EGDMA	~98	Theodoridis et al., 2003
Dopamine	MAA/EGDMA	~95	Suedee et al., 2006
Mycophenolic acid	4-VP/EGDMA	~97	Yin et al., 2006
Atropine	TFMAA/EGDMA	~98 (~4 mg g^{-1})	Nakamura et al., 2005
Verapamil	MAA/EGDMA	~95 (~5 mg g^{-1})	Moller et al., 2004
Caffeine	MAA/EGDMA	~98 (~6 mg g^{-1})	Theodoridis et al., 2004
Propranolol	MAA/EGDMA	~90 (~7 mg g^{-1})	Martin et al., 2004
Enrofloxacine	MAA/EGDMA	~91 (~6 mg g^{-1})	Martin et al., 2004
Alfuzosin (plasma)	MAA/EGDMA	~77 (~5 mg g^{-1})	Chapius et al., 2006

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Conclusions and perspectives

The advantages that MIPs offer as selective sorbents have been demonstrated. MIPs are easy to obtain, and, in some studies, it has been shown that their selectivity is extremely high. Moreover, the applicability of MIPs in SPE procedures demonstrates the feasibility of using a MIP in several formats for extracting numerous templates from different samples. Nowadays, its applicability is not only for pharmaceuticals targets, but also for environmental pollutants. The use of several toxical and carcinogeneous compounds, as hormones, herbicides, pesticides and pharmaceuticals/drugs causes pollutions to the environmental area due to their effluents. So, except for the other target molecules (dyes, ions, phenols, etc), the deposit of these hazardous compounds have been studied in order to succeeded their binding via molecular imprinting. The capability of binding in high selectivity percentages, is the key of MIPs to use successfully in many and crucial environmental targets.

References

Amalric L., Mouvet C., Pichon V., Bristeau S., 2008. Molecularly imprinted polymer applied to the determination of the residual mass of atrazine and metabolites within an agricultural catchment (Brévilles, France). J. Chromatogr. A. 1206, 95-104.

Andersson H.S., Nicholls I.A., 1997. Molecular imprinting: recent innovations in synthetic polymer receptor and enzyme mimics. Recent Res. Dev. Pure Appl. Chem. 1, 133-157.

Arshady R., Mosbach M., 1981. Synthesis of substrate-selective polymers by host-guest polymerization. Macromol. Chem. Phys.-Makromol. Chem. 182, 687-692.

Baggiani C., Giovannoli C., Anfossi L., Tozzi C., 2001. Molecularly imprinted solid-phase extraction sorbent for the clean-up of chlorinated phenoxyacids from aqueous samples. J. Chromatogr. A. 938, 35-44.

Biju V.M., Gladis J.M., Rao T.P., 2003. Ion imprinted polymer particles: synthesis, characterization and dysprosium ion uptake properties suitable for analytical applications, Anal. Chim. Acta 478, 43-51.

Brambilla G., Fiori M., Rizzo B., Crescenzi V., Masci G., 2001. Use of molecularly imprinted polymers in the solid-phase extraction of clenbuterol from animal feeds and biological matrices. J. Chromatogr. A. 759, 27-32.

Britschgi M., von Greyerz S., Burkhart C., Pichler W.J., 2003. Molecular aspects of drug recognition by specific T cells. Curr. Drug. Targets. 4, 1-11.

Bruggemann O., Visnjevski A., Burch R., Patel P., 2004. Selective extraction of antioxidants with molecularly imprinted polymers. Anal. Chim. Acta 504, 81-88.

Caro E., Marce R.M., Cormack P.A.G., Sherrington D.C., Borrull F., 2003. On-line solid-phase extraction with molecularly imprinted polymers to selectively extract substituted 4-chlorophenols and 4-nitrophenol from water. J. Chromatogr. A 995, 233-238.

Caro E., Marce R.M., Cormack P.A.G., Sherrington D.C., Borrull F., 2004. Molecularly imprinted solid-phase extraction of naphthalene sulfonates from water. J. Chromatogr. A. 1047, 175-180.

Caro E., Masque N., Marce R.M., Borrull F., Cormack P.A.G., Sherrington D.C., 2002. Non-covalent and semi-covalent molecularly imprinted polymers for selective on-line solid-phase extraction of 4-nitrophenol from water samples. J. Chromatogr. A. 963, 169-178.

Chapius F., Pichon V., Lanza F., Sellergren B., Hennion M.C., 2004. Retention mechanism of analytes in the solid-phase extraction process using molecularly imprinted polymers: Application to the extraction of triazines from complex matrices. J. Chromatogr. B 804, 93-101.

