

Application of molecularly imprinted polymers in wastewater treatment: a review

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Abstract Molecularly imprinted polymers are synthetic polymers possessing specific cavities designed for target molecules. They are prepared by copolymerization of a cross-linking agent with the complex formed from a template and monomers that have functional groups specifically interacting with the template through covalent or noncovalent bonds. Subsequent removal of the imprint template leaves specific cavities whose shape, size, and functional groups are complementary to the template molecule. Because of their predetermined selectivity, molecularly imprinted polymers (MIPs) can be used as ideal materials in wastewater treatment. Especially, MIP-based composites offer a wide range of potentialities in wastewater treatment. This paper reviews the latest applications of MIPs in wastewater treatment, highlights the development of MIP-based composites in wastewater, and offers suggestions for future success in the field of MIPs.

Keywords Molecularly imprinted polymers · Wastewater treatment · Determination · Adsorption · Catalysis · Composites

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Introduction

Water pollution is a global menace. Over the past several decades, a wide range of chemical contaminants have been released to the environmental water by various industries, agriculture, and long-term drought (Chong et al. 2010; Cundy et al. 2008; Foo and Hameed 2009). The surface water and groundwater have been severely contaminated by heavy metal, inorganic pollutants, organic pollutants, especially dyes, polycyclic aromatic hydrocarbons (PAHs), and pesticides (Aksu 2005; Oller et al. 2011; Ferrer et al. 2000). All of these chemicals have great harmful effect on public health and aquatic ecosystems due to its high toxicity and bioaccumulation (Auriol et al. 2006; Ternes and Gunten 2010; Reungoat et al. 2010). Consequently, advanced treatments of wastewater have to be envisaged to removal contaminants.

Several technologies have been developed to remove pollutants from wastewater, including physical adsorption (Snyder et al. 2007; Malik 2003; Huang and Chen 2009), oxidation (Snyder et al. 2006; Lee et al. 2008; Gottschalk et al. 2009), and bioremediation (Onesios et al. 2009; Huang et al. 2006; Guo et al. 2010). However, for some micropollutants such as endocrine-disrupting compounds (EDCs), which concentration are extremely low (typically at levels of parts per billion or parts per trillion), most of these treatments cannot completely remove them. Additionally, these techniques may remove various pollutants simultaneously but cannot effectively remove specific pollutants in wastewater. For these reasons, new methods that are both effective and selective to removal pollutants are urgently needed. More recently, molecularly imprinted polymers (MIPs) are attracting widespread attention due to their prominent selectivity. MIPs are synthetic polymers possessing specific cavities designed for target molecules. They are prepared by copolymerization of a cross-linking agent with the complex formed from a template and monomers that have functional

groups specifically interacting with the template through covalent or noncovalent bonds. Subsequent removal of the imprint template leaves specific cavities whose shape, size, and functional groups are complementary to the template molecule (Shen et al. 2012; Lavignac et al. 2004; Advincula 2011) (Fig. 1). Furthermore, in contrast to these conventional methods, MIPs have other outstanding advantages such as relative ease and low cost of preparation, high stability, physical robustness, resistance to elevated temperature, and pressure and potential application to a wide range of target molecules (Xu et al. 2004; Bui and Haupt 2010; Vasapollo et al. 2011).

MIPs, the polymeric matrices obtained by the imprinting technology, are robust molecular recognition elements able to mimic natural recognition entities such as antibodies and biological receptors (Advincula 2011; Ge and Turner 2008; Bossi et al. 2007), exhibiting high affinity and selectivity for the given analyte or its structure analogs. Therefore, MIPs have been widely utilized in many areas such as chromatograph separation (Byun et al. 2010), membrane separations (Sueyoshi et al. 2010), solid phase extraction (Yin et al. 2010), sensor (Javanbakht et al. 2008; Fuchs et al. 2012), and reactive catalysis (Strikovskiy et al. 2003). Recently, the molecular imprinting technique also has applied for the determination and removal of pollutants from the wastewater and drink water.

This review describes the latest applications of MIPs in wastewater treatment, highlights the development of MIP-based composites in wastewater, and offers suggestions for future success in the field of MIPs. Primary attention is given to the developments of MIPs used as sorbent materials for quantitative determination and purification of contaminants in environmental water, followed by critical discussion on their application as catalysts. Furthermore, the applications of MIP-based on fluorescence sensor for selective recognition of pollutants are discussed. Simultaneously, we pay special attention to the development of MIP-based composites in

wastewater treatment. Finally, challenges are offered to inspire more exciting developments in this still young yet very promising field in the future. The structure of this review is illustrated in Fig. 2.

Molecularly imprinted polymers

The history of molecular imprinting technology seems to be somewhat complicated. The first appearance of molecularly imprinted technique (MIT) dates back to the early 1930s. Polyakov (1931) explained the selectivity effects in terms of a template effect, although the additives were included after polymerization. In the 1940s, Pauling (1940) first put forward the idea about molecular imprinting, which involved a protein antibody self-assembly with an antigen acting as a template. However, no significant advances in molecular imprinting have been made in the following 20 years. And, it was not until in 1972 that Wulff and Sarhan (1972) laid the foundation for the current field with the first report of organic polymers which were prepared by reversible chemical bonds. In the early 1980s, Vlatakis et al. (1993) have successfully prepared the MIPs by using noncovalent molecular imprinting technology. Based on these pioneering studies, molecular imprinting technology started to grow rapidly (Hu et al. 2007).

Generally, there are three binding interactions between template and monomers such as covalent, noncovalent, and semicovalent. The covalent approach was first introduced by Wulff and Sarhan (1972), which involves the formation of reversible covalent bonds between template and monomers prior to polymerization. The obvious advantage of this technique is that binding sites are more homogenous due to the high stability of the template–monomer interaction (Martín-Esteban 2013). However, the interactions between template and monomers are so strong that it is difficult to thoroughly remove the template.

In contrast, Arshady and Mosbach (1981) developed a noncovalent approach which combines the template and monomer in situ by noncovalent interactions such as electrostatic forces, hydrogen binding, or van der Waals forces and so on. Due to the weak interaction, this procedure is rather simple, and a large number of monomers able to interact with a wide range of templates are commercially available. This approach is by far the most used for the preparation of MIPs (Tamayo et al. 2007; Bergmann and Peppas 2008; Malitesta et al. 2012). However, it is not free of some drawbacks occurring because of the low-selectivity binding sites.

Semicovalent is a method that combines the covalent and noncovalent methods. MIPs are synthesized by covalent interactions and then re-recognize the template via a noncovalent molecular imprinting process because of the reversible bond (Fuchs et al. 2012; Zhan et al. 2013). Thus, semicovalent imprinting combines the main advantages of the above two techniques, the stable and stoichiometric complex

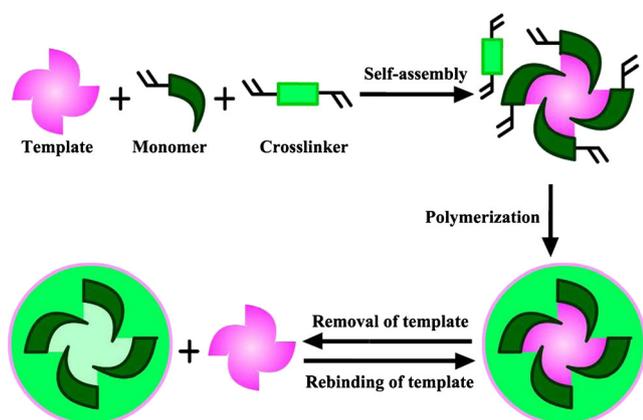
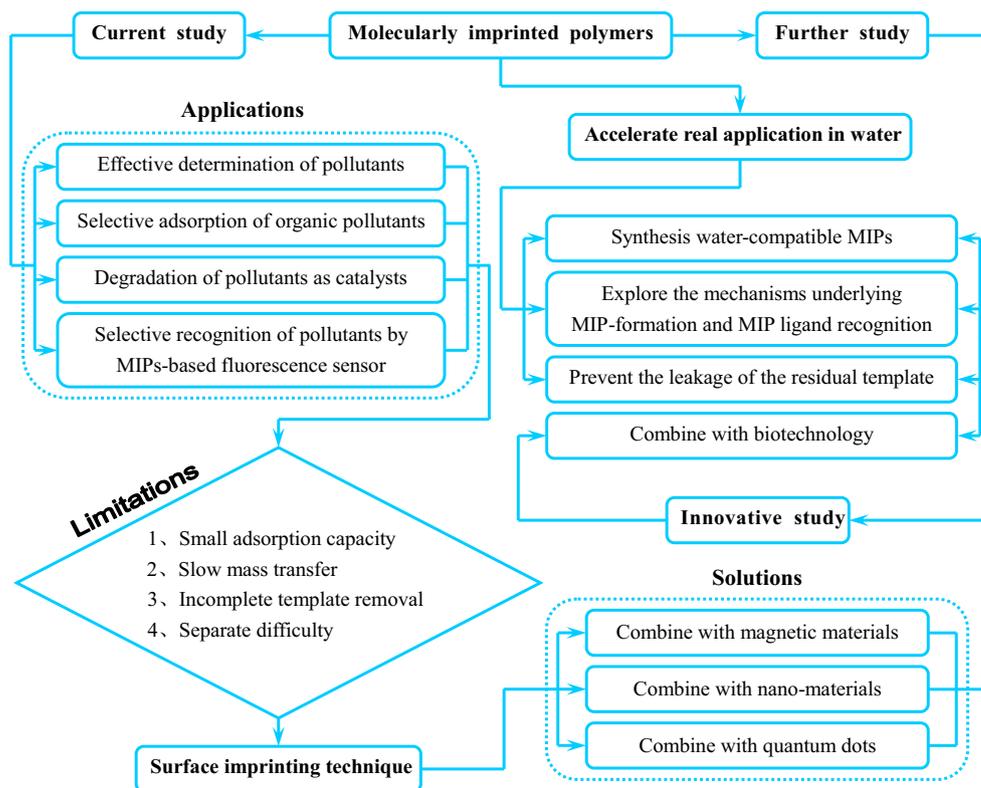


Fig. 1 Schematic representation of principle of molecular imprinting (adopted from Shen et al. 2012)

Fig. 2 Overview of review structure



in covalent imprinting, and the fast guest binding in noncovalent imprinting.

