

## Review Article

# Molecular Imprinting for High-Added Value Metals: An Overview of Recent Environmental Applications

**George Z. Kyzas and Dimitrios N. Bikiaris**

*Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki,  
541 24 Thessaloniki, Greece*

Correspondence should be addressed to George Z. Kyzas; [georgekyzas@gmail.com](mailto:georgekyzas@gmail.com)

Received 26 January 2014; Accepted 11 February 2014; Published 7 April 2014

Academic Editor: Margaritis Kostoglou

Copyright © 2014 G. Z. Kyzas and D. N. Bikiaris. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

One of the most hot topics of recent research is the reuse of some compounds existing as pollutants in environment. These compounds (molecules, ions, complexes, etc.) are of high-added value and it will be ideal to selectively bind them with any environmental application and reuse them in their initial or modified form. The latter can be achieved using molecular imprinting. In the present review article, an overview of the recent attempts for the selective binding of some precious metals (i.e., gold, silver, and platinum) of high-added value is done using molecular imprinted polymers (MIPs) as materials. The simplicity of their use, their relatively low cost, and the broad range of possible guest molecules (small organic molecules, ions, metals, and also biological macromolecules) have since led to the important development of molecular imprinting.

## 1. Introduction

One of the most hot topics of recent research is the reuse of some compounds existing as pollutants in environment. These compounds (molecules, ions, complexes, etc.) are of high-added value and it will be ideal to selectively bind them with any environmental application and reuse them in their initial or modified form. The latter can be achieved using molecular recognition. 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 and bind with each other using noncovalent forces, including hydrogen bonds, electrostatic interactions, hydrophobic interactions, and weak metal coordination [1]. Therefore, a specific technology has been bloomed and redesigned in the last 30 years, which is called molecular imprinting (MI). The whole process is based on adsorption technology, which is already one of the most successful techniques for pollutants removal [2–8].

MI is not a recent science. The earliest reports of imprinting go back to the early 1930s when a Soviet chemist Polyakov [9] 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. In 1955 a senior student of Linus Pauling, Dickey, observed that after removal of the “patterning” dye the silica would rebind with the same dye in preference to the others [10]. However, in 1972 a step change in molecular imprinting occurred when the group of Guenter Wulff reported that they had successfully prepared a molecularly imprinting organic polymer (MIP) [11]. 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 [12], ketal/actal [13], and Schiff’s base formation [14] to prepare template monomers. Subsequently, throughout the 1970s and 1980s, Wulff’s group published extensively using this approach.

The second major breakthrough in organic polymer imprinting occurred in 1981 when Arshady and Mosbach

reported that they had prepared an organic MIP using non-covalent interactions only [15]. This approach was termed the “noncovalent approach” as opposed to the covalent approach favoured by Wulff, and it was this approach, with its simple, seemingly trivial methodology, that triggered the explosion in molecular imprinting that occurred during the 1990s. Noncovalent 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 noncovalent 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 et al. reported an intermediate approach that combines the advantages of both approaches [16]. This approach relies on covalent interaction during the polymerization stage, but noncovalent interactions during rebinding. Importantly, in order to improve subsequent noncovalent binding geometry, Whitcombe’s approach incorporated a sacrificial spacer group that was designed to be lost during template removal. The noncovalent 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 [17]. 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, and also biological macromolecules) have since led to the important development of this technique, as illustrated by the increasing numbers of publications over recent years (Figure 1).

It is a great of interest to prepare/design materials, which only selectively remove carcinogenic pollutants from wastewaters, as ions, phenols, and drugs/pharmaceuticals. Nowadays, MIPs are highly cross-linked polymeric phases with predetermined selectivity for a single molecule or a group of structurally related molecules (template), employed in separation processes of environmental pollutants (chromatography, solid-phase extraction, membrane separations, and adsorption), artificial antibodies, and sensors recognition elements [14].

This review aims to gather and report (i) recent synthesis routes of MIPs and (ii) their environmental applications for “hot pollutants” of high-added value metals discharged in environmental ways. The novelty of this work is clear given the lack of review articles or overviews regarding the use of MIPs for high-added value metals. Scopus, which is one of the largest abstract and citation database of peer-reviewed works, gives 136 results after searching with terms as “Molecularly Imprinted.” However, none of them are special for metals (or precious metals).