Chapuis F., Mullot J., Pichon V., Tuffal G., Hennion M.C., 2006. Molecularly imprinted polymers for the clean-up of a basic drug from environmental and biological samples. J. Chromatogr. A. 135, 127-134.

Sorption processes and pollution edited by Grégorio Crini and Pierre-Marie Badot

Chapuis F., Pichon V., Lanza F., Sellergren B., Hennion M.C., 2003. Optimization of the class-selective extraction of triazines from aqueous samples using a molecularly imprinted polymer by a comprehensive approach of the retention mechanism. J. Chromatogr. A. 999, 23-33.

Chassaing C., Stokes J., Venn R.F., Lanza F., Sellergren B., Holmberg A., Berggren C., 2004. Molecularly imprinted polymers for the determination of a pharmaceutical development compound in plasma using 96-well MISPE technology. J. Chromatogr., B 804, 71-81.

Chen B.N., Piletsky S., Turner A.P.F., 2002. Molecular recognition: design of "keys". Comb. Chem. High Throughput Screen 5, 409-427.

Chen H., Olnstead M.M, Albright R.L., Devenyi J., Fish R.H., 1997. Metal-ion-templated polymers: Synthesis and structure of N-(4-vinylbenzyl)-1,4,7-triazacyclononanezinc(n) complexes, their copolymerization with divinylbenzene, and metal-ion selectivity studies of the demetalated resins - evidence for a sandwich complex in the polymer matrix. Angew. Chem., Int. Ed. Engl. 36, 642-645.

Crescenzi C., Bayoudh S., Cormack P.A.G., Klein T., Ensing K., 2001. Determination of clenbuterol in bovine liver by combining matrix solid-phase dispersion and molecularly imprinted solid-phase extraction followed by liquid chromatography/electrospray ion trap multiple-stage mass spectrometry. Anal. Chem. 73, 2171-2177.

Crini G., 2006. Non-conventional low-cost adsorbents for dye removal: A review. Bioreour. Technol. 97, 1061-1085.

Daniel S., Gladis J.M., Rao T.P., 2003. Synthesis of imprinted polymer material with palladium ion nanopores and its analytical application Anal. Chem. Acta 488, 173-182.

Dickey F.H., 1949. Specific adsorbents. Proc. Natl. Acad. Sci. 35, 227-229.

Dirion B., Lanza F., Sellergren B., Chassaing C., Venn R., Berggren C., 2002. Selective solid phase extraction of a drug lead compound using molecularly imprinted polymers prepared by the target analogue approach. Chromatographia 56, 237-241.

Dong X., Wang N., Wang S., Zhang X., Fan Z., 2004. Synthesis and application of molecularly imprinted polymer on selective solid-phase extraction for the determination of monosulfuron residue in soil. J. Chromatogr. A 1057, 13-19.

Feng Q.-Z., Zhao L.-X., Wei Y., Lin J.-M., Zheng Z.-X., 2009. Molecularly imprinted solid-phase extraction combined with high performance liquid chromatography for analysis of phenolic compounds from environmental water samples. J. Hazard. Mater. 167, 282-288.

Ferrer I., Lanza F., Tolokan A., Horvath V., Sellergren B., Horvai G., Barcelo D., 2000. Selective trace enrichment of chlorotriazine pesticides from natural waters and sediment samples using terbuthylazine molecularly imprinted polymers. Anal. Chem. 72, 3934-3941.

Gladis J.M., Rao T.P., 2004. Effect of porogen type on the synthesis of uranium ion imprinted polymer materials for the preconcentration/ separation of traces of uranium, Mikrochim. Acta 146, 251-258.

Guney O., Yilmaz Y., Pekcan O., 2002. Metal ion templated chemosensor for metal ions based on fluorescence quenching. Sens. Actuators. B. Chem. 85, 86-89.

Haupt K., Mosbach K., 2000. Molecularly imprinted polymers and their use in biomimetic sensors. Chem. Rev. 100, 2495-2504.

Hofstadler S.A., Griffey R.H., 2001. Analysis of noncovalent complexes of DNA and RNA by mass spectrometry. Chem. Rev. 101, 377-390.

Hu S.G., Li L., He X.W., 2005. Solid-phase extraction of esculetin from the ash bark of Chinese traditional medicine by using molecularly imprinted polymers. J. Chromatogr. A 1062, 31-37.

Kala R., Gladis J.M., Rao T.P., 2004. Preconcentrative separation of erbium from Y, Dy, Ho, Tb and Tm by using ion imprinted polymer particles via solid phase extraction. Anal. Chim. Acta 518, 143-150.