MIPs are being increasingly used as selective adsorbents in different applications. To satisfy the different application purposes, MIPs with well-controlled physical forms in different size ranges are highly desirable. Generally, MIPs have been prepared as monoliths by traditional bulk polymerization. In this polymerization, functional monomers, template, cross-linking, and initiator are dissolved by suitable solvent in a test tube. Subsequently, the mixture is purged with nitrogen to remove oxygen, and the test tube is sealed under vacuum. Finally, bulk monoliths are downsized by grinding and sieving, which result in irregularly shaped particles. Bulk polymerization is by far the most widely used method for the preparation of MIPs due to the simplicity and universality (Pérez-Moral and Mayes 2004; He et al. 2007). However, it has some serious problems such as time-consuming and labor-intensive, and less than 50 % of the ground polymer is recovered as useable particles (Zheng et al. 2013; Poma et al. 2010; Yoshimatsu et al. 2007).

To overcome these drawbacks, several polymerizations have been proposed for the direct preparation of spherical particles in desired size. Suspension polymerization is one of the simplest and the most common approaches for the production of the MIP beads. In conventional suspension polymerization, all the components involved in the polymerization process are dispersed in water phase in the presence of

stabilizer and surfactant. However, the use of water as a dispersing agent reduces the binding site number and strength between the functional monomer and template (Mayes and Mosbach 1996). Liquid perfluorocarbons are largely immiscible with most organic compounds and hence become an appropriate continuous phase for suspension polymerization. Precipitation polymerization is one of the most well-suited methods to obtain MIP microspheres with the desired characteristics. In this reaction system, the functional monomers, template, cross-linking, and initiator are dissolved in a larger amount of porogen than those typically used in the bulk polymerization. But, as the polymerization proceeds, the growing polymer chains become insoluble in the porogen and tend to precipitate. The advantage of this method includes that it requires no surfactant and can obtain a micron size range of MIPs by controlling the polymerization conditions (He et al. 2007; Yan et al. 2007). Two-step or multiple swelling polymerizations are another common method for preparing MIP beads, but it is also one of the more laborious procedures (Hu et al. 2007; Turiel and Martin-Esteban 2004). In this technique, preformed uniform-sized seed particles are suspended in water, and after several additions of suitable organic solvents, the initial particles swell to a final size with desirable performance.

More recently, surface imprinting technique has attracted significant interest as a new alternative for improving the performance of MIPs. In the most common MIP strategy,

surface imprinting, the imprinted binding sites are located at or very near the surface of the polymer. The special characteristic solves the problem of limited mass transfer, small binding capacity, and incomplete template removal which often associated with materials by previous molecular imprinting methods (Gao et al. 2007, 2008). Surface imprinting polymers were usually prepared by either synthesizing a thin polymer film using similar approaches to those in bulk imprinting or by attaching the template on the surface of a substrate (flat or spherical) with polymerization.

Use of molecularly imprinted polymers in wastewater treatment

In recent years, several research began to study the use of MIPs for wastewater treatment. The applications of MIPs in contaminated water can be divided into four aspects: (i) technologies which use MIPs as selective tools for determination of pollutants in wastewater, (ii) technologies which use MIPs as a kind of effective sorbent for purification of pollutants, (iii) technologies which use MIPs to improve the efficiency of catalytic for organic matters, and (iv) those which apply MIP-based fluorescence sensor to recognize and directly quantify target analytes. Due to the advantages of high selectivity and strong affinity, MIPs become an efficient method for selective recognition, separation, determination, and purification of pollutants in wastewater.

Effective determination of pollutants

As an alternative, MIPs have been already successfully used as selective tools in several analytical fields such as sensors, solid phase extraction (SPE), and chromatograph due to their favorable molecular recognition capabilities and stability. In particular, SPE is the most advanced application of the area of MIPs, which provides a simple and effective pretreatment method in complicated samples (Sellergren 2000; Whitcombe and Vulfson 2001; Haupt and Mosbach 2000). Molecular imprinted SPE (MISPE) has opened a new window for selective extraction and recognition of target molecules from the complex matrices (Turiel and Martín-Esteban 2010). In recent years, several publications have described the success of MISPE for the extraction and determination of a broad range of compounds from water sample, including carbaryl (Sánchez-Barragán et al. 2007), water-soluble acid dyes (Luo et al. 2011a), bisphenol A (Ou et al. 2006), catechol (Tarley and Kubota 2005), carbamazepine (Beltran et al. 2007), benzimidazole compounds (Cacho et al. 2009), 17 β -estradiol (Watabe et al. 2006), herbicides (Sambe et al. 2007), mercury (Liu et al. 2006), and cyanide (Say et al. 2004).

When MIPs act as SPE sorbents for the selective extraction of target analytes from water samples, the retention of the

analytes is mainly due to nonspecific hydrophobic, electrostatic interaction or hydrogen bonding (Sun and Qiao 2008) with the polymer matrix, as well as selective retention mechanism between the target and the surface function monomer. In general, the intermolecular hydrogen-bonding between analyte and the polymer is weak in aqueous solution because of the competition from the high concentration of water molecules (Ou et al. 2006). MISPE coupled to high-performance liquid chromatograph can effectively separate pollutants from water samples. For example, Xu et al. (2009) studied on a MISPE coupled to high-performance liquid chromatograph for separation and determination of trace estrone in environment. Due to the specific recognition sites from the molecular imprinted process, MIPs show high selectivity toward estrone. Results also showed that the limit of detection was 5.7 ng L⁻¹ (S/N=3), and the relative standard deviations for nine replicate extractions of 0.5 μ g L⁻¹ estrone were less than 10.0 %. This novel-developed method is capable of being applied for monitoring the existing estrone residue in water.

Most MIPs are synthesized by using the target analyte as a template to show high selectivity, but residual template leaking may happen in the SPE procedure, which would have a serious impact on the accuracy of identification and quantitation of the trace compounds (Andersson et al. 1997). To solve this problem, the strategy of surface molecular imprinted polymers with dummy templates has been applied to prepare the sorbents. With this strategy, the bleeding template can be separated from the target molecules and would not interfere with trace analysis. Furthermore, SMI greatly increases the efficiency of adsorption and desorption, reducing the leakage of the residual template to a great extent. For example, Zhao et al. (2010) prepared dummy template imprinted polymers at surface of silica microparticles for the selective extraction of trace bisphenol A from water samples. The analogs of BPA, such as DDBP and TBBPA, were used as the dummy templates instead of BPA, to prevent inaccurate determination of trace BPA in water samples in case of the leakage of residual BPA in the MIPs. And, the resulting dummy MIPs (DMIPs) showed large sorption capacity, high recognition ability, and fast binding kinetics for BPA.

With the development of MISPE, some drawbacks of MISPE emerged and greatly restricted its widespread application. For example, the small particle sizes bring difficulties when trying to separate them from aqueous sample, which eventually lead them far from real application. It was excited for scientists to find that giving MIP magnetism was an effective approach to overcome the disadvantages of MISPE (Ansell and Mosbach 1998; Lu et al. 2006a, b). Lin et al. (2012) performed the combination of imprinting polymers and magnetic particles for selective extraction and detection of bisphenol A (BPA) from aqueous samples. As magnetic molecular imprinted polymers (MMIPs) were adopted as the adsorbents of SPE for detecting BPA in real water samples,

the recoveries of spiked samples ranged from 84.7 to 93.8 % with the limit of detection of 2.50 pg mL^{-1} , revealing that the MMIPs were efficient SPE adsorbents and were reliable for selective extraction and determination of BPA. These MMIPs not only have selectivity for the target molecules from complex matrix, but also are easily collected and separated by an external magnetic field without additional centrifugation, filtration, and membrane separation, which greatly facilitate the lab work. Similarly, other MMIPs have been synthesized for the determination of different contaminants (Zhu et al. 2013; Mehdinia et al. 2013; Kong et al. 2012).

Selective adsorption of organic pollutants

As a well-known wastewater treatment, adsorption process has been widely applied to remove chemical pollutants from water. It has numerous advantages in terms of cost, flexibility, and simplicity of design/operation, and in many cases, it well generate high-quality-treated effluent (Rafatullah et al. 2010; Ahmad et al. 2009; Zeng et al. 2007). The adsorption process is a surface phenomenon in which the adsorbates are attracted to the surface of solid adsorbent and form attachments via physical or chemical bonds (Foo and Hameed 2010, 2011). To date, various materials including activated carbon (Kobya et al. 2005), iron oxide nanomaterials (Xu et al. 2012), graphene-based materials (Wang et al. 2013), etc., have been applied to removal of pollutants from water. Among these available adsorbents, it seems that MIPs, possessing high selectivity for target analyte and favorable capacity to organic pollutants, are most promising ones for pollutant removal from aqueous systems. Currently, MIPs are being explored for organic contaminant adsorption, particularly for the treatment of trace contaminants in large-volume water samples. A lot of experiments have been undertaken to examine the removal efficiency of organic pollutants by using MIPs for organic pollutants. Table 1 lists recent reports on the adsorption of organic compounds by MIPs.

According to the previous research, mechanisms of contaminant adsorption in aqueous phase by MIPs can be classified into two types: nonspecific adsorption and specific adsorption. Nonspecific adsorption results from the hydrogen bonding, hydrophobic interaction, or van der Waals force, while specific adsorption comes from the selectivity recognition cavities which were introduced in imprinting process. Furthermore, two types of adsorption may simultaneously occur in aqueous solution. For instance, Dai et al. (2011) synthesized MIPs for the selective removal of diclofenac (DFC) from the complex surface water. The prepared MIPs exhibited outstanding adsorption ability for DFC with a maximum binding site capacity (Q_{max}) of 324.8 mg g^{-1} . In comparison, nonimprinted polymers (NIPs) only absorbed less than 20 % of DFC, and the Q_{max} value of NIPs was 45.2 mg g^{-1} . The result demonstrated that nonspecific

adsorption and specific adsorption simultaneously occur in the adsorption process, and specific imprinting sites favored the adsorption of the target molecule in aqueous solution. In addition, MIPs show excellent regeneration characteristics and can be reused at least 12 times without significant loss of loading capacity. It was recommended that MIPs were selective and effective adsorbents for rapid removal of organic pollutants from contaminated water.

