

INTERFACE SCIENCE AND TECHNOLOGY

Advanced Low-Cost Separation Techniques in Interface Science

Edited by
George Z. Kyzas
Athanasios C. Mitropoulos



Advanced Low-Cost Separation Techniques in Interface Science

Interface Science and Technology

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New trends in molecular imprinting techniques

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1. Introduction

Molecular imprinting technology (MIT) is an umbrella term for all the methods and approaches involved in molecularly imprinted polymer (MIP) synthesis process [1]. The as-synthesized MIPs can be implemented in many fields including biological and electrochemical sensors [2,3], separation and adsorption technologies [4] as well as sample preparation applications mainly in analytical chemistry for solid-phase extraction (SPE), microextraction, and others. First in 1931 by Polyakov and then in 1949 by Dickey [5], the effect of participating solvent in polymerization process and the resulting affinity of the synthesized polymer to the “pattern molecule” led to a more elaborative investigation on the topic by researchers globally. The MIP technology gained popularity during the last two decades, acquiring its present sense through an enormous number of studies and review articles. In fact, a brief research through scientific publications database (ScienceDirect and Scopus) of related literature showed that a great amount of work done is within a time frame of 2015 to present, with 2017 being the year of the most published studies on the topic. Also, a closer review of the available literature can lead to estimations regarding the trends both in synthesis and evaluation of MIP. In this respect, the specific chapter aims to cover the recent development within MIP technology, providing examples from recently published works.

2. Synthesis of molecularly imprinted polymers

The synthesis of MIP is considered an easy and effective process requiring (1) a template which is essentially the target molecule, (2) one or more functional monomer(s), (3) cross-linker(s), (4) initiator(s), (5) a porogenic solvent, and (6) a solvent for template extraction after polymerization of the complex (Fig. 7.1). The resulted material is a three dimensional polymer with formed cavities in shape and size that can bind and take in, via functional groups of the polymer, only a molecule with the same specifications. Thus, MIPs are characterized by high degree of selectivity for a predetermined compound, rapid mass transfer and kinetics, low-cost and easy synthesis procedure for trace analytes binding. Detailed description of the common synthesis protocol is given in multiple literature reviews [7], textbooks [8,9], and studies [10], therefore it is omitted from the specific work.

A successful metaphor to describe this mechanism is lock and key hypothesis that was postulated by Emil Fisher in 1894 in his work upon enzymes selectivity [11]. Actually, MIPs are artificial materials that mimic such behavior of natural occurring processes (i.e., antibodies) being though superior due to the fact that they provide [9] the ability to bind even compounds that are not present in nature while the number of binding sites is

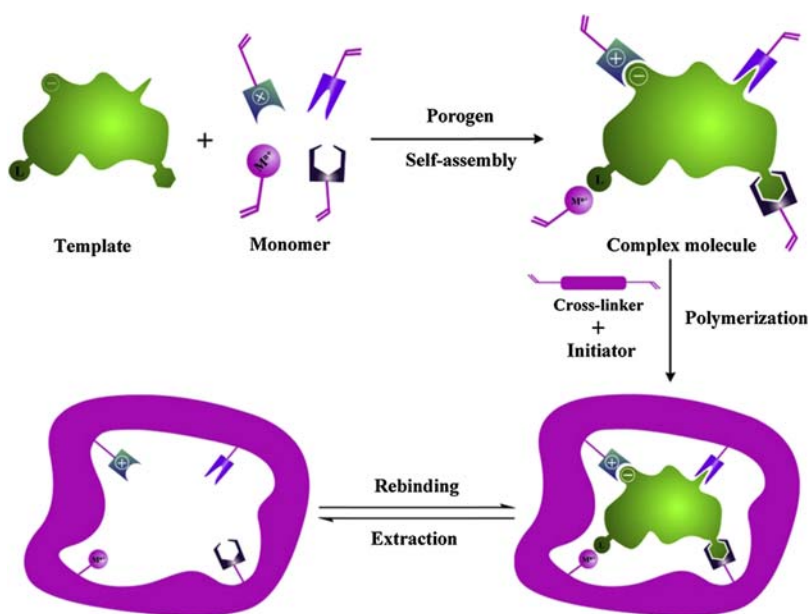


FIGURE 7.1 Schematic representation of molecularly imprinted polymer synthesis [6].

increased by many orders of magnitude. Fig. 7.1 represents schematically the whole process and outcomes of each step.

In MIP technology, many subgroups can be formed under various criteria; a classification could be done, for example, according to the MIP synthesis approach (solid-phase method, polymerization, surface imprinting, etc.) or the resulted MIP type (inorganic–organic molecularly imprinted polymer (IMIP), magnetic molecularly imprinted polymer (MMIP), multitemplate MIP, nanoparticles composite molecularly imprinted polymer (MIP-NP), etc.), the list can be endless due to versatile nature of MIPs. Another way for MIP categorization could be by application or target molecule. So ever, MIP technology is one of the emerged technologies with rapid development. The amount of studies conducted so far indicates the maturity level of MIT and hence MIP. The present work gives an overview of hot topics of the moment and the conducted studies upon the latest trends. Table 7.1 presents some of the new trends of this technology.