Koeber R., Fleischer C., Lanza F., Boos K.S., Sellergren B., Barcelo D., 2001. Evaluation of a multidimentional solid-phase extraction platform for highly selective on-line cleanup and high throughput LC-MS analysis of triazines in river water samples using molecularly imprinted polymers. Anal. Chem. 73, 2437-2444.

Koide Y., Shoshenji H., Maeda M., Takagi M. 1998. Molecular and Ionic Recognition with Imprinted Polymers. In: Bartsch R.A., Maeda M., eds. American Chemical Society, Washington, DC, USA, pp. 264.

Kuchen W., Schram J., 1988. Metal-ion-selective exchange resins by matrix imprint with methacrylates. Angew. Chem. Int. Ed. Engl. 27, 1695-1697.

Sorption processes and pollution edited by Grégorio Crini and Pierre-Marie Badot

Kyzas G.Z., Bikiaris D.N., Lazaridis N.K., 2009. Selective separation of basic and reactive dyes by molecularly imprinted polymers (MIPs). Chem. Eng. J. 149, 263-272.

Lai J.P., R. Niessner, D. Knopp, 2004. Benzo[a]pyrene imprinted polymers: Synthesis, characterization and SPE application in water and coffee samples. Anal. Chim. Acta 522, 137-144.

Li Q., Su H., Li J., Tan T., 2007. Studies of adsorption for heavy metal ions and degradation of methyl orange based on the surface of ion-imprinted adsorbent. Process Biochem. 42, 379-383.

Li Y., Yang T., Qi X.L., Qiao Y.W., Deng A.P., 2008. Development of a group selective molecularly imprinted polymers based solid phase extraction of malachite green from fish water and fish feed samples. Anal. Chim. Acta 624, 317-325.

Lin Y., Shia Y., Jiang M., Jin Y., Peng Y., Lu B., Dai K., 2008. Removal of phenolic estrogen pollutants from different sources of water using molecularly imprinted polymeric microspheres. Environ. Pollut. 153, 483-491.

Liu Y.W., Chang X.J., Wang S., Guo Y., Din B.J., Meng S.M., 2004. Solid-phase extraction and preconcentration of cadmium(II) in aqueous solution with Cd(II)-imprinted resin (poly-Cd(II)-DAAB-VP) packed columns. Anal. Chim. Acta 519, 173-179.

Maeda M., Murata M., Tsukagoshi K., Takagi M., 1994. Template dependent metal adsorptivity of dialkyl phosphate-type resins prepared by surface template polymerization technique. Anal. Sci. 10, 113-115.

Mhaka B., Cukrowska E., Tse Sum Bui B., Ramström O., Haupt K., Tutu H., Chimuka L., 2009. Selective extraction of triazine herbicides from food samples based on a combination of a liquid membrane and molecularly imprinted polymers. J. Chromatogr. A. 1216, 6796-6801.

Martin P., Jones G.R., Stringer F., Wilson I.D., 2004. Comparison of extraction of a β-blocker from plasma onto a molecularly imprinted polymer with liquid-liquid extraction and solid phase extraction methods. J. Pharm. Biomed. Anal. 35, 1231-1239.

Masque N., Marce R.M., Borrull F., Cormack P.A.G., Sherrington D.C., 2000. Synthesis and evaluation of a molecularly imprinted polymer for selective on-line solid-phase extraction of 4-nitrophenol from environmental water. Anal. Chem. 72, 4122-4126.

Mayes A.G., Andersson L.I., Mosbach K., 1994. Sugar binding polymers showing high anomeric and epimeric discrimination by non-covalent molecular imprinting. Anal. Biochem. 222, 483-488.

Moller K., Nilsson U., Crescenzi C., 2004. Investigation of matrix effects of urine on a molecularly imprinted solid-phase extraction. J. Chromatogr. B. 811, 171-176.

Muldoon M.T., Stanker L.H., 1997. Molecularly imprinted solid phase extraction of atrazine from beef liver extracts. Anal. Chem. 69, 803-808.

Müller R., Andersson L.I., Mosbach K., 1993. Molecularly imprinted polymers facilitating a β-elimination reaction. Makromol. Chem. Rapid. Commun. 14, 637-641.

Nakamura M., Ono M., Nakajima T., Ito Y., Aketo T., Haginaka J., 2005. Uniformly sized molecularly imprinted polymer for atropine and its application to the determination of atropine and scopolamine in pharmaceutical preparations containing Scopolia extract. J.Pharm. Biomed. 37, 231-237.

