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Recent advancements in molecularly imprinted polymers for the removal of heavy metal ions and dyes

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ABSTRACT

Contamination set off by highly toxic metal ions and dyes is a big threat to the environment and living beings. Various industries like metal plating, mining, pesticides, battery manufacturing, and dyeing release metal ions and toxic dyes directly into the water. It is necessary to remove these toxic substances from the environment. Molecular imprinting technology (MIT) got a lot of attention in the last two decades because of several advantages over conventional adsorption technologies. Molecularly imprinted polymers (MIPs) are compatible with natural antibodies having the highest selectivity due to specific recognition sites for the template molecules. Selectivity is the major advantage of MIP, any targeted heavy metal ions and dyes can be separated efficiently. Various polymerization procedures can be used for the MIP preparation started by self-assembled monomers surrounding the molecules of the template because of the "monomer functional groups and template" interchange. Various studies have been made for the removal of metal ions and dyes from water and excellent results have been attained. Continuous research developments are being done for real applications of MIPs to remove toxic environmental substances that are not only harmful to humans and other organisms but also disturb the ecological balance. This review represents the development of current MIPs, advantages as well as disadvantages exhibited from various angles to complete a roadmap towards industrial and commercial use of MIPs.

Keywords: Heavy metals; Dyes; Environmental toxicity; Molecularly imprinted polymers; Adsorption

1. Introduction

Environmental pollution is a global threat because of various serious health concerns to living organisms [1–3]. Heavy metal ions and dyes are fatal because they cause cancer, brain tumor, cardiovascular disease, and serious health issues. Rapid urbanization and industrialization have triggered the production of heavy metals and their accumulation in the aqueous environment. Different types of chemicals containing heavy metals are discharged directly into the water as agriculture and industrial waste [4–8]. Modern industries like metal plating, mining, pesticides, and battery manufacturing release heavy metals directly into the water [9,10]. Similarly, textile, dyeing, tannery, paint, paper, and pulp industries are responsible for dye release in the environment [11,12]. Heavy metals and dyes not only affect human health but also cause serious problems to all major species of the ecosystem [13]. Even low exposure to heavy metals and dyes impairs various important biological processes of the human body and food chains [14]. Various techniques are in practice for the elimination of metal ions and dyes from wastewater like membrane processes, extraction, chemical precipitation, ion exchange, and adsorption [15–17]. All process has some deficiencies,

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especially regarding the selectivity issues and also cross-reactions of substances to adsorbent materials. Among various adsorbent technologies related to heavy metal ions and dye adsorption, molecular imprinting technology (MIT) has gained a lot of attention.

2. Molecularly imprinting technology

MIT is currently a well-established and excellent technique based on the synthesis of polymeric substances compatible with natural antibodies with a specific ability to recognize the analyte molecules [18,19]. The cavities generated after the subsequent exclusion of target molecules are size, shape, and geometrically identical to the template [20,21]. Thus, template rebinding is preferentially ensured with high specificity. Molecular imprinting mechanism can be described in three phases as shown in Fig. 1 [22]. (a) Template and monomer form pre-polymerized complex through non-covalent or covalent interactions, (b) polymerization is processed by the addition of cross-linker molecules, (c) template is removed leaving behind binding interactions by washing polymer matrix with some suitable solvent and template-oriented cavities are generated [23]. The unique characteristics of molecularly imprinted polymers (MIPs) including high stability, easy synthesis, significant reusability, hollow morphology, low cost, and especially high selectivity made them the ideal candidate for various applications [24,25].

MIP composites are similarly formed to improve the sensitivity and selectivity of the material. Silica-based materials are very significant in providing support by resisting swallowing and shrinking of the material [26] but there are limitations regarding the limited modification capabilities and denaturation of material at extreme pH. Magnetic nanoparticles increase the efficiency of the materials by facilitating the sorption process; exhibiting high surface-to-volume area and good dispersibility [27], but functionalization is required to avoid agglomeration and oxidation. With the extension of MIT, the use of carbon-derived materials has increased. Carbon-derived materials have a high surface area, good durability, and adsorption capacity [28] but their aggregation effect the sorption capacity negatively, and also surface modification is required before use. Furthermore, biopolymers are also being widely used because they are environment friendly and have a high binding capacity [29], but contain less selectivity.

2.1. Green chemistry and MIPs

Environmental protection is one of the major responsibilities of researchers because human activities directly influence the environment. In view of this, Anastas and Warner [30] established 12 green chemistry principles in 1998, which were primarily oriented to synthetic chemistry but some of them could be used in analytical chemistry. Gałuszka et al. [31] revised and suggested 12 principles of green analytical chemistry which include effective concepts of waste reduction, risk, and prevention of hazardous side effects. Furthermore, the 12 principles were again proposed by permitting the assessment of 3 complementary areas that are red, green, and blue for analytical efficiency, environmental safety, friendliness, and economical aspects, respectively [32,33].

MIP synthesis is a hit-and-trial method that takes time and even many MIPs are prepared and tested before getting