3. Inorganic molecularly imprinted polymer

According to the recent literature, a small yet portion of scientists have shown interest in using hybrids of organic–inorganic compounds in MIP synthesis instead of pure organic ones. This can be attributed to the fact that such hybrid materials can overcome some drawbacks. The as-synthesized MIPs, with traditional organic monomers, suffer from low performance in aqueous media, and many times there are difficulties of obtaining uniform particle size, some of the most important aspects considered especially in biological applications such as drug delivery [25] and therapeutic/diagnostic procedures [26]. For the latter case, “shell-” and “core-” like MIPs are implemented where “shell” is referred to imprinting the surface layer of nanosphere-shaped polymer [27] while “core” usually constitutes from a silica-based [28] or Fe_2O_3 [29] nanoparticles.

The embedment of inorganic particles into organic matrices leads to high-quality materials regarding mechanical strength, thermal and chemical stability, high selectivity performance, and other properties prerequisite for adsorption applications. Hence, this new generation of MIP materials is not restricted only to biological applications, but they are used in extend as adsorbents for effective decontamination of aqueous media. A large number of studies has been conducted upon investigation of IMIPs efficacy as adsorbents in many aspects including environmental [30], food processing [31], drug [32], and valuable metals recovery technology [33] and others.

Immobilization of template combined by solid-phase method for MIP nanoparticles synthesis has been first introduced in 2013 by Poma and associates [34]. The team achieved to fully automate the synthesis process in a device producing reuseable immobilized templates eliminating extreme operation conditions. Since then, the specific method has been utilized

TABLE 7.1 Few examples of new trends in molecular imprinting technology (MIT).

MIP type	Approach	Target molecule	Monomer/cross-linker/initiator	Chain transfer agent	Porogen	Solvent	References
IMIP-NP	Solid phase	Vancomycin	MAA/EGDMA, TRIM/DABE	PETMP			[12]
IMIP-NP	Solid phase	IBA					[13]
IMIP-NP	Solid phase	4-Ethylphenol	4VP, FER/EDMA, RIM/INEFETER	Pentaerythritol tetrakis (3-mercaptopropionate)	Acetonitrile, tetrahydrofuran	—	[14]
IMIP-NP	Solid phase	Trypsin	Nipam, BIS, TBA, NAPMA, AA/BIS, EGDMA, TRIM, NAPMA, AAm/ammonium persulfate aqueous solution, TEMED	—	—	—	[15]
IMIP-NP	Solid phase	THC	BIS, EGDMA, TRIM, NAPMA, AAm/PETMP, INIFETER			DMF, ACN	[15]
MIP	Bulk polymerization	Ketoprofen	2-Vinylpyridine/ethylene glycol dimethacrylate, 1,1'/azobis (cyclohexanecarbonitrile)	—	Toluene/ acetonitrile	—	[16]
Multi-template MIP	Bulk polymerization	Naproxen, ibuprofen and diclofenac	2-Vinylpyridine/ethylene glycol dimethacrylate	—	Toluene	—	[17]
SPI-MIPs	Bulk polymerization	Spiramycin	MAA/EGDMA/AIBN	—	—	Methanol	[18]

SBA-15@MIP	Surface molecular imprinting	dicyandiamide	DCD/EGDMA/AIBN	—	Tetrahydrofuran-ethanol	Methanol	[19]
SiO ₂ @MIPs	Surface molecular imprinting	17 β -Estradiol	APTES/CTAB/BTEB	—	Ammonia	Na ₂ CO ₃	[20]
Sol-gel MIPs	Surface molecular imprinting	Gossypol	APTES/TEOS/-	—	Acetic acid	Methanol/HCL	[21]
MMIPs	Precipitation polymerization	CDNB	EGDMA/MDI/-	Phloroglucinol	Tetrahydrofuran	Methanol/acetic acid	[22]
MMIPs	RAFT polymerization	BPA	4-Vinylpyridine and β -CD/TRIM/AIBN	—	—	Acetic acid/methanol	[23]
MMIPs	Surface polymerization	Folic acid	Acrylonitrile/EGDMA/AIBN	—	Ethanol	Methanol/acetic acid	[24]

IMIPs, inorganic–organic molecularly imprinted polymers; *MIPs*, molecularly imprinted polymers; *MMIPs*, magnetic molecularly imprinted polymers.

successfully by many other researchers for various purposes. Commonly, immobilization of the template is achieved by grafting covalently organic molecules on an inorganic substrate either heterogeneously or homogeneously [35].

A silica-based hybrid was evaluated for Hippuric acid (HA) extraction by solid-phase method [36]. The inorganic part of this composite material was a silica-based compound, and the target molecule recognition site was formed by 3-aminopropyl trimethoxysilane as the functional monomer cross-linked by tetraethoxysilane while methacryloxypropyltrimethoxysilane provided the ability of MIP surface acrylamide coating. The resulted material is characterized as restricted access material (RAM) due to the formation of hydrophilic barriers-like network. Furthermore, Arabi et al. [36], performed routine MIP characterization techniques for morphological evaluation including transmission electron microscope (TEM), scanning electron microscope (SEM), and FTIR as well as investigations of MIP performance by applying SPE of HA in a cartridge packed with the resulted material. After optimization of the methodology, the template to monomer ratio was found to be 1:5. Chromatography analysis of simple MIP was compared with that of RAM-MIP which demonstrated higher performance and repeatability while its reusability was determined to be high after a number of SPE cycles.