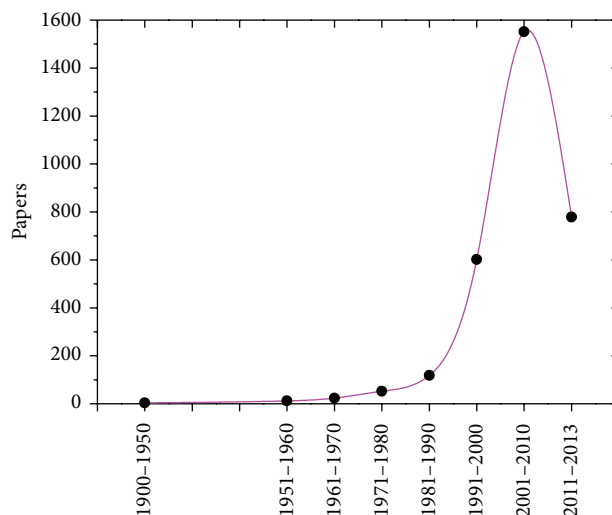


FIGURE 1: Works published for “molecular imprinted polymers” term (data after search in Scopus).

## 2. Design and Synthesis 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 reversibly covalent or noncovalent (hydrogen, ionic, van der Waals,  $\pi$ - $\pi$ , 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 reinsertion 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) noncovalent interactions, and (iii) double approach: covalent plus noncovalent.

The second step is the polymerisation step of the monomers around the complex formed in the first step [18]. 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 (a,a'-azobutyronitrile as initiator, denoted as AIBN), 45°C (azobis valeronitrile as initiator, denoted as ABDV) 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 [19].

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 noncovalent 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  $\mu$ moles 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 optimized to obtain yields of over 99%. 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 the literature for the preparation of MIPs, presenting their main differentiation in the phase. The main organic solvents used are dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), acetonitrile, toluene, and chloroform, while deionized water is also used as solvent [20]. Moreover, it is notable 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 divinylbenzene (DVB), ethylene glycol dimethacrylate (EGDMA), ethylene bis acrylamide (EBA), and trimethyl propane trimethacrylate (TRIM). The groups of Wulff et al. [21] and Sibrian-Vazquez and Spivak [22] have systematically studied the effect of cross-linkers on the recognition properties of MIPs.

Another important point is that the synthesis is related to the template used. For example, the synthesis of MIP and the binding forces between template and polymeric matrix can be strongly influenced by the valence of the template. Therefore, other reagents are selected in order to form a polymeric matrix for monovalent metal as templates and other for others.

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 are spectroscopy (NMR, FTIR), swelling tests, and BET analysis [17, 23].

In summary, a very characteristic scheme/example was found in the literature describing the synthesis and selective binding of dye molecules (as templates) with two types of MIPs either for basic (Figure 2(a)) or reactive dyes

(Figure 2(b)) [24]. Essentially two strategies for molecular imprinting have been established based on whether the template is associated with interactive monomers using covalent bonds or noncovalent interactions. Of the two strategies, the noncovalent approach has been used more extensively for three reasons: (i) noncovalent methodology is easier because it does not require synthetic steps toward the prepolymer complex and 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 functionalities can be introduced into the MIP binding site using noncovalent methods.

Prior to its use in experiments, an 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. Chromatographic evaluation allows measurement of capacity factors ( $k'$ ) and imprinting factors (IF) of MIPs. 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 (nonimprinted polymer which is synthesized just the same as MIP but without the target compound). 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 [25], 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 [25].

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 is calculated [26]. Some of these experiments are based on radioligand binding, which is a very highly sensitive method to study the population of binding sites with the strongest binding characteristics [13]. 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.

### 3. Selective Binding of High-Added Value Compounds

Numerous studies have been reported regarding the imprinting of ions and the use as adsorbents for the selective capture/binding from environmental media. Many ions/metals have been selectively bound from MIPs presenting impressively high selectivity coefficients.

For example, Tsukagoshi et al. [27] 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