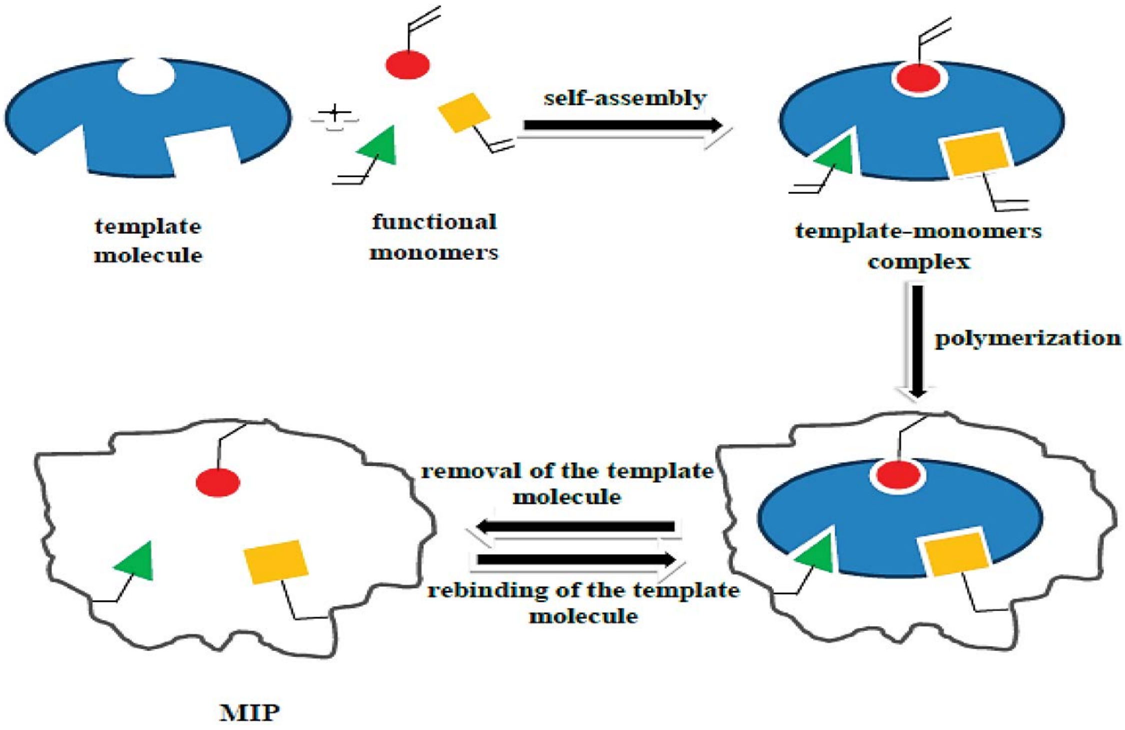


Fig. 1. Schematic illustration of the molecularly imprinting technique [22].

the final product. The other non-functional MIPs are waste and thus leading to enormous solid waste. There are also some other necessary steps involved for the polymers produced by bulk polymerization, including grinding, sieving, time consumption, and high energy [34]. Developments are being done for attaining the MIP in a greener way.

Recently, 14 principles of green MIT were proposed by Arabi et al. [18] with the GREENIFICATION acronym which could assist as a guide for MIP GREENIFICATION as shown in Fig. 2. Despite such a guide, there is a lack of quantitative information on the environmental impact of the entire chemical procedure, thus the already existing assessment tools would assist to produce the actual green MIP-based sample preparation techniques. Far as we know, no specific tool exists which could perform the greener assessment in molecular imprinting fields. However, other assessment tools like AGREE tool [35] and EcoScale [36] can be used for green assessment of MIP development and use in sample preparations following the rules of green analytical chemistry. It is expected that more research is to come in the next years because a lot of things have to do with green improvement in terms of MIP synthesis and performance.

This review focuses on the chemistry of molecularly imprinted polymers fundamentals, synthesis processes, and their application for the adsorption of heavy metal ions and dyes. Finally, a brief review of recent trends and future prospects in MIPs is also presented in this paper as a roadmap for future work. Functional monomers, cross-linkers, templates, porogen solvents, and initiators are required to synthesize MIPs.

2.2. Monomer

Monomer choice is very important to synthesize MIP successfully because monomer and template molecule interactions form a pre-polymerization complex [37]. Most of the functional monomers contain two group units in their structure; one is a polymerizable unit and the other is a recognition unit [38]. MIP binding capacity and cavities generation is directly related to the amount of monomer in the pre-polymerized complex mixture. Sometimes multiple monomers are used for MIP synthesis, and their reactivity ratios should be properly managed during the pre-polymerization process. Le Chatlier principle governs the relationship between template and monomer in complex solutions [39]. Monomer classification is based on the nature of the covalent, non-covalent, and semi-covalent interactions [40]. Many monomers can be used for the synthesis of MIP, but methacrylic acid (MAA) is known as a universal functional monomer due to its H-bond donor and acceptor