Enantiomers of albendazole sulfoxide (ABZSO), a drug usually used in veterinary as an antihelminthic for sheep, were successfully extracted from water by a poly(methacrylic-acid)silica-based IMIP. According to the study of Anacleto et al. [30], the so-named MIP-poly(MAA)-SiO₂ was synthesized and evaluated and compared with nonimprinted polymer (NIP) for its adsorption capacity, kinetics, and the effect of pH for the optimal performance. The results of the analysis showed that adsorption equilibrium was reached after 20 min of contact in aqueous solution of pH 9.0, while pseudo-second-order equation was that best fitted to kinetics analysis giving the same R value in both cases. This outcome leads to estimations that both examined materials adsorbed the target compound onto their external surfaces although at equilibrium MIP-poly-(MAA)-SiO₂ adsorbed up to 70% of enantiomers while NIP adsorbed only 50%. Additionally, the agreement with Langmuir isotherm indicates that monolayer molecule adsorption was performed giving information on adsorption capacity which was 140 and 35 mg/g for MIP-poly(MAA)-SiO₂ and NIP-poly(MAA)-SiO₂, respectively. Finally the specific work concluded that such MIPs can be implemented efficiently for separation and removal purposes of pharmaceuticals in water, providing reusability of the material as well.

In another work, organic–inorganic MIPs were synthesized on selenium (Se) nanoparticles for cholesterol binding. Specifically, two different monomers were polymerized namely 2-hydroxyethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EGDMA) and stabilized by poly(vinyl pyrrolidone) (PVP) by Polyakova et al. [37]. Pickering microemulsion was used

as synthesis method; the resulted sorbent was evaluated by chemical and morphological evaluation techniques. In order to compare, same examination was done for NIP as well. SEM micrographs revealed that synthesized MIPs had better porous microstructure while adsorption properties investigation indicated that the initial concentration of cholesterol plays a significant role in material's overall performance. Langmuir isotherm model describes better the adsorption process which seems to be monolayer deposition of the target compound, hence material's imprinted surface can be considered as advantage for cholesterol extraction from blood plasma.

4. Magnetic molecularly imprinted polymer

MMIPs are a new class of materials attracting an increased attention during past years mainly due to their easier after-treatment processes which are much more convenient and effective than those of conventional MIPs. An additional factor for their preference is the selectivity, for the target molecule, that they perform [38]. As it is rational, MMIPs are synthesized following surface imprinting technique where the polymeric surface layer of coated magnets is imprinted by the target analogue. Specifically, as a common methodology, emulsion polymerization take place in order to obtain core particles covered with imprinted shells [39]. A schematic representation of a common utilized methodology for MMIP synthesis is illustrated in Fig. 7.2 [39]. Besides many other advantages of core-shell structured materials, the obtained uniformity regarding the size and shape of the resulted particles as well as the greater overall efficiency makes this approach highly attractive in many aspects.

High internal phase emulsion polymerization by Pickering method was the methodology of choice for porous MMIP tailoring used for λ -cyhalothrin (LC) adsorption [40]. After its synthesis, material was evaluated regarding kinetics, adsorption capacity, and selectivity by competitive recognition test. The adsorption capacity was investigated under no vibration and although the equilibrium was reached after 2 h, the amount that could be adsorbed was roughly determined at 1 h of the contact with the pesticide. Isothermal sorption measurements at ambient temperature estimated the adsorption capacity to 404.4 $\mu\text{mol/g}$, while from the thermodynamic point of view, the one-layer molecular deposition occurred spontaneously. Finally, in order to qualitatively define the MMIP selectivity, one similar to λ -cyhalothrin compound, namely fenvalerate (FL), and a nonanalogue such as diethyl phthalate (DEP) were examined as well. The test revealed that the MMIP presented higher affinity to LC and its analogue while no selectivity to DEP was observed. The authors attribute this behavior to the fact that LC and FL is bound to MMIP by hydrogen bonds while DEP lacks them, limiting its ability to get into the formed cavities despite its small molecule.

Zhang et al. [41] managed to successfully bind salicylic acid (SA) onto core-shell MMIP. In fact, comparative experiments of synthesized MMIP by

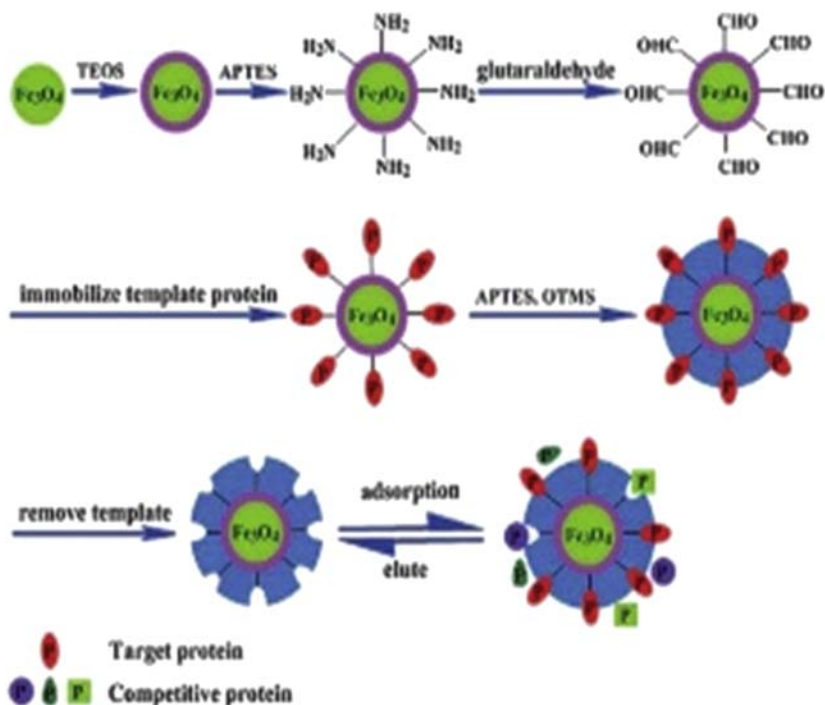


FIGURE 7.2 A schematic illustration of core-shell magnetic molecularly imprinted polymer synthesis. Fe_3O_4 nanoparticle is used as core and coated with a silica shell. After processing with tetraethoxysilane (TEOS), $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ is produced. Further, reaction with 3-aminopropyltriethoxysilane (APTES) take place in order to obtain amino groups on its surface, while further reaction with glutaraldehyde (GA) leads to surface modification by creating aldehydes. Then, a 3D polymeric structure is formed under siloxane copolymerization by APTES and octyltrimethoxysilane after target compound had been immobilized via covalent approach onto the modified surface. The created network constitutes protein complex in which protein is removed leaving cavities of specific characteristics concerning shape, size, and functionality [39].