Navarro-Villoslada F., San Vicente B, Moreno-Bondi M.C., 2004. Application of multivariate analysis to the screening of molecularly imprinted polymers for bisphenol A. Anal. Chim. Acta 504, 149-162.

Nishide H., Deguchi J., Tsuchida E., 1977. Adsorption of metal ions on crosslinked poly(4-vinylpyridine) resins prepared with a metal ion as template. J. Polym. Sci. Polym. Chem. 15, 3023-3029.

O'Shannessy D.J., Ekberg B., Mosbach K., 1989. Molecular imprinting of amino acid derivatives at low temperature (0°C) using photolytic homolysis of azobisnitriles. Anal Biochem 177, 144-149.

Panasyuk T., Dallorto V.C., Marrazza G., Elskaya A., Piletsky S., Rezzano I., 1998. Molecular imprinted polymers prepared by electropolymerization of Ni-(protoporphyrin IX). Anal. Lett. 31, 1809-1824.

Pap T., Horvath V., Tolokan A., Horvai G., Sellergren B., 2002. Effect of solvents on the selectivity of terbutylazine imprinted polymer sorbents used in solid-phase extraction. J. Chromatogr. A. 973, 1-12.

Piletsky S.A., Piletska E.V., Karim K., Freebairn K.W., Legge C.H., Turner A.P.F., 2002. Polymer cookery: Influence of polymerization conditions on the performance of molecularly imprinted polymers. Macromolecules 35, 7499-7504.

Polyakov M.V., 1931. Adsorption properties and structure of silica gel. Zhur. Fiz. Khim. 2, 799-805.

Sorption processes and pollution edited by Grégorio Crini and Pierre-Marie Badot

San Vicente B., Navarro-Villoslada F., Moreno-Bondi M.C., 2004. Continuous solid-phase extraction and preconcentration of bisphenol A in aqueous samples using molecularly imprinted columns. Anal. Bioanal.Chem. 380, 115-122.

Sambe H., Hoshina K., Haginaka J., 2007. Molecularly imprinted polymers for triazine herbicides prepared by multistep swelling and polymerization method. J. Chromatogr. A 1152, 130-137.

Say R., Ersoz A., Turk H., Denizli A., 2004. Selective separation and pre-concentration of cyanide by a column packed with cyanide-imprinted polymeric microbeads. Sep. Purif. Technol. 40, 9-14.

Sellergren B., 1994. Imprinted dispersion polymers. New easily accessible affinity stationary phases. J. Chromatogr. 673, 133-141.

Sellergren B., Shea K.J., 1993. Influence of polymer morphology on the ability of imprinted network polymers to resolve enantiomers. J. Chromatogr. 635, 31-49.

Sellergren B., Andersson L., 1990. Molecular recognition in macroporous polymers prepared by a substrate-analog imprinting strategy. J. Org. Chem. 55, 3381-3383.

Shea K.J., Sasaki D.Y., 1991. An analysis of small-molecule binding to functionalized synthetic polymers by 13CP/MAS NMR and FT-IR spectroscopy. J. Am. Chem. Soc. 113, 4109-4120.

Sibrian-Vazquez M., Spivak D.A., 2004. Characterization of molecularly imprinted polymers employing crosslinkers with nonsymmetric polymerizable groups. J. Polym. Sci. A. Polym. Chem. 42, 3668- 3675.

Spivak D.A., Shea K.J., 1997. Evaluation of binding and origins of specificity of 9-ethyladenine imprinted polymers. J. Am. Chem. Soc. 119, 4388-4393.

Suedee R., Seechamnanturakit V., Canyuk B., Ovatlarnporn C., Martin G.P., 2006. Temperature sensitive dopamine-imprinted (N,N-methylene-bis-acrylamide cross-linked) polymer and its potential application to the selective extraction of adrenergic drugs from urine. J. Chromatogr. A. 1114, 239-249.

Sundberg E.J., Mariuzza R.A., 2002. Molecular recognition in antibody-antigen complexes. Adv. Protein Chem. 61, 119-160.

Theodoridis G., Zacharis C.K., Tzanavaras P.D., Themelis D., Economou G., 2004. Automated sample preparation based on the sequential injection principle: Solid-phase extraction on a molecularly imprinted polymer coupled on-line to high-performance liquid chromatography. J. Chromatogr. A. 1030, 69-76

Theodoridis G., Kantifes A., Manesiotis P., Raikos N., Tsoukali-Papadopoulou H., 2003. Preparation of a molecularly imprinted polymer for the solid-phase extraction of scopolamine with hyoscyamine as a dummy template molecule. J.Chromatogr.A. 987, 103-109.