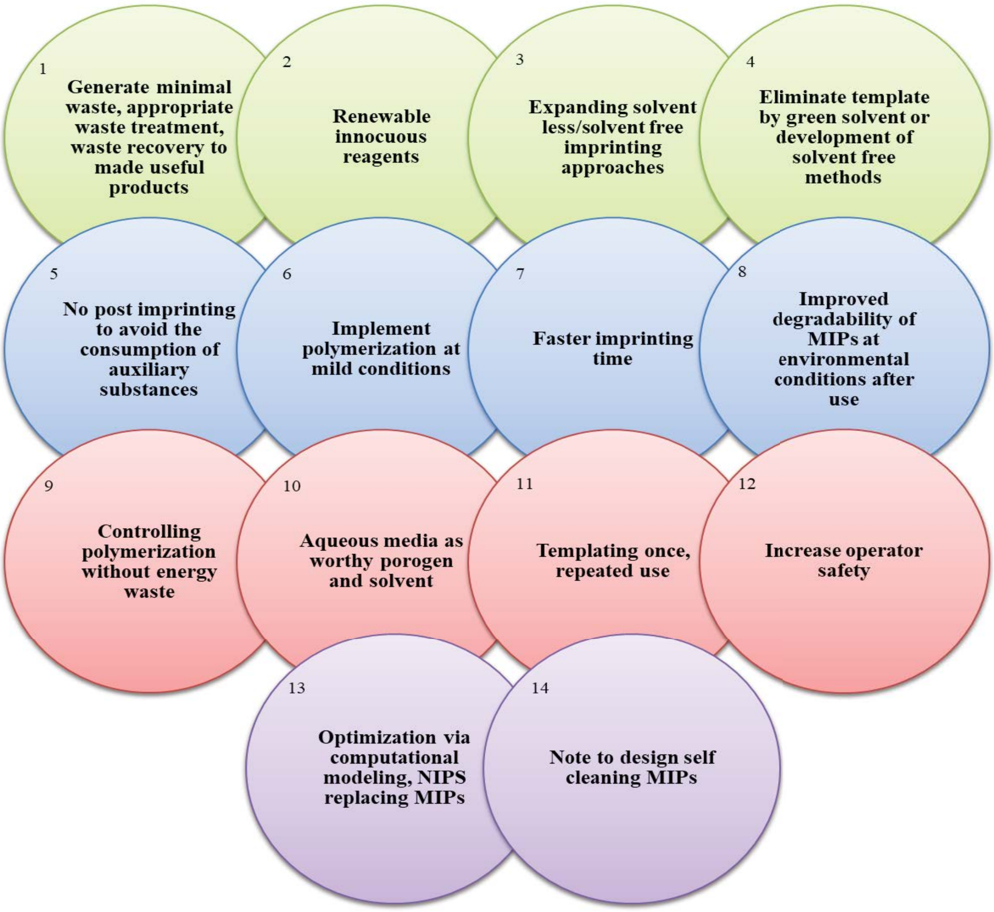


Fig. 2. 14 principles of green molecular imprinting expressed as the mnemonic device "GREENIFICATION" [18].

sites. MAA has a good binding capacity and larger porosity which makes it unique in the class of functional monomers [41]. The number of functional monomers is small, hence researchers are focusing to develop new monomers for improving the various template imprinting.

Furthermore, room temperature Ionic liquids (RTILs), were primarily considered a class of green solvents due to their negligible vapor pressure, non-flammability, and tuneable properties [42], though recent reports have warned about their poor biodegradability and lethal toxicity [43,44]. Various RTILs have been discovered as reagents for MIPs because the RTILs can interact with various analytes by hydrogen bonding, hydrophobic, electrostatic, ion exchange, and π–π interactions. High porosity and flexibility of RTILs made them important chemicals for MIT [45,46]. Wang et al. used vinylimidazole RTIL as a monomer for the first time in the fabrication of chlorsulfuron MIPs [47]. A large number of monomers exist for the non-covalent MIT technique as compared to other fabrication approaches due to their high sensitivity, flexibility, and versatility [47]. Methyl methacrylate (MMA), styrene, acrylic acid (AA), and 4-vinylpyridine (non-covalent technique); 4-vinyl benzaldehyde, 4-vinyl aniline, and 4-vinyl benzene boric acid (covalent procedure); 3-isocyanato-propyltriethoxysilane (IPTS) (semi covalent); and Fe^{2+}/MMA complex and Cu(II)-iminodiacetate-derivatized vinyl (ligand exchange) are the examples of various functional monomers for different preparatory approaches [48]. Fig. 3 shows the chemical structures of some commonly used functional monomers in MIT.

2.3. Cross-linkers

Cross-linkers are very important substances for controlling the polymeric matrix structure of MIPs, and these agents are responsible for functional monomer aggregation and connection with each other [49]. Cross-linkers also play a vital role in the polymerization process, proper cavities generation by stopping functional monomers displacement, and template separation. Cross-linker molecule selection should be appropriate because these are also responsible for polymeric matrix morphology, stability of imprinted bonding spots, and mechanical stability with high porosity [50]. A fixed amount of cross-linkers is needed to obtain a stable porous polymeric complex because binding sites are affected by the amount of cross-linkers. High cross-linker amount is necessary for the generation of mechanically stable porous structure and binding site strength [51,52]. Three-dimensional structure of the polymer is achieved with a high proportion of cross-linker that guaranteed the shape, size, and functionality groups alike as template molecules. Binding sites become close to each other and imprints do not work properly if less amount of cross-linker is added in the polymeric solution. If the ratio is too high, the polymer will become hard due to less swallowing preventing MIP from expanding and lowers the recognition ability [53–55]. Some cross-linkers are categorized with regards to fabrication techniques; bis-(1-(tert-butylperoxyl)-1-methylethyl)-benzene (BIBP), triallyl isocyanurate (TAIC) (Covalent procedure); benzoic acid, ethylene glycol dimethacrylate (EGDMA), *N,N*-methylenediacrylamide (MDAA), divinylbenzene (DVB) (non-covalent process); diphenyldiethoxysilane (DPDES), and tetramethoxysilane (TMOS) (sol–gel method) [48]. Some frequently used cross-linkers are shown in Fig. 4.

2.4. Porogens

Porogens are very significant substances in the MIP fabrication process. Porogens play an important role not only in dissolving the various agents during the polymerization