sol-gel polymerization and the same not imprinted material demonstrated a greater binding capacity by many times while its recovery was up to 108%. Therefore the particular synthesis strategy is suggested by the research team as a multifaceted method for production of materials for harsh and complex environments.

Another study on core-shell structured MIP nanoparticles, conducted by Wu and his team [42], proposes the synthesized MMIP for tetrabromobisphenol A (TBBPA) extraction from water. Fe_3O_4 nanoparticles were coated by imprinted SiO_2 , and evaluation of the material revealed its high efficiency toward TBBPA removal. Specifically, MMIP adsorbed 2.3 times more of the target compound than MNIP at a minimal equilibrium time of 40 min presenting also high reusability, while its stability did not show to decrease even after seven cycles of TBBPA extraction by adsorption.

5. Dummy-template molecularly imprinted polymer

Environmental safety is one of the most significant concerns in many fields of science. Green technology and all the subsequent aspects have been developed in recent years and the number of firm supporters is ever increasing. In the field of chemistry, some of the major issues arise are the logical use of reactants, the minimization of energy consumption, the reusability of the produced material, and the optimization of the whole process; so it could be considered eco-friendly and safe to be implemented [43]. In this sense, the participation of computational chemistry in MIP synthesis process is essential. During the past years many works have been conducted and published supporting computational approach for synthesis optimization. In most of the cases, computational tools such as density functional theory and molecular dynamics [10] are used for an efficient screening of monomers in order to find the suitable for the intent use, thus avoiding the generation of unusable waste like it happens when trial-and-error approach is implemented. MIPs synthesis is considered easy to do, but there are some steps of the process that are crucial for the final result; template manipulation is one of them. The main advantage of an MIP is its capability to recognize even traces of a particular compound, that is why it is preferred for sample preparation in already mentioned methods. In many cases, the target compound may be toxic or valuable enough so any leakage from the MIP matrix is undesirable. To solve this problem, dummy templates are used instead of original compounds. As a dummy template for MIP synthesis (DMIP) is an analogue to the target molecule; another molecule of similar shape, size, and functionality but not toxic or valuable.

In order to overcome low selectivity for SA of MIPs due to its weak hydrogen bonding ability with conventional monomers, Xiang et al. [44] used ionic liquid as functional monomer for polymerization of proposed MIP in aqueous medium. As template they replaced SA with a dummy compound which was benzoic acid while MCM-48 was the porous substrate. During this study, parameters such as the kind of template, the analogy of template–monomer–cross-linker, and porogen selection were optimized for synthesizing an MIP of high adsorption capacity and improved selectivity. The resulted material was a hollow porous MIP presenting better properties than any reported MIP fabricated traditionally or by surface imprinting technology. The affinity of fabricated MIP to SA was determined by means of adsorption capacity and imprinting factor. Imprinting factor was the ratio of adsorption capacity of MIP and an NIP as reference material, and it was found 5.61 with adsorption capacity of MIP being 29.75 mg/g. BET analysis provided information about surface area which was 543.9 m²/g, while kinetics test showed that reaction equilibrium was reached after 25 min of contact following Freundlich equation and described by pseudo-second-order model. Finally, the

recovery rate was found to be up to 94.5%, implying the specific MIP can be applied successfully for SA extraction.

One additional challenge in analytical chemistry is the ability for a material to be multifunctional, in other words, to possess the ability to recognize and bind more than one compounds simultaneously. MIP offers this opportunity by suitable design and optimization. For example, Song et al. [45] synthesized a dual template MIP for detection of 16 compounds, 8 fluoroquinolones (FQs), and 8 sulfonamides (SAs). As dummy templates, pipemidic acid (PA) and nalidixic acid (NA) were selected for FQs while sulfanilamide (SA) and sulfabenzamide (SB) were found to be suitable for SAs. Theoretical results of simulation modeling tool and experiments were compared in order to examine the performance of the fabricated MIP for FQs and SAs affinity. Then the optimized materials were used for mentioned drugs detection in pork and chicken meat by SPE column as sample preparation method for ultra performance liquid chromatography. The results obtained indicated the good potentials of the specific MIP with maximum drug adsorption at 74.2 μg and recovery up to 99% even after eight times of column usage. As it is implied in Fig. 7.3, the prepared MIPs present high affinity to specific analytes that can be observed from high recovery of the target compounds while other competitor compounds are not recognized by any of the MIPs.