Currently, MIPs used in most studies were limited to one target enrichment and adsorption. To further improve the utilization efficiency of MIPs, a few studies recently developed multifunctional MIPs, aiming for simultaneously removing lots of pollutants rather than single pollutant during adsorption process. In a study performed by Dai et al. (2012), multitemplate MIPs were prepared by using acidic pharmaceuticals mixture (ibuprofen (IBP), naproxen (NPX), ketoprofen (KEP), diclofenac (DFC), and clofibric acid (CA)) as the templates for the removal of acidic pharmaceuticals from contaminated water. Due to the specific imprinting cavities and nonspecific interaction between adsorbent and adsorbate, the prepared MIPs exhibited outstanding selectivity affinity toward five pharmaceuticals with high binding capacity. Furthermore, MIPs can be reused for at least 15 times without loss of performance, indicating that the multitemplate MIPs are economic and practical materials for removing lots of pollutants.

When it comes to the application of MIPs in adsorption of pollutants from environment water, the efficiency and cost must be taken into account. In previous research, great efforts have been made to optimize the polymerization and improve efficiency. Recently, there has been research on combination with other efficient materials to widen their potential applications in wastewater treatment. Pan et al. (2011b) synthesized MMIPs for the selective recognition of 2,4-dichlorophenol (2,4-DCP). The prepared MMIPs exhibited high magnetic property ($M_s=5.67 \text{ emu g}^{-1}$) and great adsorption capacity (145.79 mg g^{-1}). Due to their high magnetic susceptibility, MIPs could be easily separated from the suspension, leading to a fast and selective removal of 2,4-DCP from aqueous solutions. Gao et al. (2011) reported the preparation of carbon nanotubes (CNTs) functionalized with MIPs for advanced removal of estrone from water samples. The prepared MIP nanocomposites showed excellent selectivity and high removal efficiency (ranged from 96.14 to 98.03 %) toward estrone due to the high specific surface area of CNTs and the specific recognition sites of MIPs. Thus, the combination of the selectivity properties of MIPs and superior adsorption performance of materials tends to be a promising way to deal with a variety of environmental problems.

Laboratory studies indicated that MIPs could effectively remove a range of organic pollutants, including BPA, 2,4-DCP, estrone, and DFC. However, MIP-based technology for organic adsorption is still at a relatively early stage for

Table 1 Previous research in the utilization of molecularly imprinted polymers as adsorbents for the removal of organic pollutants in wastewater

Target analytes	Adsorption capacity	Reference
Diclofenac	The adsorbent showed a maximum of 324.8 mg g ⁻¹ uptake capacity for diclofenac.	(Dai et al. 2011)
α-Estradiol	The MIPs showed outstanding affinity toward α-estradiol with a binding capacity of 380 nmol mg ⁻¹ .	(Meng et al. 2005)
17β-Estradiol	The adsorption capacity of MIPs for 17β-estradiol was 15 mg/g.	(Lai et al. 2010)
Clofibric acid	The maximum adsorption capacity for Clofibric acid was 359 mg g ⁻¹ .	(Dai et al. 2013a)
2,4-Dichlorophenol	The removal efficiency of 2,4-dichlorophenol reached 83.2 %.	(Li et al. 2009)
2,4-Dinitrophenolic	The removal efficiency of 2,4-dinitrophenolic was very high with all above 92 %.	(Jing et al. 2014)
Carbamazepine	The adsorption amount of MIPs for CBA and CA reached 74.2 and 82.2 mg g ⁻¹ , respectively.	(Dai et al. 2013b)
Clofibric acid		
Polycyclic aromatic hydrocarbons (PAHs)	The removal efficiency of PAHs reached more than 80 % within 45 min.	(Krupadam et al. 2010)
Estrogenic compounds	The maximum adsorption capacity of MIPs for estrone, E2, 17α-ethinylestradiol and BPA were 92.8, 95.8, 115.4, and 57.4 μ mol g ⁻¹ polymers, respectively.	(Zhongbo and Hu 2008)

wide application. It is recognized that there is much room for further improvement, and the transfer of MIPs from laboratory to field-scale application involves many complexities. With increasing trends in contaminant removal treatment, more data of MIPs will become available on performance and cost, which can provide additional information for large-scale industrial application.

Degradation of pollutants as catalysts

Considerable efforts have been made to investigate the possible use of MIPs for catalytic applications (Brüggemann 2001; Sharabi and Paz 2010; Resmini 2012; Sun et al. 2013; Zhang et al. 2013). The obvious advantage of MIPs can withstand aggressive conditions, including high temperature and pressure, extreme pH, and organic solvents, making the new MIP-based catalysts attractive for diverse practical applications. In addition, MIP catalysts are able to mimic the active center of enzymes which are generally utilized as catalysts in several reactions and have high selectivity toward substrates. For these reasons, MIPs can be employed instead of enzymes or natural catalytic antibodies and offer potential for developing tailored catalysts for special substrates.

There have been many reports about MIPs as enzyme-mimetic catalysts for organic catalysis. For example, Chen et al. (2002) successfully synthesized MIP-based catalysts for catalytic ester hydrolysis by using *p*-nitrophenyl phosphate as a transition state analog. In the study, the effects of pH and contact time were studied to evaluate the catalytic activity of MIPs. And, results demonstrated that rate enhancement of the hydrolysis by MIPs was 60-folds over the uncatalyzed solution reaction. Nowadays, the MIP catalysts were mainly prepared by two approaches. The first one involves introduction of suitable catalytic groups such as metal ions into a defined orientation in the active sites and subsequently exhibits high

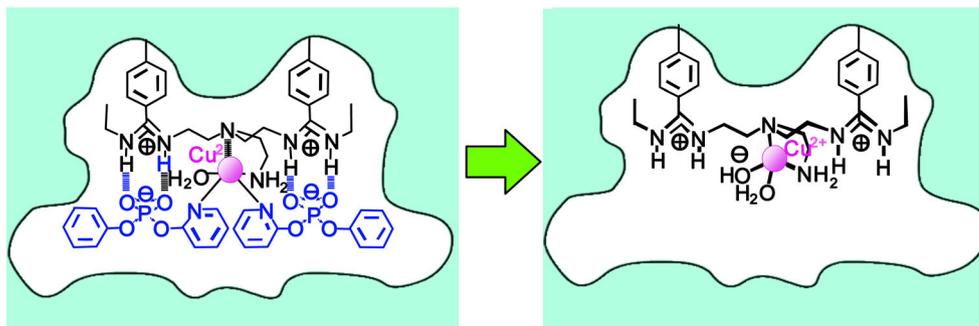
catalytic efficiency in the presence of true substrates. For example, Liu and Wulff (2008) prepared an artificial model of carboxypeptidase A by combination of molecular imprinting and the introduction of americium groups and copper (II) or zinc (II) into the active site in predetermined orientation (Fig. 3). The results demonstrated that the molecular imprinted polymers offer an excellent possibility to mimic the active sites of natural enzymes. Furthermore, it has been seen that the introduction of metal ions into the TSA-imprinted active sites resulted in a strong increase in catalytic activity. Therefore, constructing a catalytically active center with a special structure and function in MIP-imprinted cavities would open up new ways for the design of highly active new catalysts.

The second approach is based on the immobilization of metal or metal complex of low molecular weight exhibiting catalytic properties. Titania (TiO₂) is one of the most common photocatalysts and has been well-studied with concern for environmental protection. But, because TiO₂ has poor selectivity it is difficult to selectively catalyst specific pollutants from complicated wastewaters in the presence of other pollutants. Shen et al. (2008) synthesized MIP-coated TiO₂ photocatalysts for the degradation of 2-nitrophenol and 4-nitrophenol via surface molecular imprinting. The prepared MIP-coated photocatalysts not only enhanced the activity toward the photodegradation of target pollutants but also showed great selectivity compared to the conventional TiO₂.

Selective recognition of pollutants by MIP-based fluorescence sensor

In recent years, MIP-based fluorescence sensors, which are based on surface MIPs and fluorescence signal, have been used for the specific recognition and quantitative detection of

Fig. 3 Schematic representation of the copper (II) into the active site in predetermined orientation of the imprinted polymers (adopted from Liu and Wulff 2008)



target analytes. Kim et al. (2012) prepared a highly sensitive molecularly imprinted fluorescent sensor by using a CdSe quantum dot (QD) as a signal transducer and a mesoporous silica nanoparticle as an imprinting material for fluorescent sensing of BPA. Liu et al. (2014) synthesized nanoshell sensor using the molecular imprinted polymer on the surface of the $\text{YVO}_4:\text{Eu}^{3+}$ for detection of λ -Cyhalothrin (LC). The as-prepared core–shell structured nanocomposite ($\text{YVO}_4:\text{Eu}^{3+}@\text{MIPs}$), which was composed of lanthanide doped $\text{YVO}_4:\text{Eu}^{3+}$ as fluorescent signal and surface molecular imprinted polymers as molecular selective recognition sites, could selectively and sensitively optosense the target analytes. Quenching of the luminescence emitted by the core–shell structured nanoparticles allowed the determination of LC as low as 1.76 μM . The obtained sensor was proven to be suitable for the detection of residues of LC in real examples.