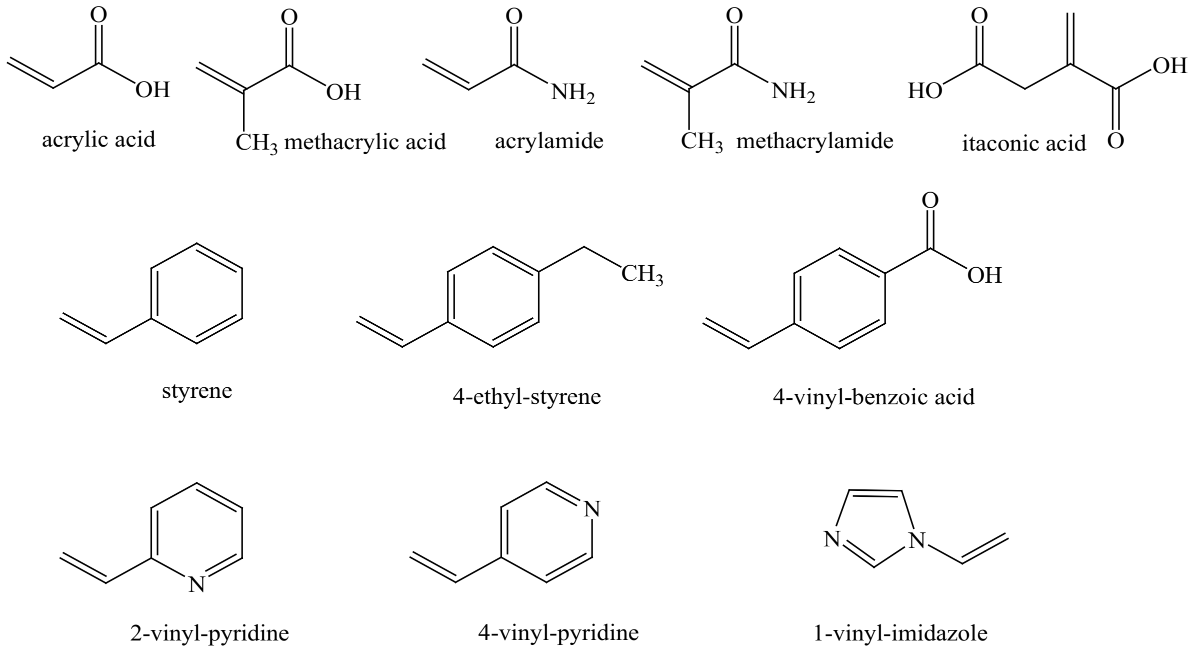


Fig. 3. Chemical structure of some common functional monomers used in molecularly imprinting technology.

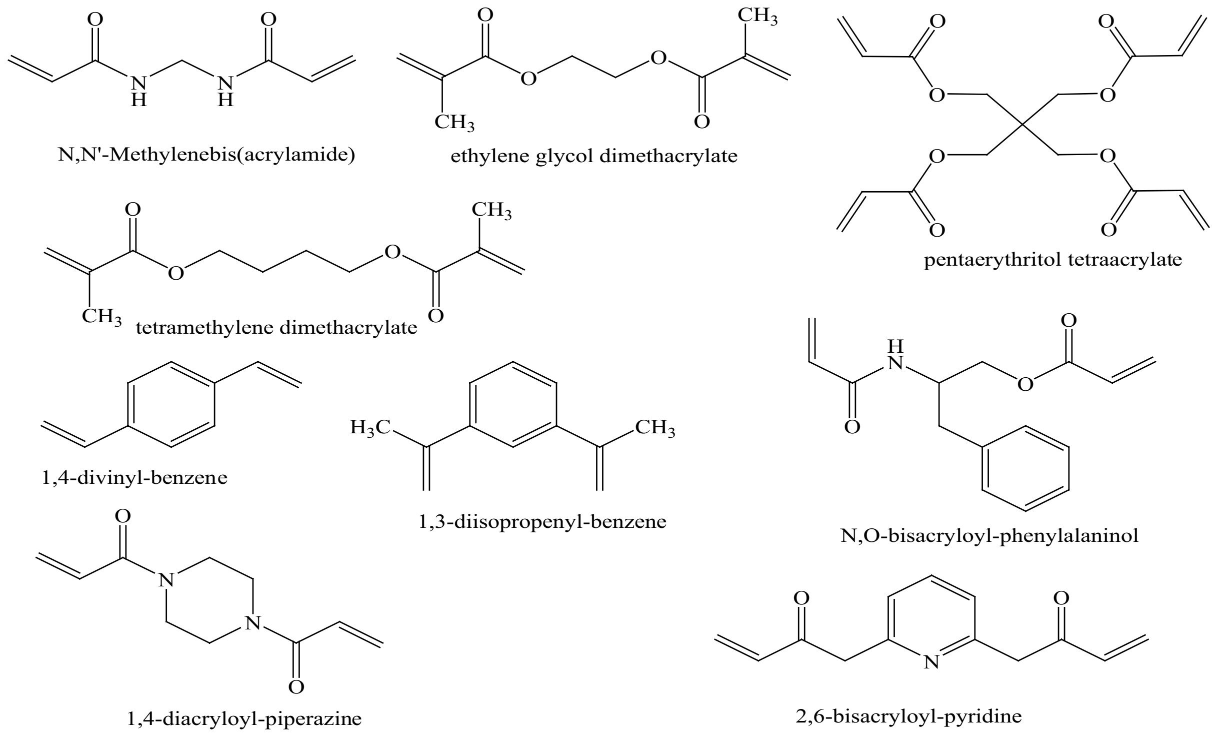


Fig. 4. Chemical structures of some cross-linkers used in the molecularly imprinting technology.

process but are also very significant for the MIP porous structure development [56]. Stability is also related with porogens because porogen must not chemically interact with the monomer-template complex. Thus, proper reagents must be chosen during the MIP synthesis process to get the desired effects [57]. Mostly, polar solvents are preferred for covalent MIP synthesis and non-polar organic solvents are used in non-covalent MIP synthesis mechanism [58]. Polymer morphology and adsorption properties are also dependent on the porogenic solvents. The selectivity and sensitivity for the template molecules are influenced by the monomers and solvents used in the MIP process [59]. Acetonitrile, tetrahydrofuran, methanol, chloroform, toluene, 2-methoxyethanol, N,N-dimethylformamide, and dichloroethane are common solvents used for the synthesis of MIP [60]. Green chemistry is getting a lot of attention worldwide; therefore a lot of focus is on the development of safe, ecofriendly, and economical solutions. ILs are being used for the synthesis of MIP over conventional porogens due to novelty, noninflammability, and high dispersion strength. ILs have been successfully employed in bulk polymerization and surface molecularly imprinting technology [61] but there is a demand to explore new solvents after toxicological studies of ILs. Room temperature ILs including [BMIM][BF_4], [BMIM][PF_6], [HMIM][PF_6], and [OMIM][PF_6] gained enormous attention and were listed in the potential porogenic solvent [62].