In some cases, synthetic template preparation is restricted by high cost and complexity, hence other solutions should be provided. One clever way to overcome such issues is to structurally divide the target compound producing fragments that are same or similar to it like He et al. [46] achieved in order to selectively extract gonyautoxins from seawater by SPE. The research team followed a multitemplate MIP method for dummy template preparation using fragments of dummy analogues (2,4,6-triaminopyrimidine, 4-hydroxy-2-butanone, and imidazole). Bulk polymerization was the selected approach

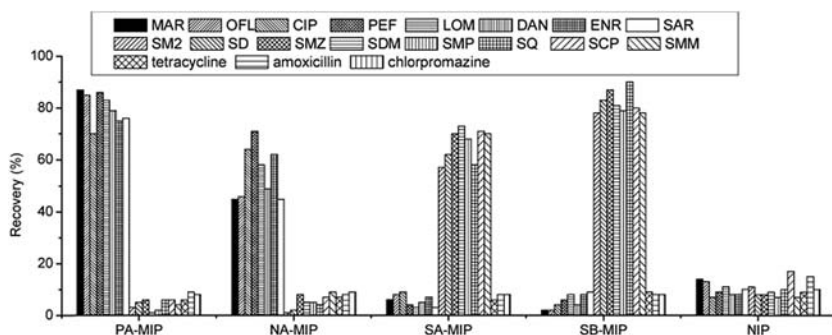


FIGURE 7.3 Recoveries of fluoroquinolones and SAs by four prepared molecularly imprinted polymers compared with blank nonimprinted polymer material [45].

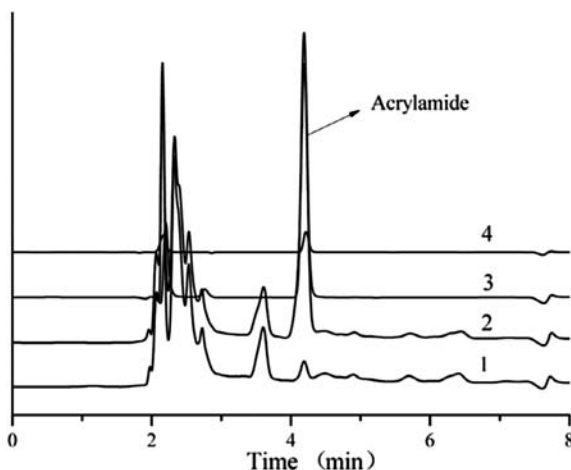


FIGURE 7.4 HPLC–UV chromatograms of food samples. The collected spectra shows (1) not spiked, (2) spiked with 4 ng/g acrylamide and without extraction, (3) spiked with 4 ng/g acrylamide and with AMDSMIPsGOF Fe_3O_4 extraction, and finally, (4) spiked with 4 ng/g acrylamide and the remaining solution after extraction [47].

for MIP synthesis involving prepolymerization by sonication for template and monomers dissolution. After this process, cross-linkers were added and mixed by stirring. The template was removed by a mixture of methanol/acetic acid of 9:1 in a Soxhlet after the polymerization was completed. The most significant remarks of this study was the results obtained by comparison of the fabricated multitemplate MIP with that of monotemplate, prepared in the previous work of the same team for 1 and 4 gonyautoxins isolation. It was revealed that MIP prepared by multitemplate method had lower adsorption capacity than that prepared by monotemplate method, authors attribute this outcome to incorrect combination of template fragments into the MIP synthesis leading to binding sites not suitable for the specific analyte.

The above spectra (Fig. 7.4) make clear the high selectivity of an MIP for acrylamide detection and removal from food. Specifically, Ning et al. [47], fabricated for the first time MIP selective to acrylamide. The difficulty in such case is that, usually, acrylamide is used a cross-linker making restrictions to its manipulation as template. Moreover, acrylamide is toxic and cancerogenic, hence its usage is preferred to be avoided. Instead acrylamide, the mentioned group introduced an analog to acrylamide; the so-named propionamide. The most remarkable of the work, was that the as-synthesized magnetic graphene oxide MIP (AMDSMIPsGOF Fe_3O_4) presented high selective recognition of the target compound even from fried foods, with high recovery yield.

6. MIP performance

6.1 Characterization and performance evaluation methods

Materials such as MIPs can be characterized by means of many methods including morphological and chemical evaluation. The most common techniques for morphological characterization of MIPs are TEM and SEM, while chemical analysis is provided by methods of liquid chromatography, FTIR, mass spectroscopy, and others. Binding efficiency can be determined by sorption test of the examined material, providing information about its kinetics and adsorption capacity of the target pollutant onto its surface, while surface properties can be further estimated by methods such as N_2 porosimetry in order to obtain the surface area. However, MIP properties are significantly affected by some factors both from the perspective of selected reagents and the followed synthesis approach. Following, effect of porogenic solvent, template removal method, and synthesis process on the resulted MIPs are presented by some examples of the recent literature.

6.2 Effect of the porogenic solvent on MIP efficiency

Porogen plays an important role within MIP synthesis process. Porogen is responsible not only for dissolving properly all the agents during polymerization but also for the development of porous structure of the MIP. Additionally, porogen must not interact with the formed template–monomer complex retaining its stability [49]. Thus, reagent used as porogen must be selected thoughtfully for MIP synthesis regarding the desired results and MIPs usability.