MIPs have been successfully used with fluorescence sensors, and several methods have been used to achieve a close integration of the fluorescence sensors with the polymer. There are some papers using fluorescence functional monomers to synthesize MIP-based fluorescence sensors. Tong and coworkers (2002) have used zinc(II)–protoporphyrin (ZnPP) as fluorescent reporter/functional monomer to synthesize MIP sensor for the selective recognition of histamine. Results demonstrated that the fluorescence intensity of the MIP decreased upon exposure to histamine. As an alternative to integrate MIPs with fluorescence sensors, Turkewitsch et al. (1998) developed fluorescent chemosensor for adenosine 3':5'-cyclic monophosphate (cAMP) by incorporation of a fluorescent dye (trans-4-[p-(N,N-dimethylamino) styryl]-N-vinylbenzylpyridinium chloride) into the binding sites. The fluorescent dye is serving as both the recognition element and the measuring element for the fluorescence detection of cAMP in aqueous media. Quenching of the dye was observed upon rebinding of the template cAMP molecule to the MIP. In addition, Ng and Narayanaswamy (2006) also developed a novel aluminium ion-specific sensor. This sensor adopted Al^{3+} as the template molecule and 8-hydroxyquinoline sulfonic acid ligand as the fluorescence tag. 8-Hydroxyquinoline sulfonic acid (8HQs) was adopted as the ligand owing to its

ability to react with Al^{3+} ion to form a complex with good optical properties. The fluorescence signal during metal–ligand complexation was detected using a fiber optic cable. Results demonstrated that the synthesized MIPs showed a promising quantitative response over a range of different Al^{3+} ion concentrations within a very short period of time.

Moreover, MIP-based fluorescence sensor can also be developed by imprinting of fluorescence transduction platform. The MIPs on the surface of fluorescence transduction platform, as a recognition element, can specially bind the trace target analyte in complicated matrix, which bring about the fluorescence quenching of the sensor, and the degree of quenching may be related to the amount of the target analyte. Several groups have fabricated molecularly imprinted film on the surface of semiconductor quantum dots (such as Mn^{2+} doped ZnS QDs, CdSe QDs, CdTe QDs) (Wang et al. 2009; Zhang et al. 2012). Ge et al. (2011) developed a fluorescence nanosensor based on CdTe quantum dots and MIPs for the determination of deltamethrin (DM). The CdTe– SiO_2 –MIPs is employed as a novel and highly sensitive luminescence probe for optical recognition of DM. Zhou et al. (2014) reported a novel fluorescent sensor based on MIP-coated graphene quantum dots (GQDs) for determination of paranitrophenol (4-NP) in water sample. The novel fluorescent sensor possesses prominent merits, such as stable fluorescence, eco-friendly property, rapid response, and good recognition specificity.

Leakage of the residual template molecules is one of the biggest challenges for application of MIP in fluorescence sensors, which would impair the accuracy of sensors. SMI with dummy templates may be a good alternative to solve this problem. Xu et al. (2013b) reported a novel DMIP@QDs sensor with trinitrophenol (TNP) as a dummy template molecule for the detection of TNT on the surface of QD. In the study of Chen et al. (2012), molecularly imprinted film with diphenolic acid (DPA) as dummy template molecule has been grafted on the surface of Mn-doped ZnS quantum dots (QDs) to develop a selective and sensitive sensor for rapid determination of tetrabromobisphenol A (TBBPA) in water. The obtained DPA-MIP-QDs sensor has distinguished selectivity and high binding affinity to TBBPA. The sensor has been successfully applied to determine the TBBPA in water, and the

average recoveries of the TBBPA at various spiking levels ranged from 80.2 to 96.5 % with relative standard deviation below 8.0 %.

Application of MIP-based composites in wastewater treatment

Molecular imprinting technique has become a promising way to prepare MIPs with tailored selectivity for target analytes. The prepared MIPs exhibit an affinity for the template molecule over other structurally related compounds. However, traditional MIPs suffer from many limitations in practical application, such as incomplete template removal, low-affinity binding, and slow mass transfer. Recently, molecular imprinting technique combines with nanomaterials (Chen et al. 2014; Pan et al. 2011c), magnetic particles (Mehdinia et al. 2013; Li et al. 2012), or quantum dots to prepare surface MIP composites (Table 2), which enable the imprinting sites situated at the polymer surface or close to the surface, which have received considerable attention. Because the composites possess the advantages of both MIPs and nanomaterials, magnetic particles, or quantum dots, it shows great selectivity, favorable affinity, and fast association/dissociation kinetics toward analytes. Many approaches have been explored to develop these surface MIP composites, including free radical polymerization (FRP), reversible addition fragmentation

chain transfer (RAFT) polymerization, atom transfer radical polymerization, and sol–gel method, etc.

MIP-magnetic particle composites in wastewater treatment

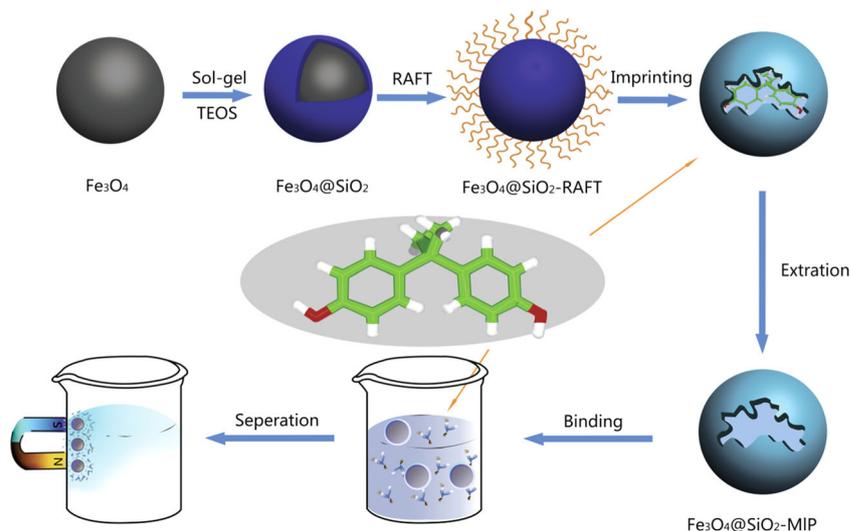
Magnetic particles (Fe_3O_4) have drawn considerable attention because of the fundamental scientific interest and the promising applications in separation, catalysis, and biological and environmental remediation. Additionally, Fe_3O_4 also shows advantages such as low toxicity, low cost, and eco-friendliness which serves as a stabilizer. More recently, there has been an increasing interest in combining magnetic particles with molecular imprinting technique for the comprehensive benefits in selectivity and sensitivity. It is expected that the marriage of the magnetic particles and MIPs will provide a new approach toward separation application and broaden the use of MIPs in wastewater treatment. When magnetic particles are encapsulated inside of imprinted polymers, the resulting MMIPs cannot only selectively recognize the target analytes, but also can be quickly isolated from the complex matrix with an external magnetic field (one of the polymerizations of preparation magnetic MIP composites is shown in Fig. 4).

Guo et al. (2011) successfully synthesized magnetic MIPs based on kaolinite/ Fe_3O_4 composites for the selective adsorption and separation of BPA from aqueous solutions. In the study, the effects of pH, initial BPA concentration, contact time, and temperature of the medium on the adsorption were

Table 2 Recent reports about the application of MIP-based composites in wastewater treatment

Materials	Target analytes	Application	Reference
MIPs/ Fe_3O_4	Estrogens	Determination of estrogens in water samples.	(Lin et al. 2013)
MIPs/ Fe_3O_4	4-Nitrophenol	Selective determination of 4-nitrophenol in aqueous water.	(Mehdinia et al. 2013)
MIPs/ Fe_3O_4	4-Nitrophenol	Selective adsorption of 4-nitrophenol from wastewater	(Tang et al. 2012)
MIPs/ Fe_3O_4	Sulfonamides	Fast determination of sulfonamides from water.	(Chen et al. 2013)
MIPs/ Fe_3O_4	BPA	Rapid determination of BPA in environmental water.	(Ji et al. 2009)
MIPs/ Fe_3O_4	Water-soluble acid dyes	Removal of water-soluble acid dyes from water environmental.	(Luo et al. 2011b)
MIPs/ Fe_3O_4	EDCs	Removal of EDCs from aqueous environmental.	(Xia et al. 2013)
MIPs/kaolinite/ Fe_3O_4	BPA	Selective adsorption and separation of BPA from aqueous solution.	(Guo et al. 2011)
MIPs/chitosan/ Fe_3O_4	Carbamazepine	Separation of carbamazepine from environmental water bodies.	(Yu et al. 2011)
MIPs/Au nanoparticles	BPA	Selective determination BPA in real water samples.	(Xue et al. 2013)
MIPs/ TiO_2 nanotubes	Estrogenic compounds	Removal of estrogenic compounds from second effluents.	(Zhang et al. 2013)
MIPs/carbon nanotubes	Triclosan	Determination of triclosan in water samples.	(Gao et al. 2010)
MIPs/carbon nanotubes	Estrone	Selective removal of estrone from water samples.	(Gao et al. 2011)
MIPs/multiwalled carbon nanotubes	2,4-dichlorophenoxy acetic acid	Determination of 2,4-dichlorophenoxyacetic acid in environmental water.	(Yang et al. 2013)
MIPs/halloysite nanotubes	2,4,6-trichlorophenol	Recognition of 2,4,6-trichlorophenol from environmental samples.	(Pan et al. 2011c)
MIPs/carbon nanoparticles	Fluoroquinolone antibiotics	Removal of fluoroquinolone antibiotics in aqueous solution.	(Tan et al. 2013)

Fig. 4 Synthesis route of surface imprinted core-shell magnetic beads (adopted from Li et al. 2010)



studied to examine the removal efficiency of the prepared adsorbents. And, the resulting MMIPs showed an outstanding affinity toward BPA in aqueous samples with the adsorption capacity of 142.86 mg g⁻¹ at 298 K. Furthermore, the separation and recycling of MMIPs became much easier due to incorporating Fe₃O₄. Similar to adsorption of pollutants by MIPs, MMIPs adsorb on BPA also by imprinting sites and nonspecific interactions. In addition, MMIPs have successfully applied to SPE pollutants from aqueous phase. For example, Chen et al. (2013) prepared MMIPs for the extraction and enrichment of sulfonamide antibiotics and their acetylated metabolites from environmental water. Results showed that the detection limits of the method are in the range of 0.38–1.32 ng L⁻¹ and the relative standard deviations of intraday and interday are in the range of 1.3–6.8 and 1.7–9.1 %, respectively. The MMIPs with saturation magnetization value of 16.7 emu g⁻¹ could be separated from the environmental water samples easily by the application of an external magnetic field, reducing the time consumption of pretreatment.