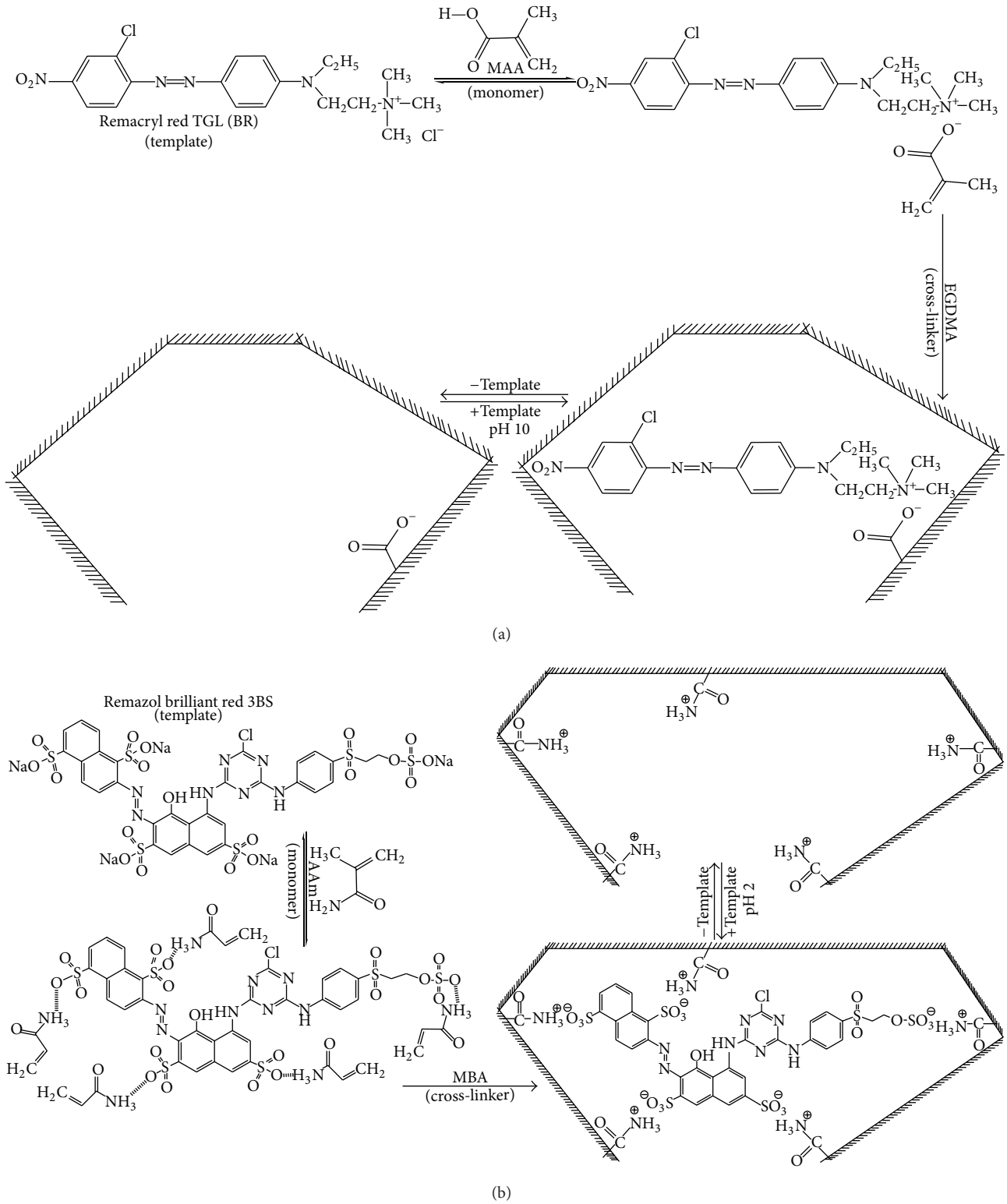


FIGURE 2: Schematic representation of the imprinting process for (a) basic and (b) reactive dye.

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. Furthermore, in another work [28], monomer-type functional surfactants (2-(p-vinyl benzylamino)-alkanoic acid and N,N-dialkyl derivatives) have been used as both ligand and emulsifier for the preparation of surface-template resins. The surfactants were adsorbed at the toluene-water interface and emulsified DVB-styrene in a  $\text{Cu}^{2+}$  or  $\text{Zn}^{2+}$  solution. Emulsion polymerization using a  $\text{K}_2\text{S}_2\text{O}_8$  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. Another brief example was given by Chen and coworkers [29] who 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  $\text{Zn}^{2+}$  complexes with the cross-linking agent DVB (80%) and the use of AIBN as initiator provided highly cross-linked macroporous polymers. However, attempts to prepare a Cu IIP or a blank polymer were unsuccessful. The overall order of metal-ion selectivity for  $\text{Zn}^{2+}$  as the imprint ion MIPs is  $\text{Mn}^{2+} < \text{Ni}^{2+} < \text{Zn}^{2+} < \text{Co}^{2+} \ll \text{Cu}^{2+}$ , which somewhat, but not exactly, follows the Irving-Williams order of stability. Chen et al. [29] have postulated that  $\text{Zn}^{2+}$  imprinting (the ionic radius of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  being comparable) accounts for the selectivity for the  $\text{Cu}^{2+}$  ion over the  $\text{Fe}^{3+}$  ion because usually the  $\text{Fe}^{3+}$  ion can readily compete for any polymer-pendant ligand site because of its favorable charge-to-radius ratio.

$\text{Ca}^{2+}$ - and  $\text{Mg}^{2+}$ -ion-selective sorbents were prepared by ion imprinting using N,N'-dimethyl-(N,N'-bis-4-vinyl phenyl)-3-oxapentane diamide; then they were 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  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions were found to bind  $\text{Ca}^{2+}$  ions with 6 and 1.7 times lower  $K_{\text{diss}}$  values (constant of dissociation), respectively, when compared with reference polymers prepared in the absence of metal ions. In addition, the number of binding sites for  $\text{Ca}^{2+}$  ions, determined for the respective polymer preparation, fitted well with theoretical values calculated from the stoichiometry of the complexation of the ionophore by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, respectively.