As it was mentioned in a previous section, green chemistry perspectives are appealing to chemists worldwide, therefore a lot of focus has been put on finding more eco-friendly, safer, and lower cost solutions whenever it is possible. Such an example is the usage of ionic liquids instead of conventional reagents in MIP synthesis process. Due to their nature, ionic liquids among other properties demonstrate nonvolatility, nonflammability, and also they are highly dispersible in inorganic/organic solvents, thus they have been implemented in recent studies substituting conventional monomers or/and cross-linker [50] in bulk polymerization or as functional substrate in surface MIT [51]. Ionic liquid can also be successfully used as porogen, adding special characteristics to MIPs. As an example, Booker and her team have conducted a series of studies upon the performance of ionic liquids as porogen within MIP synthesis for trans-aconitic acid 1 and cocaine 2. Investigations of porogen volumes and process temperature conditions as well as polymerization method were included. Comparisons with MIP prepared in volatile organic carbon VOC solvents such as CH_3CN were performed as well. In the initial study, acetonitrile and chloroform porogen performance for MIP preparation of aforementioned target compounds was compared with that of (BMIM) (BF4)

and (BMIM) (PF6) ionic liquids for the same purpose. Two different polymerization methods were implemented, namely bulk and precipitation polymerization at 5 and 60 °C. Remarkably, it was revealed that conventional porogens failed to develop 3D polymer complexation at low temperature in both polymerization methods. In contrast, ionic liquids as porogen achieved to form MIP and by temperature increase the polymerization rate was found to be significantly greater than the respective of conventional ones. Subsequent study of the same research team [48] generated additional MIPs characterized by SEM as well. Cocaine MIPs were prepared as monolithic when 5 mL of porogen was used and by precipitation method (25 mL of porogen). Obtained MIP characterization by SEM (Fig. 7.5) supports the results concluding that porogen nature impacts significantly MIP morphology.

As it was mentioned, MIPs are widely used in sensor technology for trace detection and monitoring as they are a good alternative of biological receptor-based methods whose usage is restricted by their stability and cost. A carbon paste electrode with appropriate MIP was proposed as sensor for histamine monitoring by Akhoundian et al. [52]. In their study, two different porogen solvents were used in MIP synthesis; acetonitrile and methacrylic acid following bulk polymerization method. For determination of porogen influence of MIP selectivity, optical rebinding test was performed by UV-VIS spectroscopy, after the MIP/histamine (at concentrations from 0 to 1 mM for 4 h of contact at ambient temperature) suspension was centrifuged, for both MIPs and their respective NIPs (Fig. 7.6).

The obtained results reveal that MIP synthesized in chloroform as porogen solvent performs better than MIP prepared in MeCN. This is attributed to the different polarities of the two porogens and to the fact that histamine binding is based mainly on hydrogen bonds in the presence of the methacrylic acid (as monomer) and chloroform (as porogen) combination. The latter is confirmed

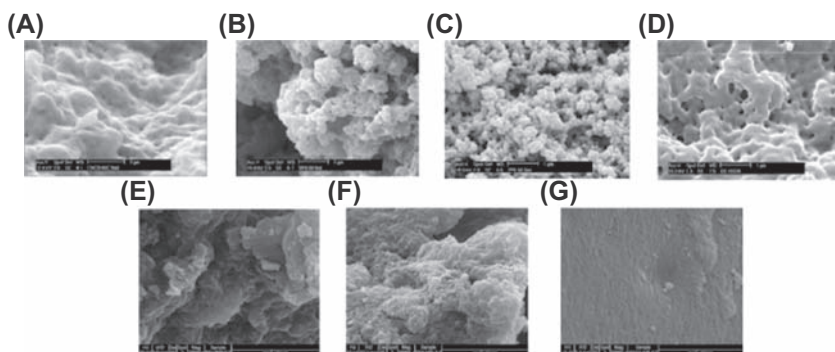


FIGURE 7.5 SEM images of cocaine-imprinted polymers prepared in 5 mL porogen at 60 and 0 °C [48]. (A) CHCl₃-60-5; (B) [bmim]BF₄-60-5; (C) [bmim]PF₆-60-5; (D) [bmim]HSO₄-60-5; (E) [bmim]BF₄-0-5; (F) [bmim]PF₆-0-5; (G) [bmim]HSO₄-0-5.

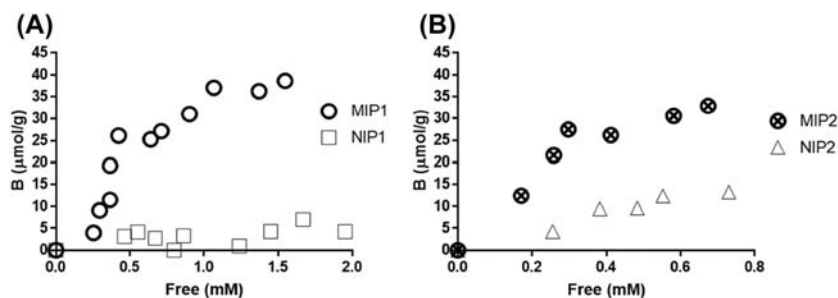


FIGURE 7.6 Rebinding isotherm of histamine examined by UV-VIS spectroscopy for (A) MIP1, NIP1; (B) MIP2, NIP2 in 50 mM PBS buffer (pH 7.4). MIP1 and MIP2 (corresponding NIPs) were prepared in CHCl_3 and MeCN, respectively [52].

by Triikka and her team [54] investigating binding and recognition properties of MIPs by conducting combinational NMR and UV-VIS spectroscopy analysis.

Supercritical fluids implementation is an emerged technology and can be considered as another route for meeting green technology requirements. To this direction, supercritical fluid such as scCO_2 has recently been used as porogen solvent for MIP prepolymerization phase. Due to its inherent characteristics, scCO_2 has been reported as a promising solution for sustainable, clean and with low environmental impact solvent. Moreover, scCO_2 apolar nature makes it perfect for porogen solvent while it does not interact with template—monomer complex resulting in MIP of controlled structural properties [55]. In order to fabricate a bisphenol A selective MIP, Rebocho and group synthesized a ferrocenyl-based MIP [56]. The polymerization process was occurred in a specially designed cell where all reactants were mixed at CO_2 environment with the assistance of sonication bath to ensure solids' dissolution (for detailed methodology refer to specific work).