MIP–nanoparticle composites in wastewater treatment

At present, diverse nanotechniques are employed for the imprinting polymers. Among these techniques, the combination of surface imprinting with nanostructure, especially imprinting of target molecules on the surface of nanosized support materials, has recently attracted much more interest (Ma et al. 2011). Up to now, a large number of nanostructure materials have been used as supporting material in the preparation of imprinted polymers, including carbon nanotubes (Gao et al. 2011), nanosilica (Wei et al. 2013), magnetic nanoparticle (Wang et al. 2011), multiwalled carbon particles (MCNs) (Yang et al. 2013), TiO₂ nanotubes (Zhang et al. 2013), gold nanoparticles (Xu et al. 2013a), and silver colloidal particles

(He et al. 2008). These nanomaterials that combine with surface molecular imprinting have been successfully synthesized core-shell MIPs. Such core-shell MIPs can be endowed with the following additional features: (i) The templates within thin imprinted shells can be completely removed to form effective recognition sites; (ii) the size or form of the imprinted materials can be readily regulated by that of the preformed supports; and (iii) the multifunctional composites possess good dispersibility, high surface-to-volume ratio, and rapid binding kinetics.

MIPs in conjunction with nanomaterials have widespread applications in wastewater treatment, including recognition, separation, and adsorption pollutants from environmental water. For example, Gao applied surface molecular imprinting technique to anchoring MIP shell onto the surface of CNTs for determination of trace triclosan (TCS) in environmental water (Gao et al. 2010) (Fig. 5). The prepared MIP nanocomposites combined the merits of surface molecular imprinting and carbon nanotubes. Results showed that the recoveries of MIP nanocomposites in river water and lake water sample ranged from 92.1 to 95.3 and 90.7 to 93.6 %, respectively. The relative standard deviation was less than 8.4 %. Tan et al. (2013) successfully synthesized core-shell MIPs for adsorption of fluoroquinolone antibiotics (FQs) in aqueous solution. The synthesized process combined a surface technique with sol-gel process based on mesoporous carbon nanoparticles (MCNs). The prepared MIP–nanoparticle composites showed fast adsorption and good selectivity for ofloxacin due to the specific adsorption and nonspecific adsorption (electrostatic interaction and hydrogen-bonding interactions). In addition, nano-MCN/MIPs could be reused at least five rounds for removing of FQs without any loss of performance, indicating the potential applications of the nano-MCN/MIPs for selective removal of FQ residues in waters.

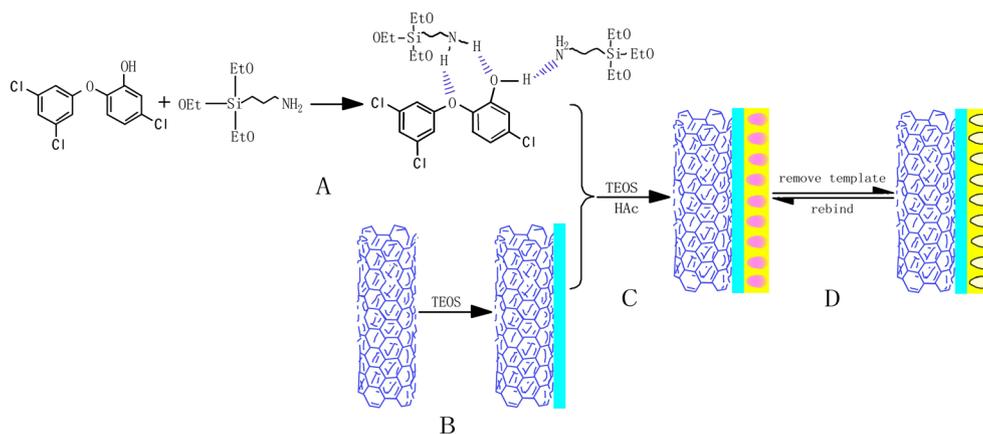


Fig. 5 Scheme of the synthetic route for CNTs@TCS-MIPs: **a** formation of template (TCS)-aminosilica monomer (APTES) complex; **b** transformation of the surface of purified CNTs to silica shell by a sol-gel process using TEOS and APTES in the presence of CTAB to obtain core@shell

CNTs@SiO₂; **c** reaction of CNTs@SiO₂ with template silica monomer complex to produce silica surface functionalized with TCS-imprinted polymer; **d** removal of the TCS from polymer shells and the CNTs@TCS-MIPs were obtained (adopted from Gao et al. 2010)

MIP quantum dot composites in wastewater treatment

Over the past decade, quantum dots (QDs) have attracted intensive research interest for sensing and recognizing the organic and inorganic compound pollutants due to their prominent advantages, such as great photostability, high photoluminescence efficiency, size-dependent emission wavelengths, and sharp emission profile (Liu et al. 2013; Van Tilborg et al. 2006). However, the selectivity of QDs may be restricted by the similar fluorescence response to structural analogs of the template molecules. And, the nonspecific binding causes a high level of background fluorescence, limiting target specificity and detection sensitivity—a major barrier for the widespread application of QDs in real. To our knowledge, molecular imprinting is a well-established technique widely used for synthesizing MIPs with tailor-made molecular recognition binding sites for recognition. Therefore, combining the high selectivity of molecular imprinting technology and excellent fluorescent characteristics of QDs could develop new method for target analyte recognition.

The QDs@MIP composites were widely used as sensors for the recognition of pollutants. Liu et al. (2010) reported the preparation of MIP anchored on the surface of Mn-doped ZnS QDs for chemiluminescence detection of 4-nitrophenol in tap water. Zhao et al. (2011) developed composite QDs@MIP nanospheres for specific recognition and direct fluorescent quantification of pesticides in aqueous media. These QDs–MIP nanospheres demonstrated high recognition selectivity in aqueous media and relatively fast adsorption and desorption kinetics. Based on the fluorescence quenching via template analyte (diazinon) rebinding into the recognition cavities in the polymer matrixes, the QDs–MIP nanospheres were successfully applied to the direct fluorescence quantification of diazinon, independent of extracting templates from the MIP nanospheres, as well as further complicated and time-consuming

assays. Wang et al. (2009) have developed a type of MIP-based room temperature phosphorescence by anchoring a MIP layer on the surface of Mn-doped ZnS QDs for detecting pentachlorophenol in water. The combination of the RTP emission of Mn-doped ZnS QDs and the merits of the surface imprinting polymers not only makes the MIP-based RTP optosensor also applicable to selective detecting of nonphosphorescent analytes without the need for any inducers and derivatization but also improves the RTP selectivity of the QDs.

Combining the selectivity properties of MIPs and the superior adsorption performance, magnetism and fluorescent characteristics of these special materials tend to be a promising approach to deal with a variety of environmental problems. MIP-based nanoadsorbents, magnetic adsorbents, and QD composites provide opportunities for selective and effective removal of pollutants from environmental water, and MIP-based catalysis could achieve the goal of selective catalysis pollutants. Although lots of nanomaterials, magnetic particles, and QDs have been investigated to combine with MIPs, more potential materials and technologies need to search in order to achieve the goal of MIP large-scale application in environmental water. At present, little information is available on combining molecularly imprinting technology with biological technology for environmental application, which may show a great application prospect by combining respective advantages of both MIPs and biomass. Further studies may focus on finding potential biomass combine with MIPs.

Critical barriers to success of MIP application in wastewater treatment

Although considerable progresses have been achieved, the real use of MIPs for water analysis and purification in its

infancy. As illustrated in this review, a range of MIP-based technologies has been proposed or is under active development for wastewater treatment, but many techniques are still at an experimental or pilot stage. Thus, there is much room for further improvement. First, the fundamental mechanisms underlying MIP formation and MIP ligand recognition have received very little attention, thus remain largely unknown (Nicholls et al. 2011). The successful preparation of MIPs mainly depends on the stability and strength of the monomer template complex prior to polymerization. It is clear that the binding interactions between the template and monomer are covalent or noncovalent (hydrogen bonding, electrostatic, and hydrophobic interactions). However, the relative importance of each of these is still in question. A better understanding of mechanism behind the molecular imprinting process is necessary to approach the goal of “rational MIP design.” More efforts should be undertaken to understand the molecular level events occurring in prepolymerization mixtures; the polymerization reaction and the factors may affect polymer–ligand recognition.

Second, the imprinting technologies to synthesis water-compatible MIPs are still required (Piletska et al. 2008). The traditional polymers are often synthesized in organic solvent and display a different swelling effect when they are used in an aqueous system. The apparently different structure after swelling makes the MIPs unable to specific recognition the target from water samples. On the other hand, water molecules will compete with the template, then making weaker or destroying noncovalent between template and function monomer. In spite of these, some progress has been made in the development of water-compatible MIPs. A new method to synthesis water-compatible MIPs is introduction of hydrophilic properties into the polymer. For example, Pan et al. (2011a) reported a highly efficient one-pot approach to obtain dispersed water-compatible MIP microspheres by surface grafting hydrophilic polymers using reversible addition fragmentation chain transfer (RAFT) polymerization. The obtained MIP microspheres showed significant enhanced surface hydrophilicity and excellent molecular recognition ability in pure water.

Last, the potential risk for leakage of the residual template molecules during the adsorption process must be taken into account (Lin et al. 2012). Surface molecular imprinting (SMI) technique was developed to solve this problem by localizing the recognition sites on the surface of suitable substrate. However, SMI cannot completely avoid residual template leakage as there is always a small amount of templates well remained in the polymer matrix after the template-washing step. Recently, MIPs had been prepared using its structurally related analog as an alternative template molecule in order to eliminate the undesired leakage for the traditional MIPs (Yin et al. 2012). However, the selective of the dummy template is a significant problem because the interaction of template molecules with that of functional monomer, and the

conformation effects between target molecules and rebinding sites may take great influence on the properties of proper affinity and sufficient recovery.