The range of metal ions imprinted in organic polymers now includes uranium (as  $\text{UO}_2^{2+}$ ) [30], erbium [31], dysprosium [32], gadolinium [33], cadmium [34], and lead [35], among others.

However, the most interesting is a new type of works regarding precious metals as gold (Au), silver (Ag), and platinum (Pt), which are characterized as being of high-added value. The above metals have long been valued as precious metals, used in currency coins, making ornaments, jewelry, high-value tableware and utensils (hence the term silverware), and as an investment in the forms of coins and bullion. They are used industrially in electrical contacts and conductors, in mirrors, and in catalysis of chemical

reactions. Their compounds are used in photographic film and other metal compounds are used as disinfectants and microbiocides (oligodynamic effect). While many medical antimicrobial uses of the aforementioned precious metals have been supplanted by antibiotics, further research into clinical potential continues.

Ahamed et al. [36] synthesized a novel chelating ion-imprinted resin using chitosan as a scaffold material; N-ethylenediamine (1-imidazolyl ethyl)-type chitosan has been prepared and applied to the selective extraction of gold(III) chlorides from complex aqueous solutions. Batch adsorption experiments were carried out with various parameters, such as contact time, pH, initial Au(III) concentration, and temperature. The kinetic studies revealed that the adsorption process could be described by pseudo-second-order kinetic model, while the adsorption data correlated well with the Langmuir and Temkin models. The maximum adsorption capacities calculated from the Langmuir equation are 810.67 and 649.35 mg/g at pH 3 and 6, respectively. The selectivity study revealed that the ion-imprinted polymer was highly selective to Au(III) compared to Pb(II), Ni(II), Cu(II), Mn(II), and Fe(III), even at the optimum binding pH for the other metal ions (pH 5-6). The adsorbent was successfully regenerated with a 0.7 M thiourea-2 M HCl solution.

Another research team [37] developed an ion-imprinted polymer for selective extraction and determination of gold ions. To increase the adsorbent efficiency, this polymer was coated on a novel nanoporous carbon-based material, carbohydrate-derived Max-Planck Gesellschaft 1, which is also the first example of grafting imprinted polymer on nanoporous-carbon material. These particles were applied successfully for preconcentration of ultratrace amount of gold ions, following determination by flame atomic absorption spectrometry. Some effective factors on the efficiency of gold ions extraction, such as concentration and volume of eluant, sample and eluant flow rates, and also effect of interfering ions especially palladium and platinum ions, were investigated. The technique was also used to determine the concentration of gold ions in mine stone samples with satisfactory results. The accuracy of this method was investigated by determination of gold ions concentrations in several reference materials with certified gold content.

The same research team but in another work [38] developed a gold ion-imprinted polymer (GIP) by incorporating a dipyriddy ligand into an ethylene glycol dimethacrylate matrix which was then coated onto porous silica particles. The material was used for the selective extraction of ultratrace quantities of gold ion from mine stones; this was followed by its quantitation by FAAS. Similarly as above, the effects of concentration and volume of eluant, pH of the solution, flow rates of sample and eluant, and effect of potentially interfering ions, especially palladium and platinum, were investigated. In order to show the high selectivity and efficiency of the new sorbent, the results were compared to those obtained with more simple sorbents possessing the same functional groups. The accuracy of the method was demonstrated by the accurate determination of gold ions in a certified reference material. To the best of our knowledge, there is no report so

far on an imprint for gold ions that has such a selectivity over Pd(II) and Pt(II) ions.

Furthermore, another gold-imprinted polymer (IIP), based on dipyrindyl amine-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs), was synthesized as a novel magnetic adsorbent for rapid extraction, preconcentration, and determination of trace amounts of gold ions [39]. This was characterized by FTIR, SEM, elemental analysis (CHN), and TGA/DSC. The optimum conditions, including pH of sample, eluant type and concentration and also the least amount of eluant necessary for desorption of gold ions, and the time of adsorption, were obtained. The effect of various cationic interferences on the adsorption of gold, specifically Pt(II) and Pd(II) ions, was evaluated. The maximum capacity of the IIP modified magnetic nanoparticles was found to be greater than 76 mg/g. Furthermore, the accuracy of this method was confirmed using various standard materials. This method was also applied successfully for preconcentration and determination of gold ions in some real samples.