6.3 Template removal methods

The method of template desorption is crucial for the optimal performance of the fabricated MIP. Many methods have been developed to efficiently remove template from the formed 3D network leaving the desired cavities for target molecule capturing. Lorenzo and Carro [57] conducted a replete review of MIP template extraction methods providing information about technologies up to 2011. Although MIT is a rapidly developed field with new materials and composition methods emerging every now, template extraction seems not to follow the same tempo. As it is well known, a successful template removal contributes to overall success of MIP synthesis. If template remainings are still present when prepared MIP is applied, then the adsorption capacity is

decreased due to lower number of available binding sites (some of the binding sites are occupied with template). Additionally and especially for applications that requires high accuracy such as analytical methods (SPE, MSPE, etc.), a phenomenon called “template bleeding” may cause many problems leading to inaccurate estimations. Common strategies for this last step of MIP synthesis procedure include solvent extraction, microwave and ultrasound assisted extraction, pressurized-liquid extraction, and others. Template removal is considered as the least cost-effective process of MIP synthesis, thus optimization is mandatory for achieving good results at as low cost as possible but also with limited environmental impact. In fact, there are cases that, in order to remove the template, extreme conditions are applied leading most of the times to disintegration of formed cavities.

One of the latest work upon the specific topic has been conducted, and pressurized hot water extraction (PHWE) was proposed as the optimal template removal method by Batlokwa [53]. In the specific study, PHWE was compared with other common methods, namely soxhlet and ultrasonic extraction. Three MIPs were prepared and colored for distinguishing purposes. The optimal operation conditions of purge water were 220 °C at 50 bars with a flow rate of 2 mL/min. Comparative experiment for extraction efficiency (EE) was performed for all three methods revealing that PHWE not only had the highest EE percentage (99.6%) for all MIPs but also template wash-off was achieved in less time. The most interesting and worth to mention outcome of the specific study is the results from template bleeding test presented in Fig. 7.7.

As it is shown, PHWE presented no bleeding at all of chlorophyll and quercetin MIP and only a small percentage for Phthalocyanine of 0.02% compared to the rest two methods. The conclusion of this study is that water for template removal is the optimal solution while it is cheaper, readily available, and does not cause environmental damage as organic solvents do.

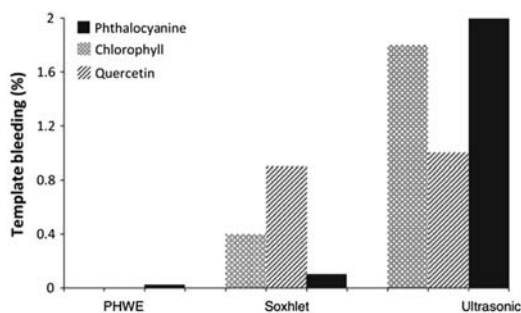


FIGURE 7.7 Percentage of template bleeding after the initial wash-off by all three template extraction methods [53].

6.4 Other parameters

An interesting perspective about the effect of MIP particle shape has been postulated by Roy et al. [58] with results that indicate the importance of MIP shape in selectivity and adsorption capacity. Silver nanoparticles (AgNPs) were synthesized acquiring spherical, hexagonal, rod, and flower shape and further modified by surface molecularly imprinting for phenformin recognition. AgNPs were subjected to characterization by UV-VIS spectroscopy, X-ray diffraction (XRD), SEM (Fig. 7.8), TEM (Fig. 7.9), while surface-modified nanoparticles were examined additionally for adsorption capacity, selectivity of the target molecule, surface area, and electrocatalytic activity.

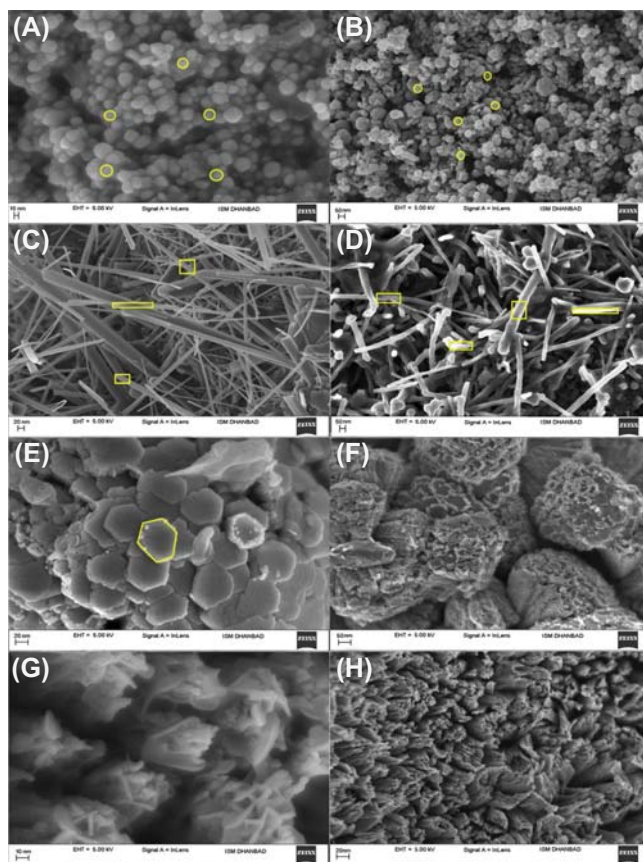


FIGURE 7.8 SEM micrographs of silver nanoparticles and the resulted molecularly imprinted polymers: (A) AgNSSs, (B) MIPAgNSSs, (C) AgNRs, (D) MIPAgNRs, (E) AgHPs, (F) MIPAgHPs, (G) AgFLs, and (H) MIPAgFLs.