Conclusions

MIPs, with high selectivity and strong affinity for target chemicals, have a particularly high potential for wastewater treatment applications. To bring the MIP development a step forward, MIP prioritization and further application prospect have been presented. As a kind of effective sorbents, MIPs have proven to be a very valuable technique for selective SPE and removal of a given analyte or a group of structurally analogous compounds. When employed as catalysts, MIPs display an important role in the degradation of pollutants. And, MIP-based fluorescence sensor provides an alternative for special recognition and determination of pollutants from real sample. In particular, MIP-based composite materials offer a wide range of potentialities in wastewater treatment. Incorporating with magnetic particles, nanoparticles, or quantum dots, MIPs can reserve their prominent selectivity and possibly induce new performance such as excellent charge separation–transportation capability, high adsorption capability. Little information is available on combining molecularly imprinted technology with biological technology; further studies may focus on finding potential biomass combine with MIPs. All these works suggest that the potential applications of MIPs for clean water are close to reality. However, there are still some challenges to face, including fundamental mechanism, the synthesis of water-compatible MIPs, and the potential leakage of residual template. Taking these things into consideration, we remain positive about the future potential of MIPs as selective adsorbents for wastewater treatment as well as a wide variety of other applications.

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References

- Advincula RC (2011) Engineering molecularly imprinted polymer (MIP) materials: developments and challenges for sensing and separation technologies. *Korean J Chem Eng* 28(6):1313–1321
- Ahmad A, Rafatullah M, Sulaiman O et al (2009) Removal of Cu (II) and Pb (II) ions from aqueous solutions by adsorption on sawdust of Meranti wood. *Desalination* 247(1):636–646
- Aksu Z (2005) Application of biosorption for the removal of organic pollutants: a review. *Process Biochem* 40(3):997–1026

- Andersson LI, Paprica A, Arvidsson T (1997) A highly selective solid phase extraction sorbent for pre-concentration of sameridine made by molecular imprinting. *Chromatographia* 46(1–2):57–62
- Ansell RJ, Mosbach K (1998) Magnetic molecularly imprinted polymer beads for drug radioligand binding assay. *Analyst* 123(7):1611–1616
- Arshady R, Mosbach K (1981) Synthesis of substrate-selective polymers by host-guest polymerization. *Makromol Chem* 182:687–692
- Auriol M, Filali-Meknassi Y, Tyagi RD et al (2006) Endocrine disrupting compounds removal from wastewater, a new challenge. *Process Biochem* 41(3):525–539
- Beltran A, Caro E, Marcé RM et al (2007) Synthesis and application of a carbamazepine-imprinted polymer for solid-phase extraction from urine and wastewater. *Anal Chim Acta* 597(1):6–11
- Bergmann NM, Peppas NA (2008) Molecularly imprinted polymers with specific recognition for macromolecules and proteins. *Prog Polym Sci* 33(3):271–288
- Bossi A, Bonini F, Turner APF et al (2007) Molecularly imprinted polymers for the recognition of proteins: the state of the art. *Biosens Bioelectron* 22(6):1131–1137
- Brüggemann O (2001) Catalytically active polymers obtained by molecular imprinting and their application in chemical reaction engineering. *Biomol Eng* 18(1):1–7
- Bui BTS, Haupt K (2010) Molecularly imprinted polymers: synthetic receptors in bioanalysis. *Anal Bioanal Chem* 398(6):2481–2492
- Byun HS, Youn YN, Yun YH et al (2010) Selective separation of aspirin using molecularly imprinted polymers. *Sep Purif Technol* 74(1):144–153
- Cacho C, Turiel E, Pérez-Conde C (2009) Molecularly imprinted polymers: an analytical tool for the determination of benzimidazole compounds in water samples. *Talanta* 78(3):1029–1035
- Chen W, Han DK, Ahn KD et al (2002) Molecularly imprinted polymers having amidine and imidazole functional groups as an enzyme-mimetic catalyst for ester hydrolysis. *Macromol Res* 10(2):122–126
- Chen YP, Wang DN, Yin YM et al (2012) Quantum dots capped with dummy molecularly imprinted film as luminescent sensor for the determination of tetrabromobisphenol A in water and soils. *J Agr Food Chem* 60(42):10472–10479
- Chen HY, Zhang YQ, Gao B et al (2013) Fast determination of sulfonamides and their acetylated metabolites from environmental water based on magnetic molecularly imprinted polymers. *Environ Sci Pollut R* 20(12):8567–8578
- Chen HC, Kong J, Yuan DY et al (2014) Synthesis of surface molecularly imprinted nanoparticles for recognition of lysozyme using a metal coordination monomer. *Biosens Bioelectron* 53:5–11
- Chong MN, Jin B, Chow CWK et al (2010) Recent developments in photocatalytic water treatment technology: a review. *Water Res* 44(10):2997–3027
- Cundy AB, Hopkinson L, Whitby RLD (2008) Use of iron-based technologies in contaminated land and groundwater remediation: a review. *Sci Total Environ* 400(1):42–51
- Dai CM, Geissen SU, Zhang YL et al (2011) Selective removal of diclofenac from contaminated water using molecularly imprinted polymer microspheres. *Environ Pollut* 159:1660–1666
- Dai CM, Zhang J, Zhang YL et al (2012) Selective removal of acidic pharmaceuticals from contaminated lake water using multi-templates molecularly imprinted polymer. *Chem Eng J* 211:302–309
- Dai CM, Zhang J, Zhang YL et al (2013a) Application of molecularly imprinted polymers to selective removal of clofibric acid from water. *PLoS one* 8(10):1–8
- Dai CM, Zhang J, Zhang YL et al (2013b) Removal of carbamazepine and clofibric acid from water using double templates–molecularly imprinted polymers. *Environ Sci Pollut R* 20(8):5492–5501
- Ferrer I, Lanza F, Tolokan A et al (2000) Selective trace enrichment of chlorotriazine pesticides from natural waters and sediment samples using terbuthylazine molecularly imprinted polymers. *Anal Chem* 72(16):3934–3941
- Foo KY, Hameed BH (2009) Utilization of biodiesel waste as a renewable resource for activated carbon: application to environmental problems. *Renew Sust Energ Rev* 13(9):2495–2504
- Foo KY, Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. *Chem Eng J* 156(1):2–10
- Foo KY, Hameed BH (2011) The environmental applications of activated carbon/zeolite composite materials. *Adv Colloid Interfac* 162(1):22–28
- Fuchs Y, Soppera O, Haupt K (2012) Photopolymerization and photostructuring of molecularly imprinted polymers for sensor applications—A review. *Anal Chim Acta* 717:7–20
- Gao D, Zhang Z, Wu M et al (2007) A surface functional monomer-directing strategy for highly dense imprinting of TNT at surface of silica nanoparticles. *J Am Chem Soc* 129(25):7859–7866
- Gao B, Wang J, An F et al (2008) Molecular imprinted material prepared by novel surface imprinting technique for selective adsorption of pirimicarb. *Polymer* 49(5):1230–1238
- Gao RX, Kong X, Su FH et al (2010) Synthesis and evaluation of molecularly imprinted core-shell carbon nanotubes for the determination of triclosan in environmental water samples. *J Chromatogr A* 1217(52):8095–8102
- Gao RX, Su XQ, He XW et al (2011) Preparation and characterisation of core-shell CNTs@MIPs nanocomposites and selective removal of estrone from water samples. *Talanta* 83(3):757–764
- Ge Y, Turner APF (2008) Too large to fit? Recent developments in macromolecular imprinting. *Trends Biotechnol* 26(4):218–224
- Ge SG, Lu JJ, Ge L et al (2011) Development of a novel deltamethrin sensor based on molecularly imprinted silica nanospheres embedded CdTe quantum dots. *Spectrochim Acta A* 79(5):1704–1709
- Gottschalk C, Libra JA, Saupe A (2009) Ozonation of water and waste water: A practical guide to understanding ozone and its applications. John Wiley & Sons, New York
- Guo HJ, Luo SL, Chen L et al (2010) Bioremediation of heavy metals by growing hyperaccumulator endophytic bacterium *Bacillus* sp. L14. *Bioresour Technol* 101(22):8599–8605
- Guo WL, Hu W, Pan J et al (2011) Selective adsorption and separation of BPA from aqueous solution using novel molecularly imprinted polymers based on kaolinite/Fe₃O₄ composites. *Chem Eng J* 171(2):603–611
- Haupt K, Mosbach K (2000) Molecularly imprinted polymers and their use in biomimetic sensors. *Chem Rev* 100(7):2495–2504
- He CY, Long YY, Pan JL et al (2007) Application of molecularly imprinted polymers to solid-phase extraction of analytes from real samples. *J Biochem Bioph Meth* 70(2):133–150
- He CY, Long YY, Pan JL et al (2008) A method for coating colloidal particles with molecularly imprinted silica films. *J Mater Chem* 18(24):2849–2854
- Hu X, Hu Y, Li G (2007) Development of novel molecularly imprinted solid-phase microextraction fiber and its application for the determination of triazines in complicated samples coupled with high-performance liquid chromatography. *J Chromatogr A* 1147:1–9
- Huang SH, Chen DH (2009) Rapid removal of heavy metal cations and anions from aqueous solutions by an amino-functionalized magnetic nano-adsorbent. *J Hazard Mater* 163(1):174–179
- Huang DL, Zeng GM, Jiang XY et al (2006) Bioremediation of Pb-contaminated soil by incubating with *Phanerochaete chrysosporium* and straw. *J Hazard Mater* 134(1):268–276
- Javanbakht M, Eynollahi Fard S, Mohammadi A et al (2008) Molecularly imprinted polymer based potentiometric sensor for the detection of hydroxyzine in tablets and biological fluids. *Anal Chim Acta* 612:65–74
- Ji YS, Yin JJ, Xu ZG et al (2009) Preparation of magnetic molecularly imprinted polymer for rapid determination of bisphenol A in environmental water and milk samples. *Anal Bioanal Chem* 395(4):1125–1133