Another precious metal is silver and has been selectively bound from imprinted polymers. Using blends of chitosan and polyvinyl alcohol as film-forming materials, the metal ion-imprinted membrane was prepared with silver ions as template [40]. The DSC curve shows that the membrane does not exhibit the heat resistance very well but the favorable compatibility. FTIR analysis implies that the coordinating atoms may be N atom of amino group in chitosan and O atom of -OH in polyvinyl alcohol. The results of the experiment of competitive adsorption indicate that silver-MIP has the ability of specificity and recognition to Ag(I). The large adsorption capacity for Ag(I) indicates that silver-MIP can be used in silver enrichment and separation from waste solutions as an effective material.

Another study reports the preparation of chitosan hydrogels and imprinting by silver with different mass ratios [41]. Compared with the native chitosan hydrogel sample, the optimally imprinted sample (Agim75) presents a significantly enhanced Ag I adsorption capacity as well as a high selectivity. This is attributed to the specific cavities formed by the template Ag(I) ions in the polymer matrix. The effects of the adsorption conditions and desorption process were also studied.

A more detailed study investigates the synthesis of ion-imprinted polymers (IIPs) for selective extraction of Ag(I) ions from aqueous solution by a precipitation polymerization method using two functional monomers, 4-vinyl pyridine (4-VP) and 1-vinyl imidazole (1-VID), and N,N-ethylene bisacrylamide (EBAm) as the cross-linker [42]. Batch adsorption experiments were carried out as a function of Ag(I) imprinted polymer amount, agitation time, pH, and initial Ag(I) concentration. The kinetic studies indicated that pseudo-second-order kinetic model best describes the adsorption behavior, while the adsorption data correlated well with the Langmuir isotherm. Furthermore the selectivity studies revealed that the ion-imprinted polymers had a higher absorption capacity and a higher selectivity, for the Ag(I) ions, than the control polymers.

The selective binding of platinum was also studied using MIPs in some recent works. A new Pt-imprinted polymer

was synthesized by bulk polymerization by using platinum-iodide-vinyl pyridinium ion ternary ion association complex as a template with 2-hydroxy ethyl methacrylate (functional monomer) and ethylene glycol dimethacrylate (cross-linking monomer) in the presence of 2,2'-azo-bis-isobutyronitrile as initiator [43]. The synthesis was carried out thermally at 60°C in methanol medium and the resultant polymer material was dried and filtered to get unleached polymer particles. The imprinting anionic species were removed by stirring the above particles for 18 h with 6 M HCl to obtain leached polymer particles. These leached polymer particles will now selectively rebind with [PtI<sub>6</sub>]<sup>2-</sup> species. NIPs were similarly prepared without the template. Control, unleached, and leached polymer particles were characterized by XRD, UV-Vis spectrophotometric, and SEM studies. Various parameters that influence the recovery of platinum from dilute aqueous solutions were systematically studied and the results obtained are described in this paper. In all these studies the imprinting effect was noticed. Furthermore, the percent recoveries obtained with leached and control polymer particles for platinum and other noble metals and base metals which are likely to coexist with platinum in its minerals were also studied. These studies indicate the possibility of selective recovery of platinum from its minerals.

Another ion-imprinted polymer (IIP) was obtained by copolymerization of methacrylic acid (as a functional monomer) and ethylene glycol dimethacrylate (as a cross-linking agent) in the presence of various chelating agents for Pt(II) ion and using 2,2'-azo-bis-isobutyronitrile as the initiator [44]. Specifically, acetaldehyde thiosemicarbazone (AcTSn) and benzaldehyde thiosemicarbazone (BnTSn) were used as chelators. The IIPs were applied as sorbents for solid-phase extraction of Pt(II) and Pt(IV) ions from aqueous solutions. The effects of acidity and flow rate of the sample, of elution conditions, and of potentially interfering ions were investigated. The imprinting effect of analyte is clearly demonstrated by the fact that only the IIP is capable of quantitative retention of Pt(II) and Pt(IV) ions. The method works best in the pH range from 0.5 to 1 and from 3.5 to 9.5. The ions can be recovered with an acidic solution of thiourea. The Pt-AcTSn polymer displays better sorption properties for the separation of analytes. The selectivity coefficients of the Pt-AcTSn and control polymers for Pt(IV) in the presence of Pd(II), Rh(III), Ru(III), Al(III), and Cu(II) were calculated, and the sorbent capacity for Pt(IV) was found to be 4.56 mg/g. The method was successfully applied to the determination of Pt(IV) by electrothermal atomic absorption spectrometry in tap water, tunnel dust, and anode slime samples.

In summary, the rebinding capacity of Ag, Au, Pt, - MIPs is ranged from a very small number of  $\mu\text{g/g}$  to even 85 mg/g [36, 41–44]. The latter was related from the synthesis and polymerization conditions.