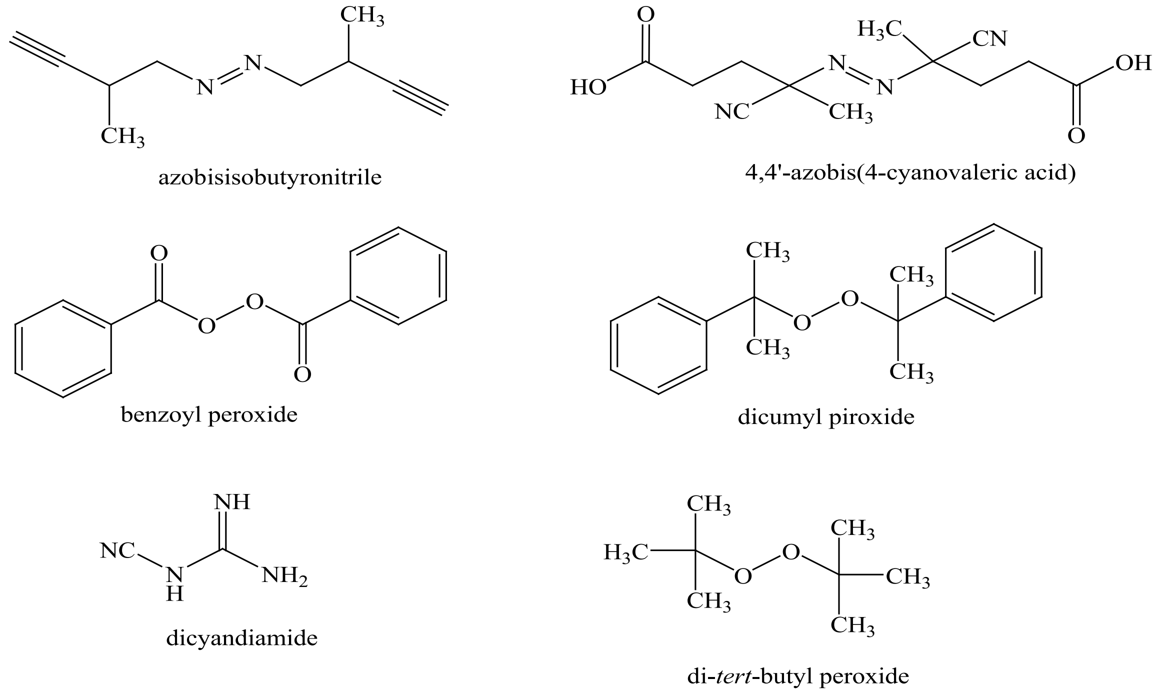
Additionally, the use of organic solvents can also be reduced in the MIP preparation by using the medium of supercritical carbon dioxide ($scCO_2$) in a heterogeneous reaction system [63]. Lee et al. [64] synthesized MIP for the removal of carbamazepine(CMZ) by using $scCO_2$ and adsorption properties were measured. MAA, CMZ, and EGDMA were used as functional monomers, templates, and cross-linkers, respectively. The prepared MIP was selective and sensitive toward the target molecule of carbamazepine (CMZ).

2.5. Initiator

MIPs are synthesized by various processes including electropolymerization, free radical polymerization (FRP), and photopolymerization. Photochemical or thermal ways are used to initiate FRP process for a wide range of analyte structures and functional groups. Various azo and peroxy compounds are widely used in the MIP synthesis process [65,66]. Azobisisobutyronitrile (AIBN) as initiator. A successful polymerization process requires an inert gas, argon, or nitrogen atmosphere [67]. Some important initiators for MIP are shown in Fig. 5.

2.6. Template

MIT has gained a lot of attraction and a variety of analytes/templates are being targeted for environmental, chemical, biological, industrial, and biological interests [68]. There are three requirements for an ideal template: (i) polymerization should not be prevented by the functional groups of templates; (ii) template functional groups should be interacted with functional monomers to form complexes; (iii) template should be chemically stable during the polymerization process [69]. So far, MIT has exhibited promising progress by imprinting a large variety of templates of small organic molecules. Additionally, imprinting of big biomolecules is still a challenging task. Firstly, high cross-linked



azobisisobutyronitrile

4,4'-azobis(4-cyanovaleric acid)

benzoyl peroxide

dicumyl piroxide

dicyandiamide

di-*tert*-butyl peroxide

Fig. 5. Some initiators used in the molecularly imprinting technology.

gels hinder the mass transfer of the template for large template molecules. Furthermore, template crosslinking to the network can also cause immobilization. Secondly, imprinting generally can be done in aqueous medium while the biomacromolecule has a sensitive structure and different soluble properties which limit the choice of the monomer. Thirdly, the complexity of biomacromolecules and strongly varied physicochemical properties in different regions may cause cross-reactivity and a specific binding [70]. Despite the challenges, many successful efforts have been done for biomacromolecule imprinting. In a study, Venkataraman et al. [71] produced molecularly imprinted hydrogels and demonstrated that polymer composition determines the polymer recognition characteristics.

Furthermore, metal ions have been successfully imprinted to generate ion-imprinted polymers. Selectivity was a major concern in the imprinting of metal ions of the same charges having similar properties and ionic radii. Ion imprinting has been improved by the incorporation of a method of using ligand complex and metal ions as actual template material for the imprinting process. Ligand selection is also important because ion recognition process includes ion chelation. The important ligand are those which have one or more chelating groups for the interaction with polymer matrix and template by heteroatoms [72]. Ligand complex and metal ions are easily pre-polymerized with the monomers and polymerization reactions proceeded successfully. Metal ions are eliminated by elution and template-oriented cavities are generated in the polymer matrix which donates high specificity and adsorption efficiency for metal ions [73,74]. Mergola et al. [75] produced a imprinted Hg(II)-diphenylcarbazone complexes for the removal of mercury. The prepared Hg-MIP exhibited excellent selectivity and specificity over other metal ions.