- Jing T, Wang J, Liu M et al (2014) Highly effective removal of 2, 4-dinitrophenolic from surface water and wastewater samples using hydrophilic molecularly imprinted polymers. *Environ Sci Pollut Res* 21(2):1153–1162
- Kim Y, Jeon JB, Chang JY (2012) CdSe quantum dot-encapsulated molecularly imprinted mesoporous silica particles for fluorescent sensing of bisphenol A. *J Mater Chem* 22(45):24075–24080
- Kobyas M, Demirbas E, Senturk E et al (2005) Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. *Bioresour Technol* 96(13):1518–1521
- Kong X, Gao RX, He XW et al (2012) Synthesis and characterization of the core-shell magnetic molecularly imprinted polymers (Fe_3O_4 @MIPs) adsorbents for effective extraction and determination of sulfonamides in the poultry feed. *J Chromatogr A* 1245:8–16
- Krupadam RJ, Khan MS, Wate SR (2010) Removal of probable human carcinogenic polycyclic aromatic hydrocarbons from contaminated water using molecularly imprinted polymer. *Water Res* 44(3):681–688
- Lai EPC, Maleki ZD, Wu SY (2010) Characterization of molecularly imprinted and nonimprinted polymer submicron particles specifically tailored for removal of trace 17 β -estradiol in water treatment. *J Appl Polym Sci* 116(3):1499–1508
- Lavignac N, Allender CJ, Brain KR (2004) Current status of molecularly imprinted polymers as alternatives to antibodies in sorbent assays. *Anal Chim Acta* 510(2):139–145
- Lee Y, Escher BI, Von Gunten U (2008) Efficient removal of estrogenic activity during oxidative treatment of waters containing steroid estrogens. *Environ Sci Technol* 42(17):6333–6339
- Li Y, Li X, Li YQ et al (2009) Selective removal of 2, 4-dichlorophenol from contaminated water using non-covalent imprinted microspheres. *Environ Pollut* 157(6):1879–1885
- Li Y, Li X, Chu J et al (2010) Synthesis of core-shell magnetic molecularly imprinted polymer by the surface RAFT polymerization for the fast and selective removal of endocrine disrupting chemicals from aqueous solutions. *Environ Pollut* 158(6):2317–2323
- Li H, Xu WZ, Wang NW et al (2012) Synthesis of magnetic molecularly imprinted polymer particles for selective adsorption and separation of dibenzothiophene. *Microchim Acta* 179(1–2):123–130
- Lin ZK, Cheng WJ, Li YY et al (2012) A novel superparamagnetic surface molecularly imprinted nanoparticle adopting dummy template: an efficient solid-phase extraction adsorbent for bisphenol A. *Anal Chim Acta* 720:71–76
- Lin ZK, He QY, Wang LT et al (2013) Preparation of magnetic multifunctional molecularly imprinted polymer beads for determining environmental estrogens in water samples. *J Hazard Mater* 252:57–63
- Liu J, Wulff G (2008) Functional mimicry of carboxypeptidase A by a combination of transition state stabilization and a defined orientation of catalytic moieties in molecularly imprinted polymers. *J Am Chem Soc* 130(25):8044–8054
- Liu ZH, Huan SY, Jiang JH et al (2006) Molecularly imprinted TiO_2 thin film using stable ground-state complex as template as applied to selective electrochemical determination of mercury. *Talanta* 68(4):1120–1125
- Liu JX, Chen H, Lin Z et al (2010) Preparation of surface imprinting polymer capped Mn-doped ZnS quantum dots and their application for chemiluminescence detection of 4-nitrophenol in tap water. *Anal Chem* 82(17):7380–7386
- Liu HL, Liu DR, Fang GZ et al (2013) A novel dual-function molecularly imprinted polymer on CdTe/ZnS quantum dots for highly selective and sensitive determination of ractopamine. *Anal Chim Acta* 762:76–82
- Liu CB, Song ZL, Pan JM et al (2014) A simple and sensitive surface molecularly imprinted polymers based fluorescence sensor for detection of λ -Cyhalothrin. *Talanta* 125:14–23
- Lu SL, Cheng GX, Pang X (2006a) Protein-imprinted soft-wet gel composite microspheres with magnetic susceptibility. II. Characteristics. *J Appl Polym Sci* 99(5):2401–2407
- Lu SL, Cheng GX, Zhang HG et al (2006b) Preparation and characteristics of Tryptophan-imprinted Fe_3O_4 /P (TRIM) composite microspheres with magnetic susceptibility by inverse emulsion-suspension polymerization. *J Appl Polym Sci* 99(6):3241–3250
- Luo XB, Zhan YC, Tu XM et al (2011a) Novel molecularly imprinted polymer using 1-(α -methyl acrylate)-3-methylimidazolium bromide as functional monomer for simultaneous extraction and determination of water-soluble acid dyes in wastewater and soft drink by solid phase extraction and high performance liquid chromatography. *J Chromatogr A* 1218(8):1115–1121
- Luo XB, Zhan YC, Huang YN et al (2011b) Removal of water-soluble acid dyes from water environment using a novel magnetic molecularly imprinted polymer. *J Hazard Mater* 187(1):274–282
- Ma J, Yuan LH, Ding MJ et al (2011) The study of core-shell molecularly imprinted polymers of 17 β -estradiol on the surface of silica nanoparticles. *Biosens Bioelectron* 26(5):2791–2795
- Malik PK (2003) Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36. *Dyes Pigments* 56(3):239–249
- Malitesta C, Mazzotta E, Picca RA et al (2012) MIP sensors—the electrochemical approach. *Anal Bioanal Chem* 402(5):1827–1846
- Martín-Esteban A (2013) Molecularly-imprinted polymers as a versatile, highly selective tool in sample preparation. *Trac-Trends Anal Chem* 45:169–181
- Mayes AG, Mosbach K (1996) Molecularly imprinted polymer beads: suspension polymerization using a liquid perfluorocarbon as the dispersing phase. *Anal Chem* 68(21):3769–3774
- Mehdinia A, Baradaran Kayyal T, Jabbari A et al (2013) Magnetic molecularly imprinted nanoparticles based on grafting polymerization for selective detection of 4-nitrophenol in aqueous samples. *J Chromatogr A* 1283:82–88
- Meng Z, Chen W, Mulchandani A (2005) Removal of estrogenic pollutants from contaminated water using molecularly imprinted polymers. *Environ Sci Technol* 39(22):8958–8962
- Ng SM, Narayanaswamy R (2006) Fluorescence sensor using a molecularly imprinted polymer as a recognition receptor for the detection of aluminium ions in aqueous media. *Analy Bioanal Chem* 386(5):1235–1244
- Nicholls IA, Andersson HS, Golker K et al (2011) Rational design of biomimetic molecularly imprinted materials: theoretical and computational strategies for guiding nanoscale structured polymer development. *Anal Bioanal Chem* 400(6):1771–1786
- Oller I, Malato S, Sánchez-Pérez JA (2011) Combination of advanced oxidation processes and biological treatments for wastewater decontamination—a review. *Sci Total Environ* 409(20):4141–4166
- Onesios KM, Jim TY, Bouwer EJ (2009) Biodegradation and removal of pharmaceuticals and personal care products in treatment systems: a review. *Biodegradation* 20(4):441–466
- Ou JJ, Hu LH, Hu LG et al (2006) Determination of phenolic compounds in river water with on-line coupling bisphenol A imprinted monolithic precolumn with high performance liquid chromatography. *Talanta* 69(4):1001–1006
- Pan GQ, Zhang Y, Ma Y et al (2011a) Efficient one-pot synthesis of water-compatible molecularly imprinted polymer microspheres by facile RAFT precipitation polymerization. *Angew Chem Int Edit* 50(49):11731–11734
- Pan J, Xu LC, Dai JD et al (2011b) Magnetic molecularly imprinted polymers based on attapulgite/ Fe_3O_4 particles for the selective recognition of 2, 4-dichlorophenol. *Chem Eng J* 174(1):68–75
- Pan J, Yao H, Xu LC et al (2011c) Selective recognition of 2, 4, 6-trichlorophenol by molecularly imprinted polymers based on magnetic halloysite nanotubes composites. *J Phys Chem C* 115(13):5440–5449
- Pauling L (1940) A Theory of the structure and process of formation of antibodies*. *J Am Chem Soc* 62(10):2643–2657