#### 4. Future Aspects

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. So, except for the other target molecules (dyes, ions, phenols, etc.), the deposit of some high-added value compounds as Au, Ag, and Pt has been studied in order to make their binding via molecular imprinting successful. The capability of binding in high selectivity percentages is the key for MIPs to be used successfully in many crucial environmental targets. Although any can doubt about the economic feasibility of MIPs use, the recovery and reuse in the case of precious metals make them very attractive for future industrial applications.

## 5. Conclusions

Molecular imprinting witnessed rapid development and can be used as technique for high-added value compounds. Given the value of some precious metals as gold, silver, and platinum, MIPs have been already successfully tested as materials for their selective binding exporting impressively high selectivity results. The capacity of these materials is not large, but MIPs use is focused on selectivity and not adsorption capacity. It is a fact that the major advantage of MIPs is not their adsorption/binding capacity but their selectivity. As it is widely known, the criteria for the selection of each material used are the combination and coevaluation of (i) cost; (ii) reuse; (iii) adsorption capacity; and (iv) selectivity. However, in the present case, where the targets are high-added value metals (Ag, Au, and Pt), a more complex selection should be done given the selective ability of MIPs to rebind the targets. Therefore, the adsorption capacity is not the principal criterion, but the selectivity.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

## Acknowledgments

The support for this study was received from the State Scholarships Foundation (IKY) of Greek Ministry of Education and Religious Affairs (in the framework of the Hellenic Republic- Siemens Settlement Agreement) through the research program "IKY Fellowships of Excellence for Postgraduate Studies in Greece-Siemens Program" under the title "Advanced Molecularly Imprinted Polymers (MIPs) as Materials for the Selective Binding and Recovery of Various High-Added Value Environmental Targets with Application to Industrial-Scale Adsorption Columns," which is highly appreciated.

## References

- [1] B. Chen, S. Piletsky, and A. P. F. Turner, "Molecular recognition: design of 'keys,'" *Combinatorial Chemistry and High Throughput Screening*, vol. 5, no. 6, pp. 409–427, 2002.
- [2] R. Srinivasan, "Advances in application of natural clay and its composites in removal of biological, organic, and inorganic contaminants from drinking water," *Advances in Materials Science and Engineering*, vol. 2011, Article ID 872531, 17 pages, 2011.
- [3] H. Sasaki, Y. Kobashi, T. Nagai, and M. Maeda, "Application of electron beam melting to the removal of phosphorus from silicon: toward production of solar-grade silicon by metallurgical processes," *Advances in Materials Science and Engineering*, vol. 2013, Article ID 857196, 8 pages, 2013.
- [4] A. Radenović, J. Malina, and T. Sofličić, "Characterization of ladle furnace slag from carbon steel production as a potential adsorbent," *Advances in Materials Science and Engineering*, vol. 2013, Article ID 198240, 6 pages, 2013.
- [5] S. M. Alahmadi, S. Mohamad, and M. Jamil Maah, "Preparation of organic-inorganic hybrid materials based on MCM-41 and its applications," *Advances in Materials Science and Engineering*, vol. 2013, Article ID 634863, 8 pages, 2013.
- [6] A. G. Balogh, K. Baba, D. D. Cohen, R. G. Elliman, W. Ensinger, and J. Gyulai, "Modification, synthesis, and analysis of advanced materials using ion beam techniques," *Advances in Materials Science and Engineering*, vol. 2012, Article ID 431297, 2 pages, 2012.
- [7] G. Jiang, T. Chen, and Q. Yang, "Photocatalytic materials," *Advances in Materials Science and Engineering*, vol. 2012, Article ID 186948, 2 pages, 2012.
- [8] Y. Mobarak, M. Bassyouni, and M. Almutawa, "Materials selection, synthesis, and dielectrical properties of PVC nanocomposites," *Advances in Materials Science and Engineering*, vol. 2013, Article ID 149672, 6 pages, 2013.
- [9] M. V. Polyakov, "Adsorption properties and structure of silica gel," *The Journal of Physical Chemistry*, vol. 2, pp. 799–805, 1931.
- [10] F. H. Dickey, "Specific adsorption," *The Journal of Physical Chemistry*, vol. 59, no. 8, pp. 695–707, 1955.
- [11] G. Wulff and A. Sarhan, "Use of polymers with enzyme-analogous structures for the resolution of racemates," *Angewandte Chemie—International Edition in English*, vol. 11, pp. 341–344, 1972.
- [12] B. Sellergren and L. Andersson, "Molecular recognition in macroporous polymers prepared by a substrate analogue imprinting strategy," *Journal of Organic Chemistry*, vol. 55, no. 10, pp. 3381–3383, 1990.
- [13] K. J. Shea and D. Y. Sasaki, "An analysis of small-molecule binding to functionalized synthetic polymers by  $^{13}\text{C}$  CP/MAS NMR and FT-IR spectroscopy," *Journal of the American Chemical Society*, vol. 113, no. 11, pp. 4109–4120, 1991.
- [14] G. Wulff, "Enzyme-like catalysis by molecularly imprinted polymers," *Chemical Reviews*, vol. 102, no. 1, pp. 1–27, 2002.
- [15] R. Arshady and K. Mosbach, "Synthesis of substrate-selective polymers by host-guest polymerization," *Macromolecular Chemistry*, vol. 182, no. 2, pp. 687–692, 1981.
- [16] M. J. Whitcombe, M. E. Rodriguez, P. Villar, and E. N. Vulfson, "A new method for the introduction of recognition site functionality into polymers prepared by molecular imprinting: synthesis and characterization of polymeric receptors for cholesterol," *Journal of the American Chemical Society*, vol. 117, no. 27, pp. 7105–7111, 1995.