3. Preparation procedures

A functional monomer interacts with a specific template molecule in the presence of a porogenic solvent. This is followed by the addition of cross-linker and initiator which lead to the generation of a stabilized 3D structure. There are four different approaches described between monomer and template namely; non-covalent, covalent, semi-covalent, and metal coordination approaches.

Non-covalent interactions were proposed by Mosbach in which monomers and templates are arranged through non-covalent interactions. These non-covalent interactions include van der Waals forces, hydrogen bonding, or π–π interactions. Non-covalent approach is the most popular imprinting technique due to its wide template range for a variety of applications. The imprinting cavities made in the pre-polymerization phase are adorned with non-covalent functionalities in which analytes rebound after polymerization and template cleavage [76]. These synthetic approaches are very easy because of relying on the commodity building blocks. The template removal needs very little effort via simple cleavage techniques. Monomer-template stoichiometric ratios are not maintained in this approach and the excess amount of monomer is required for template molecules binding, causing the development of many non-specific sites. However, MIPs prepared in this way are less selective because of non-covalent interactions nature. Comparatively, covalent imprinting produces well-defined recognition sites but lacks the extent of feasible template-monomer complexes [77].

The second most common methodology is the covalent approach which was proposed by Wulff [78]. It is less flexible and there are a smaller number of functional monomers available for covalent methodology in the MIPs which is why its applications are restricted. Covalent interactions established in Schiff base bonds, ketals, boronic ester bonds, or acetal bonds are examples of covalent interaction in molecular imprinting. High amount of cross-linker is used to obtain an insoluble rigid structure and cleavage of covalent bonds during the template extraction by chemical interaction leads to the formation of well-defined recognition sites. One of the advantages of covalent approach is that the precise stoichiometry of the template monomer complex permits the polymer preparation with binding clusters entirely placed in imprinting cavities that enhance the selectivity by reducing the non-specific interactions. The disadvantages include difficult template removal after polymer synthesis due to strong interactions, and the slow rebinding kinetics to re-establish the covalent bond limit its applications [58,79].

Another synthetic protocol for synthesizing MIPs is known as the semi-covalent approach. Semi-covalent imprinting combines the advantages of both non-covalent and covalent approaches. This method was designed to overcome the drawbacks of the covalent approach. There are two steps involved in the semi-covalent approach; (i) monomer and templated interact with each other through covalent bonding and the template is removed through hydrolysis; (ii) template-oriented imprinted sites non-covalently interact with the template molecules. Semi-covalent approach has some advantages over previous techniques including monomer template strong interaction, use of stoichiometric ratios, and facile template rebinding. The applications of this technique are also limited due to a smaller number of appropriate functional monomers [80,81].

In molecular imprinting based on metal-mediated interaction approach, metal ions can be incorporated in the imprinting method as templates or as template functional monomer interaction part. Metal-mediated interaction approaches have been employed for the production of metal-ion imprinted polymers; the cross-linkage of bifunctional component of linear chain polymers having ligands for metal binding, and surface imprinting at amphiphilic monomers on the interface of water-in-oil emulsions. The ion chelation is included in the ion recognition process, the ligand role is very significant. In most popular ligands, the chelating group exists that can interact with the templates and the polymer matrix [58,82].

Target molecule ions and polymerizable ligands complexed with the metal ions which can be charged or neutral species. The characteristics of the ligand and oxidation state of metal can effect the interaction strength, alike strong as a covalent bond. Metal ion-mediated imprinting has been used for distinct tertiary, or higher, metal complexes due to the problems associated with the synthesis and separation of these molecules. The polymers attained via this strategy have been applied to the preparation of ion-selective sensors and remediation studies [83,84]. This approach has applications in the imprinting of histidines, catalytic site construction, and the precise imprinting of sugars. Tamahkar and Denizli [85] reviewed the basic parameters for the metal coordination approach in the generation of MIP [86].

4. Smart imprinting strategies

General polymerization techniques used for the ion imprinted polymers (IIPs) include radical polymerization and sol–gel processes based on chain polymerization and stepwise polymerization mechanism [87,88]. Bulk, emulsion, suspension, and solution polymerization are composed of radical reactions [89]. Apart from these technologies, some of the smart MIP techniques including surface imprinting, stimuli-responsive imprinting, and dual/multiple components imprinting are discussed in this section for the preparation of IIPs.

4.1. Surface imprinting

Surface imprinting was first proposed by Takagi et al. in 1992 which involved emulsion polymerization [72]. A complex is formed between the amphiphilic monomer and template molecule at the emulsion interface. The template is removed after the polymerization and bindings sites formed on the material surface. Binding sites are crated near or on the polymer surface, low mass transfer is attained and complete extraction of templates is achieved. The binding sites on the shells of core-shell structured microspheres help in template ions elution and diffusion [90]. Other carriers also play auxiliary supporting roles in the imprinting method. The most popular materials are modified silica particles [91], quantum dots [92], magnetic nanoparticles [93], chitosan [94], and active polystyrenes [95].

4.2. Stimuli-responsive MIP

Stimuli-responsive polymers, also known as smart polymers, produce a relative response when subjected to external environmental stimuli like temperature, pH, magnetic, and chirality [96].

Stimuli-responsive MIPs are designed by the combination of molecular imprinting techniques and stimuli-responsive materials which produce the ability to counter external stimuli and control their interactions with the template by binding sites [97]. Currently, various smart MIPs have been reported that respond to stimuli for different medical and environmental applications [98,99].