Tsukaghoshi K., Yu K.Y., Maeda M., Takagi M., 1993. Metal ion- selective adsorbent prepared by surface-imprinting polymerization. Bull. Chem. Soc. Jpn. 66, 114-120.

Turiel E., Martın-Esteban A., Fernandez P., Perez-Conde C., Camara C., 2001. Molecular recognition in a propazine-imprinted polymer and its application to the determination of of triazines in environmental samples. Anal. Chem. 73, 5133-5141.

Uezu K., Tazume N., Yoshida M., Goto M., Furusaki S., 2001. Characterization and control of matrix for surface molecular-imprinted polymer. Kagaku Ronbunshu 27, 753-755.

Uezu K., Nakamura H., Goto M., Nakashio F., Furusaki S., 1999. Metal-imprinted microsphere prepared by surface template polymerization with W/O/W emulsions. J. Chem. Eng. Jpn. 32, 262-267.

Uezu K., Nakamura H., Kanno J., Sugo T., Goto M., Nakashio F., 1997. Metal ion-imprinted polymer prepared by the combination of surface template polymerization with post-irradiation by γ-rays. Macromolecules 30, 3888-3891.

Vigneau O., Pinel C., Lemaire M., 2003. Separation of lanthanides by ion chromatography with imprinted polymers. Chem. Lett. 32, 530-531.

Vlatakis G., Andersson L.I., Mueller R., Mosbach K., 1993. Drug assay using antibody mimics made by molecular imprinting. Nature 361, 645-647.

Watabe Y., Kondo T., Morita M., Tanaka N., Haginaka J., Hosoya K., 2004. Determination of bisphenol A in environmental water at ultra-low level by high-performance liquid chromatography with an effective on-line pretreatment device. J. Chromatogr. A. 1032, 45-49.

Sorption processes and pollution edited by Grégorio Crini and Pierre-Marie Badot

Whitcombe M.J., Rodriguez M.E., Villar P., Vulfson E.N., 1995. A new method for the introduction of recognition site functionality into polymers prepared by molecular imprinting-synthesis and characterization of polymeric receptors for cholesterol. J. Am. Chem. Soc. 117, 7105-7111.

Wulff G., 2002. Enzyme-like catalysis by molecularly imprinted polymers. Chem. Rev. 102, 1-27.

Wulff G., Vietmeier J., 1989. Enzyme-analogue built polymers: 26. Enantioselective synthesis of amino-acids using polymers possessing chiral cavities obtained by an imprinting procedure with template molecules. Makromol. Chem. 190, 1727-1735.

Wulff G., Sarhan A., 1972. Wulff: The use of polymers with enzymeanalogous structures for the resolution of racemates. Angew. Chem. 84, 364.

Xie J., Chen L, Li C., Xu X., 2003. Selective extraction of functional components derived from herb in plasma by using a molecularly imprinted polymer based on 2,2-bis(hydroxymethyl)butanol trimethacrylate. J. Chromatogr. B 788, 233-242.

Yan S., Gao Z., Fang Y., Cheng Y., Zhou H., Wang H., 2007. Characterization and quality assessment of binding properties of malachite green molecularly imprinted polymers prepared by precipitation polymerization in acetonitrile. Dyes and Pigments 74, 572-577.

Yin J., Wang S., Yang G., Yang G., Chen Y., 2006. Molecularly imprinted solid-phase extraction for rapid screening of mycophenolic acid in human plasma. J. Chromatogr. B. 844, 142-147.

Yoshida M., Uezu K., Goto M., Nakashio F., 1996. Metal ion imprinted resins with novel bifunctional monomer by surface template polymerization. J. Chem. Eng. Jpn. 29 174-176.

Yoshida M., Uezu K., Goto M., Furusaki S., 1999. Metal ion imprinted microsphere prepared by surface molecular imprinting technique using water-in-oil-in-water emulsions. J. Appl. Polym. Sci. 73, 1223-1230.

Yu K.Y., Tsukagoshi K., Maeda M., Takagi M., 1992. Metal ion imprinted microspheres prepared by reorganization of the coordinating groups on the surface. Anal. Sci. 8, 701-703.

Zhu Q.Z., P Degelmann., Niesses R., Knopp D., 2002. Selective trace analysis of sulfonylurea herbicides in water and soil samples based on solid-phase extraction using a molecularly imprinted polymer, Environ. Sci. Technol. 36, 5411-5420.

Sorption processes and pollution edited by Grégorio Crini and Pierre-Marie Badot