- [17] B. Sellergren, "Imprinted dispersion polymers: a new class of easily accessible affinity stationary phases," *Journal of Chromatography A*, vol. 673, no. 1, pp. 133–141, 1994.
- [18] S. A. Piletsky, E. V. Piletska, K. Karim, K. W. Freebairn, C. H. Legge, and A. P. F. Turner, "Polymer cookery: influence of polymerization conditions on the performance of molecularly imprinted polymers," *Macromolecules*, vol. 35, no. 19, pp. 7499–7504, 2002.
- [19] D. J. O'Shannessy, B. Ekberg, and K. Mosbach, "Molecular imprinting of amino acid derivatives at low temperature (0°C) using photolytic homolysis of azobisnitriles," *Analytical Biochemistry*, vol. 177, no. 1, pp. 144–149, 1989.
- [20] D. Spivak, M. A. Gilmore, and K. J. Shea, "Evaluation of binding and origins of specificity of 9-ethyladenine imprinted polymers," *Journal of the American Chemical Society*, vol. 119, no. 19, pp. 4388–4393, 1997.
- [21] G. Wulff, B. Heide, and G. Helfmeier, "Enzyme-analogue built polymers, 24 On the distance accuracy of functional groups in polymers and silicas introduced by a template approach," *Reactive Polymers, Ion Exchangers, Sorbents*, vol. 6, no. 2-3, pp. 299–310, 1987.
- [22] M. Sibrian-Vazquez and D. A. Spivak, "Characterization of molecularly imprinted polymers employing crosslinkers with nonsymmetric polymerizable groups," *Journal of Polymer Science A: Polymer Chemistry*, vol. 42, no. 15, pp. 3668–3675, 2004.
- [23] B. Sellergren, "Direct drug determination by selective sample enrichment on an imprinted polymer," *Analytical Chemistry*, vol. 66, no. 9, pp. 1578–1582, 1994.
- [24] G. Z. Kyzas, D. N. Bikiaris, and N. K. Lazaridis, "Selective separation of basic and reactive dyes by molecularly imprinted polymers (MIPs)," *Chemical Engineering Journal*, vol. 149, no. 1–3, pp. 263–272, 2009.
- [25] E. Caro, R. M. Marcé, P. A. G. Cormack, D. C. Sherrington, and F. Borrull, "On-line solid-phase extraction with molecularly imprinted polymers to selectively extract substituted 4-chlorophenols and 4-nitrophenol from water," *Journal of Chromatography A*, vol. 995, no. 1-2, pp. 233–238, 2003.
- [26] O. Brüggemann, A. Visnjeviski, R. Burch, and P. Patel, "Selective extraction of antioxidants with molecularly imprinted polymers," *Analytica Chimica Acta*, vol. 504, no. 1, pp. 81–88, 2004.
- [27] K. Tsukagoshi, K. Y. Yu, M. Maeda, and M. Takagi, "Metal ion-selective adsorbent prepared by surface-imprinting polymerization," *Bulletin of the Chemical Society of Japan*, vol. 66, pp. 114–120, 1993.
- [28] Y. Koide, H. Shosenji, M. Maeda, and M. Takagi, "Selective adsorption of metal ions to surface-templated resins prepared by emulsion polymerization using a functional surfactant," *ACS Symposium Series*, vol. 703, pp. 264–277, 1998.
- [29] H. Chen, M. M. Olmstead, R. L. Albright, J. Devenyi, and R. H. Fish, "Metal-ion-templated polymers: Synthesis and structure of N-(4-vinylbenzyl)-1,4,7-triazacyclononanezinc(II) complexes, their copolymerization with divinylbenzene, and metal-ion selectivity studies of the demetalated resins—evidence for a sandwich complex in the polymer matrix," *Angewandte Chemie—International Edition in English*, vol. 36, no. 6, pp. 642–645, 1997.
- [30] J. M. Gladis and T. P. Rao, "Effect of porogen type on the synthesis of uranium ion imprinted polymer materials for the preconcentration/separation of traces of uranium," *Microchimica Acta*, vol. 146, no. 3-4, pp. 251–258, 2004.