4.3. Dual/multiple components imprinting strategies

IIPs are suitable materials for the extraction and separation of heavy metal ions from the environment, but still selectivity can be improved by multiple components imprinting strategy. In this strategy, dual template ions and dual/multiple functional monomers are used and also have got attention with time [89,100]. We have added some important work in the next part of the review which contains examples of dual templates and dual/multi-functional monomer phenomena.

5. Polymerization factors affecting MIP performance

There are various polymerization factors that control the MIP performance, mainly are temperature, pressure, quantity of initiators, and polymerization time. Every polymerization process in critical and monomer-template complex stability is required during the polymerization. Low temperature is preferred due to enhanced polar interaction force and less movement of vibrational nodes. This criterion is not fixed because sometimes polymer systems behave unusual [74,101,102]. Furthermore, Sellergren et al. [103] reported the effect of pressure by preparing the same sort of MIP at high and low pressure for atrazine and ametryn. MIP prepared under high pressure had more affinity than the MIP prepared at low pressure. High-pressure effect positively on intramolecular associations and enhances binding affinity.

Time also plays important role in the conversion of monomeric units into the polymer and a long time produces the rigid polymer having well-defined imprinting sites due to prolonged reaction, resulting MIP will have high selectivity and specificity. It is crucial to maintain a medium between polymer flexibility and rigidity because rigid polymers may have decelerated binding kinetics [104,105].

The amount of initiator used in polymerization plays also important role. High amounts of initiator form rigid polymer having well-oriented cavities with high specificity and better-defined shape. On the other hand, a lower concentration of initiator reduces the temperature inside of polymerization mixture which is significant for the development of appropriate distinctive cavities of imprinting [106,107]. It concludes that MIP prepared for a long time of polymerization, with lower temperatures and low initiator concentrations has excellent binding sites and high efficiency.

6. MIPs for the removal of heavy metals

As discussed earlier, heavy metal ions discharged from industries contaminate the environment by mixing in wastewater and gases that induce toxicity in various substances. They are a serious risk to human health and the green environment nowadays [108–110]. Bioaccumulation and non-biodegradability of heavy metals raise great concern. Toxicity of metals is concerned with different factors like route, exposure, dose, chemical species, and genetics etc. [111]. Cadmium, mercury, chromium, copper, nickel, and lead are the most prominent metals which ranked the most significant related to human health. MIPs are excellent materials for the elimination of heavy metals from the environment due to their high sensitivity and selectivity over conventional methods. Table 1 represents various important studies of metal ion removal by the MIP.

6.1. Cadmium (Cd)

Cadmium is a toxic metal that causes cancer by entering in the human body through food contaminants and is recognized as a poisonous pollutant worldwide. Long-term exposure to Cd also leads to lung cancer, hematuria, kidney failure, and bone mutilation [112,113]. 10 μg·L^{-1} is the critical limit of Cd for drinking water which is determined by the World Health Organization (WHO) [114]. Cd is released during the zinc processing because Zn ores contain Cd as a general impurity. Cd has wide applications in pesticides, alloys, electroplating, Ni-Cd batteries, and much more that is why Cd has vast exposure to the living organism by contaminating water, food, and air [115,116].

Felix et al. [117] reported polymer IIP for the selective removal of Cd ion by mixing the Cd with 2-(2-thiazolylazo)-4-cresol (TAC) and polymerization were proceeded by the functional monomers of MAA along with EGDMA and AIBN. Nitric acid was used to eliminate the Cd ions from the polymer matrix. IIP showed the maximum adsorption capacity of 84.75 mg·g^{-1} that was measured by Langmuir isotherm. Limit of quantification, detection, and enrichment factor was found to be 0.46, 0.14, and 44 μg·L^{-1}, respectively. Cd ion adsorption efficiency was increased by the imprinting of Cd(II) on the aminoethyl chitosan (AECS) surface and further coating the mixture on the Fe_3O_4@SiO_2 nanoparticles. Non imprinted polymer (NIP) was also synthesized to compare the response of Cd(II)-IIP. Adsorption–desorption mechanism was investigated at optimum 6 pH for 60 min. Cd(II)-IIP adsorption capacity was measured by Langmuir equation at optimum pH and room temperature which was 26.1 mg·g^{-1} while Cd(II)-NIP exhibited the adsorption capacity of 6.7 mg·g^{-1}. Selectivity of the synthesized material was also evaluated by relative selectivity factor (βr) which were 2.061, 3.875, and 3.315 for Cd(II)/Pb(II), Cd(II)/Cr(II), and Cd(II)/Cu(II), respectively. Selectivity coefficient is defined as the ratio of the distribution coefficients of the analytes and imprinted polymer. Additionally, Cd(II)-IIP exhibited good reusability and stability with the retained adsorption capacity of 74% after 6 cycle of adsorption–desorption [118]. In an important study, Xu et al. [119] reported magnetic ion imprinted polymer (MIIP) by surface imprinting technique, using dual monomers MAA and AA, EGDMA as cross-linker, Fe_3O_4@SiO_2 as base, vinyltrimethoxysilane (VTMS) as ligand, and AIBN as initiator. Fig. 6 represents the complete steps of MIIP synthesis. MIIP exhibited excellent adsorption capacity of 46.8 mg·g^{-1} for Cd(II). Selectivity test was also performed by measuring the response of MIIP for Ni(II), Cu(II), and Pb(II) that were 2.57, 2.97, and 3.17, respectively which was higher than 1. Cd(II) was successfully extracted from the rice samples with recovery method and detection limit of 80%–103% and 0.05 ug L^{-1}, respectively with less than 4.8% relative standard deviation (RSD). With extension in technology, Guo et al. [120] synthesized poly (N-isopropyl acrylamide) imbedded graphitic carbon nitride MIIP. Pseudo-second-order (P-S-O) model and Langmuir isotherm model were used to measure the results from experimental data. Fabricated MIIP exhibited the maximum adsorption capacity of 184 mg·g^{-1} at 250 mg·L^{-1} concentration at pH 6 and 303 K temperature. MIIP was very selective for the adsorption of Cd(II) due to specific template cavities and even the adsorption capacity was 84% in five successive adsorption–desorption cycle.