- Pérez-Moral N, Mayes AG (2004) Comparative study of imprinted polymer particles prepared by different polymerisation methods. *Anal Chim Acta* 504(1):15–21
- Piletska EV, Guerreiro AR, Romero-Guerra M et al (2008) Design of molecular imprinted polymers compatible with aqueous environment. *Anal Chim Acta* 607(1):54–60
- Polyakov MV (1931) Adsorption properties and structure of silica gel. *Zhur Fiz Khim* 2:799–805
- Poma A, Turner APF, Piletsky SA (2010) Advances in the manufacture of MIP nanoparticles. *Trends Biotechnol* 28(12):629–637
- Rafatullah M, Sulaiman O, Hashim R et al (2010) Adsorption of methylene blue on low-cost adsorbents: a review. *J Hazard Mater* 177(1):70–80
- Resmini M (2012) Molecularly imprinted polymers as biomimetic catalysts. *Anal Bioanal Chem* 402(10):3021–3026
- Reungoat J, Macova M, Escher BI et al (2010) Removal of micropollutants and reduction of biological activity in a full scale reclamation plant using ozonation and activated carbon filtration. *Water Res* 44(2):625–637
- Sambe H, Hoshina K, Haginaka J (2007) Molecularly imprinted polymers for triazine herbicides prepared by multi-step swelling and polymerization method: their application to the determination of methylthiotriazine herbicides in river water. *J Chromatogr A* 1152(1):130–137
- Sánchez-Barragán I, Karim K, Costa-Fernández JM et al (2007) A molecularly imprinted polymer for carbaryl determination in water. *Sensor Actuat B-Chem* 123(2):798–804
- Say R, Ersöz A, Türk H et al (2004) Selective separation and preconcentration of cyanide by a column packed with cyanide-imprinted polymeric microbeads. *Sep Purif Technol* 40(1):9–14
- Sellergren B (2000) Molecularly imprinted polymers: man-made mimics of antibodies and their application in analytical chemistry. Elsevier, Amsterdam
- Sharabi D, Paz Y (2010) Preferential photodegradation of contaminants by molecular imprinting on titanium dioxide. *Appl Catal B-Environ* 95(1):169–178
- Shen XT, Zhu LH, Liu GX et al (2008) Enhanced photocatalytic degradation and selective removal of nitrophenols by using surface molecular imprinted titania. *Environ Sci Technol* 42(5):1687–1692
- Shen XT, Zhu LH, Wang N et al (2012) Molecular imprinting for removing highly toxic organic pollutants. *Chem Commun* 48(6):788–798
- Snyder SA, Wert EC, Rexing DJ et al (2006) Ozone oxidation of endocrine disruptors and pharmaceuticals in surface water and wastewater. *Ozone-Sci Eng* 28(6):445–460
- Snyder SA, Adham S, Redding AM et al (2007) Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Desalination* 202(1):156–181
- Strikovskiy A, Hradil J, Wulff G (2003) Catalytically active, molecularly imprinted polymers in bead form. *React Funct Polym* 54(1):49–61
- Sueyoshi Y, Fukushima C, Yoshikawa M (2010) Molecularly imprinted nanofiber membranes from cellulose acetate aimed for chiral separation. *J Membrane Sci* 357(1):90–97
- Sun H, Qiao F (2008) Recognition mechanism of water-compatible molecularly imprinted solid-phase extraction and determination of nine quinolones in urine by high performance liquid chromatography. *J Chromatogr A* 1212(1):1–9
- Sun WQ, Tan R, Zheng WG et al (2013) Molecularly imprinted polymer containing Fe (III) catalysts for specific substrate recognition. *Chin J Catal* 34(8):1589–1598
- Tamayo FG, Turiel E, Martín-Esteban A (2007) Molecularly imprinted polymers for solid-phase extraction and solid-phase microextraction: recent developments and future trends. *J Chromatogr A* 1152(1):32–40
- Tan F, Sun D, Gao JS et al (2013) Preparation of molecularly imprinted polymer nanoparticles for selective removal of fluoroquinolone antibiotics in aqueous solution. *J Hazard Mater* 244:750–757
- Tang HQ, Zhu LH, Yu C et al (2012) Selective photocatalysis mediated by magnetic molecularly imprinted polymers. *Sep Purif Technol* 95:165–171
- Tarley CRT, Kubota LT (2005) Molecularly-imprinted solid phase extraction of catechol from aqueous effluents for its selective determination by differential pulse voltammetry. *Anal Chim Acta* 548(1):11–19
- Ternes T, von Gunten U (2010) Editorial to special issue in water research: emerging contaminants in water. *Water Res* 44(2):351
- Tong AJ, Dong H, Li LD (2002) Molecular imprinting-based fluorescent chemosensor for histamine using zinc (II)-protoporphyrin as a functional monomer. *Anal Chim Acta* 466(1):31–37
- Turiel E, Martín-Esteban A (2004) Molecularly imprinted polymers: towards highly selective stationary phases in liquid chromatography and capillary electrophoresis. *Anal Bioanal Chem* 378(8):1876–1886
- Turiel E, Martín-Esteban A (2010) Molecularly imprinted polymers for sample preparation: a review. *Anal Chim Acta* 668(2):87–99
- Turkewitsch P, Wandelt B, Darling GD et al (1998) Fluorescent functional recognition sites through molecular imprinting. A polymer-based fluorescent chemosensor for aqueous cAMP. *Anal Chem* 70(10):2025–2030
- Van Tilborg GAF, Mulder WJM, Chin PTK et al (2006) Annexin A5-conjugated quantum dots with a paramagnetic lipidic coating for the multimodal detection of apoptotic cells. *Bioconjugate Chem* 17(4):865–868
- Vasapollo G, Sole RD, Mergola L et al (2011) Molecularly imprinted polymers: present and future prospective. *Int J Mol Sci* 12(9):5908–5945
- Vlatakis G, Andersson LI, Müller R et al (1993) Drug assay using antibody mimics made by molecular imprinting. *Nature* 361:645–647
- Wang HF, He Y, Ji TR et al (2009) Surface molecular imprinting on Mn-doped ZnS quantum dots for room-temperature phosphorescence optosensing of pentachlorophenol in water. *Anal Chem* 81(4):1615–1621
- Wang S, Li Y, Ding MJ et al (2011) Self-assembly molecularly imprinted polymers of 17 β -estradiol on the surface of magnetic nanoparticles for selective separation and detection of estrogenic hormones in feeds. *J Chromatogr B* 879(25):2595–2600
- Wang H, Yuan XZ, Wu Y et al (2013) Graphene-based materials: fabrication, characterization and application for the decontamination of wastewater and wastegas and hydrogen storage/generation. *Adv Colloid Interfac* 195:19–40
- Watabe Y, Kubo T, Nishikawa T et al (2006) Fully automated liquid chromatography–mass spectrometry determination of 17 β -estradiol in river water. *J Chromatogr A* 1120(1):252–259
- Wei FD, Liu XP, Zhai MJ et al (2013) Molecularly Imprinted Nanosilica Solid-Phase Extraction for Bisphenol A in Fish Samples. *Food Anal Method* 6(2):415–420
- Whitcombe MJ, Vulfson EN (2001) Imprinted polymers. *Adv Mater* 13(7):467–478
- Wulff G, Sarhan A (1972) Use of polymers with enzyme-analogous structures for resolution of racemates. *Angew Chem Int Ed Engl* 11:341
- Xia X, Lai EPC, Örmeci B (2013) Duo-molecularly imprinted polymer-coated magnetic particles for class-selective removal of endocrine-disrupting compounds from aqueous environment. *Environ Sci Pollut Res* 20(5):3331–3339
- Xu X, Zhu L, Chen L (2004) Separation and screening of compounds of biological origin using molecularly imprinted polymers. *J Chromatogr B* 804(1):61–69
- Xu ZX, Chen S, Huang W et al (2009) Study on an on-line molecularly imprinted solid-phase extraction coupled to high-performance liquid chromatography for separation and determination of trace estrone in environment. *Anal Bioanal Chem* 393(4):1273–1279
- Xu P, Zeng GM, Huang DL et al (2012) Use of iron oxide nanomaterials in wastewater treatment: a review. *Sci Total Environ* 424:1–10

- Xu GL, Yang LL, Zhong M et al (2013a) Selective recognition and electrochemical detection of p-nitrophenol based on a macroporous imprinted polymer containing gold nanoparticles. *Microchim Acta* 180:1461–1469
- Xu SF, Lu HZ, Li JH et al (2013b) Dummy molecularly imprinted polymers-capped CdTe quantum dots for the fluorescent sensing of 2, 4, 6-Trinitrotoluene. *ACS Appl Mater Inter* 5(16):8146–8154
- Xue JQ, Li DW, Qu LL et al (2013) Surface-imprinted core-shell Au nanoparticles for selective detection of bisphenol A based on surface-enhanced Raman scattering. *Anal Chim Acta* 777:57–62
- Yan SL, Gao ZX, Fang YJ et al (2007) Characterization and quality assessment of binding properties of malachite green molecularly imprinted polymers prepared by precipitation polymerization in acetonitrile. *Dyes Pigments* 74(3):572–577
- Yang WJ, Jiao FP, Zhou L et al (2013) Molecularly imprinted polymers coated on multi-walled carbon nanotubes through a simple indirect method for the determination of 2, 4-dichlorophenoxyacetic acid in environmental water. *Appl Surf Sci* 284:692–699
- Yin J, Meng Z, Du MJ et al (2010) Pseudo-template molecularly imprinted polymer for selective screening of trace β -lactam antibiotics in river and tap water. *J Chromatogr A* 1217(33):5420–5426
- Yin YM, Chen YP, Wang XF et al (2012) Dummy molecularly imprinted polymers on silica particles for selective solid-phase extraction of tetrabromobisphenol A from water samples. *J Chromatogr A* 1220:7–13
- Yoshimatsu K, Reimhult K, Krozer A et al (2007) Uniform molecularly imprinted microspheres and nanoparticles prepared by precipitation polymerization: the control of particle size suitable for different analytical applications. *Anal Chim Acta* 584(1):112–121
- Yu CM, Gou LL, Zhou XH et al (2011) Chitosan-Fe₃O₄ nanocomposite based electrochemical sensors for the determination of bisphenol A. *Electrochim Acta* 56(25):9056–9063
- Zeng GM, Huang DL, Huang GH et al (2007) Composting of lead-contaminated solid waste with inocula of white-rot fungus. *Bioresour Technol* 98(2):320–326
- Zhan J, Fang GZ, Yan Z et al (2013) Preparation of a semicovalent, molecularly surface imprinted polymer for the rapid determination of trace acid orange II in food and environmental samples. *Anal Bioanal Chem* 405(19):6353–6363
- Zhang W, He XW, Chen Y et al (2012) Molecularly imprinted polymer anchored on the surface of denatured bovine serum albumin modified CdTe quantum dots as fluorescent artificial receptor for recognition of target protein. *Biosens Bioelectron* 31(1):84–89
- Zhang WL, Li Y, Wang Q et al (2013) Performance evaluation and application of surface-molecular-imprinted polymer-modified TiO₂ nanotubes for the removal of estrogenic chemicals from secondary effluents. *Environ Sci Pollut R* 20(3):1431–1440
- Zhao WH, Sheng N, Zhu R et al (2010) Preparation of dummy template imprinted polymers at surface of silica microparticles for the selective extraction of trace bisphenol A from water samples. *J Hazard Mater* 179(1–3):223–229
- Zhao YY, Ma YX, Li H et al (2011) Composite QDs@ MIP nanospheres for specific recognition and direct fluorescent quantification of pesticides in aqueous media. *Anal Chem* 84(1):386–395
- Zheng C, Huang YP, Liu ZS (2013) Synthesis and theoretical study of molecularly imprinted monoliths for HPLC. *Anal Bioanal Chem* 405(7):2147–2161
- Zhongbo Z, Hu J (2008) Selective removal of estrogenic compounds by molecular imprinted polymer (MIP). *Water Res* 42(15):4101–4108
- Zhou Y, Qu ZB, Zeng YB et al (2014) A novel composite of graphene quantum dots and molecularly imprinted polymer for fluorescent detection of parantitrophenol. *Biosens Bioelectron* 52:317–323
- Zhu LL, Cao YH, Cao GQ (2013) Preparation and application of core-shell magnetic imprinted nanoparticles for bisphenol A. *Chin J Anal Chem* 41(11):1724–1728