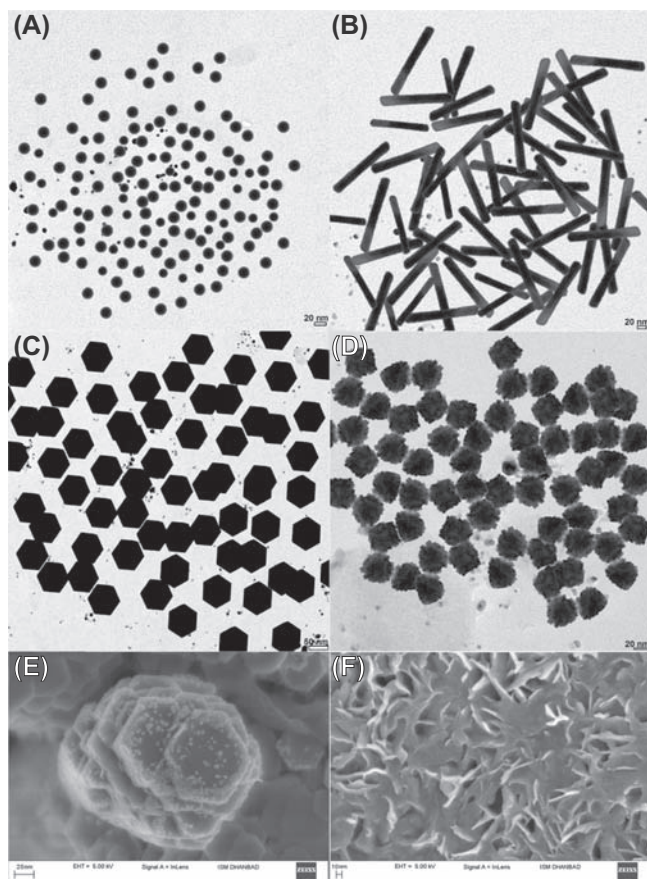


FIGURE 7.9 TEM imaging of silver nanoparticles and the resulted molecularly imprinted polymers: (A) AgNSs, (B) AgNRs, (C) AgHPs, and (D) AgFLs. High-resolution FE-SEM images of (E) MIPAgHPs and (F) MIPAgFL [58].

In another work of the same team, AgNPs of three different shapes (hexagonal, cubical, and spherical) were modified with vinyl group and used as one of the functional monomers in MIP synthesis for tramadol binding after they were embedded into the shell of Fe_3O_4 nanoparticle (NP) with high magnetism. As it was in the previous work, the scope of the study was to investigate the shape-related efficiency of the resulted MIP-NP for the morphological characterization SEM, TEM, and FE-SEM. Fig. 7.10 illustrates the whole synthesis process.

In both studies, results indicate that the shape of used MIP-NPs is crucial for their performance and this can be attributed to the fact that shape at nanoscale range alters physicochemical properties of the material as it has been reported elsewhere [60,61].

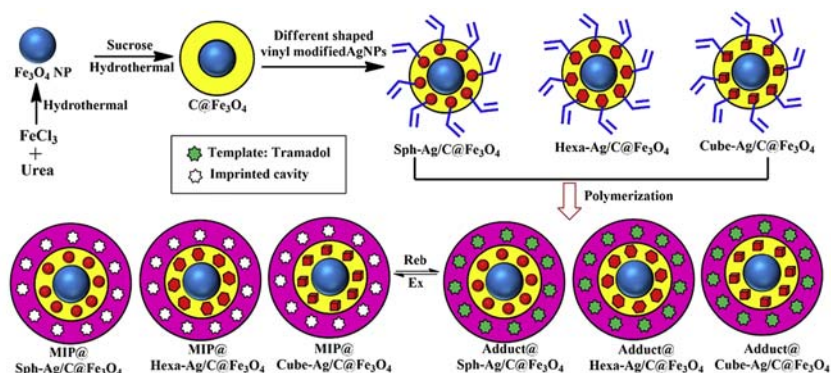


FIGURE 7.10 Synthesis process graphical illustration of resulted molecularly imprinted polymer (MIP) with different shaped AgNPs; Sph-Ag (spherical), Hexa-Ag (hexagonal), cube-Ag (cubical) [59].

7. Conclusions

Recent published studies have been reviewed and discussed. An attempt to present new trends in MIP technology and further subcategorized according to the nature of reagents and MIP utility, namely into IMIP, MIPs as magnetic particles composites (MMIP), and dummy template (DMIP) ones, was conducted. In addition, factors of major importance in MIP overall performance, such as porogenic mixture and template removal methods, as well as and other less common parameters, were highlighted. From the literature review, it was found that although there is a growing trend for MIP synthesis improvement, some involving methods (i.e., template removal) lack the appropriate attention. The latter observation indicates a misbalance between material composition and implemented methodology progress. In general, researchers have accomplished some remarkable achievements under a greener perspective. During the past 3 years, many of MIP drawbacks concerning stability, water compatibility, higher selectivity, multifunctionality, and many others have been overcome according to recently reported works.

Conflicts of interest

The authors declare no conflict of interest.

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