- [31] R. Kala, J. Mary Gladis, and T. Prasada Rao, "Preconcentrative separation of erbium from Y, Dy, Ho, Tb and Tm by using ion imprinted polymer particles via solid phase extraction," *Analytica Chimica Acta*, vol. 518, no. 1-2, pp. 143–150, 2004.
- [32] V. M. Biju, J. M. Gladis, and T. P. Rao, "Ion imprinted polymer particles: synthesis, characterization and dysprosium ion uptake properties suitable for analytical applications," *Analytica Chimica Acta*, vol. 478, no. 1, pp. 43–51, 2003.
- [33] O. Vigneau, C. Pinel, and M. Lemaire, "Separation of lanthanides by ion chromatography with imprinted polymers," *Chemistry Letters*, vol. 32, no. 6, pp. 530–531, 2003.
- [34] Y. Liu, X. Chang, S. Wang, Y. Guo, B. Din, and S. Meng, "Solid-phase extraction and preconcentration of cadmium(II) in aqueous solution with Cd(II)-imprinted resin (poly-Cd(II)-DAAB-VP) packed columns," *Analytica Chimica Acta*, vol. 519, no. 2, pp. 173–179, 2004.
- [35] O. Güneş, Y. Yılmaz, and Ö. Pekcan, "Metal ion templated chemosensor for metal ions based on fluorescence quenching," *Sensors and Actuators B: Chemical*, vol. 85, no. 1-2, pp. 86–89, 2002.
- [36] M. E. H. Ahamed, X. Y. Mbianda, A. F. Mulaba-Bafubiandi, and L. Marjanovic, "Selective extraction of gold(III) from metal chloride mixtures using ethylenediamine N-(2-(1-imidazolyl)ethyl) chitosan ion-imprinted polymer," *Hydrometallurgy*, vol. 140, pp. 1–13, 2013.
- [37] E. Moazzen, H. Ebrahimzadeh, M. M. Amini, and O. Sadeghi, "A high selective ion-imprinted polymer grafted on a novel nanoporous material for efficient gold extraction," *Journal of Separation Science*, vol. 36, no. 11, pp. 1826–1833, 2013.
- [38] H. Ebrahimzadeh, E. Moazzen, M. M. Amini, and O. Sadeghi, "Novel ion-imprinted polymer coated on nanoporous silica as a highly selective sorbent for the extraction of ultratrace quantities of gold ions from mine stone samples," *Microchimica Acta*, vol. 180, no. 5-6, pp. 445–451, 2013.
- [39] H. Ebrahimzadeh, E. Moazzen, M. M. Amini, and O. Sadeghi, "Novel magnetic ion imprinted polymer as a highly selective sorbent for extraction of gold ions in aqueous samples," *Analytical Methods*, vol. 4, no. 10, pp. 3232–3237, 2012.
- [40] X. Wang, L. Zhang, C. Ma, R. Song, H. Hou, and D. Li, "Enrichment and separation of silver from waste solutions by metal ion imprinted membrane," *Hydrometallurgy*, vol. 100, no. 1-2, pp. 82–86, 2009.
- [41] X. Song, C. Li, R. Xu, and K. Wang, "Molecular-ion-imprinted chitosan hydrogels for the selective adsorption of silver(I) in aqueous solution," *Industrial and Engineering Chemistry Research*, vol. 51, no. 34, pp. 11261–11265, 2012.
- [42] M. Ahamed, X. Y. Mbianda, A. F. Mulaba-Bafubiandi, and L. Marjanovic, "Ion imprinted polymers for the selective extraction of silver(I) ions in aqueous media: kinetic modeling and isotherm studies," *Reactive and Functional Polymers*, vol. 73, no. 3, pp. 474–483, 2013.
- [43] S. Daniel and T. Prasada Rao, "Ion imprinted polymers—a new strategy based on the utilization of ion association complex of platinum as a template," in *Proceedings of the 29th IPMI Annual Precious Metals Conference*, pp. 78–90, 2005.
- [44] B. Leśniewska, M. Kosińska, B. Godlewska-Zylikiewicz, E. Zambrzycka, and A. Z. Wilczewska, "Selective solid phase extraction of platinum on an ion imprinted polymers for its electrothermal atomic absorption spectrometric determination in environmental samples," *Microchimica Acta*, vol. 175, no. 3-4, pp. 273–282, 2011.





# Hindawi

Submit your manuscripts at  
<http://www.hindawi.com>