Agriculture wastes and beer brewing produce a lot of waste as by-products. Beer yeast is one the important waste product which is cheap and can be used as adsorbent material. Xie et al. [21] synthesized MIIP through sol-gel method by using waster beer yeast as functional monomer, tetraethyl orthosilicate (TEOS) as cross-linker, and ammonia as initiator. MSPE-graphite furnace atomic absorption technique was used to determine the Cd in environmental and food samples. MIIP and MNIP exhibited the maximum adsorption capacity of 62.74 and 32.38 mg·g^{-1}, respectively. Pseudo-second-order kinetic model was fitted for MIIP adsorption. After the four adsorption–regeneration cycles, the recovery rate was 90.7%. MIIP also recognized the Cd(II) with the LOD of 0.18 mg·L^{-1} for the 10 mg·L^{-1} standard solution.

Dual substances can also be extracted simultaneously from MIP. Rahangdale et al. [122] reported dual MIP for the simultaneous extraction of Cd and salicylic acid (SA).

Table 1
Comparative studies of ion imprinted polymer towards various heavy metal ions

Template	Monomer	Cross-linker	Initiator	Synthesis conditions	Adsorption capacity (mg·g^{-1})	References
Cd(II)	MAA	EGDMA	AIBN	60°C, 3 h	84.75	[117]
	Chitosan	Glutaraldehyde (GD)	–	60°C, 2.5 h	26.1	[118]
	MAA, AA	EGDMA	AIBN	65°C, 6 h	46.8	[119]
	N-isopropylacrylamide	Epichlorohydrin	Potassium persulfate	60°C, 10 h	184	[120]
	Waste beer yeast	Ethylenediaminetetra-acetic acid	Ammonium ferric sulfate	35°C, 24 h	62.74	[121]
	Chitosan	Epichlorohydrin	–	50°C, 4 ho	38.46	[122]
	Curcumin	EGDMA	AIBN	80°C, 24 h	106	[123]
Hg(II)	MAA/HEMA	EGDMA	Benzoyl peroxide	70°C, 2 h	1.11	[129]
	Vinyltrimethoxysilane	EGDMA	Benzoyl peroxide	70°C, 1 h	62.27	[130]
	Carboxymethyl cellulose	Epichlorohydrin	Ammonium persulfate	45°C, 24 h	80	[131]
	AA/acrylonitrile	EGDMA	AIBN	70°C, 2 h	21.6	[132]
Cu(II)	Degreasing cotton (modified)	Epichlorohydrin	Ammonium persulfate	Not mentioned	41.49	[140]
	Allyl chloride	EGDMA	AIBN	60°C, 8 h	175	[141]
	N-propyl acrylamide	*N,N*-methylene-bis-acrylamide	Ammonium persulfate	70°C, 12 h	45.46	[143]
	4-vinyl pyridine, MAA	Pentaerythritol triacrylate	Benzoyl peroxide	80°C, 6 h	2.163	[142]
Cr(VI)	MAA	EGDMA	AIBN	65°C, 24 h	169.49	[144]
	3-(2-aminoethylamino) propyltrimethoxysilane	Hexadecyltrimethyl-ammonium bromide	–	40°C, 12 h	438.1	[145]
	CAB	Glutaraldehyde	–	45°C, 6 h.	679.13	[146]
	4-vinylpyridine	EGDMA	AIBN	80°C, 5 h	0.006476	[147]
Cr(III)	Azo dye functionalized chitosan	Glyoxal	EDC	45°C, 12 h	250	[148]
Ni(II)	AA	EGDMA	AIBN	60°C, 6 h	81.73	[149]
	MAA	EGDMA	AIBN	65°C, 12 h	158.73	[150]
Pb(II)	2-(allyl sulfur) nicotinic acid	EGDMA	AIBN	70°C, 24 h	29.67	[151]
	MAA/4-VP	EGDMA	AIBN	60°C, 8 h	40.52	[152]

Biopolymer chitosan was used as functional monomer along with Cd and 4-hydroxy benzoic acid (4HBA) as inorganic and organic templates, and epichlorohydrin as cross-linker in suspension polymerization method. 4HBA was added during polymerization reaction as a dummy template for SA and generated cavities exhibited good uptake of SA. Cd and SA exhibited the rebinding capacity of 38.46 and 23.81 mg g^{-1}, respectively. Langmuir model fitted on the adsorption isotherms for Cd and SA with 0.994 and 0.995 values of R^2, respectively. Another study by Biwas et al. [123] exhibited selective removal of Cd, Co, and Pb ions by using EGDMA as cross-linker, curcumin as functional monomer, and AIBN as initiator. After polymerization, template metals were extracted from polymeric matrix by using aqueous HCl for the selective adsorption of the template metal ions. The highest adsorption intensity was measured at the optimum pH of 6 for Cd(II), Co(II), and Pb(II) as 85, 106, and 113 mg·g^{-1}, respectively. IIP exhibited excellent regeneration ability after 10 cycles of adsorption–desorption without any significance change in adsorption capacity.

6.2. Mercury

Mercury is a naturally occurring metal and is mainly released by various geothermal activities. Hg forms organic complexes and inorganic salts; and is found in both oxidative states [124]. Methylmercury is the most toxic form of Hg because of its good affinity with sulfhydryl ligands present in amino acids which lower the protein vicissitudes and causes dysfunction [125]. Hg is the most poisonous metal among all toxic elements. Every year, 2220 metric tons of mercury contaminate the environment [126], and terrestrial soil contains 95% remainder residues of mercury [127]. Anthropogenic activities originate 70% of mercury pollutants in the environment [128]. Khairi et al. reported a mercury imprinted copolymer by using the stock solution

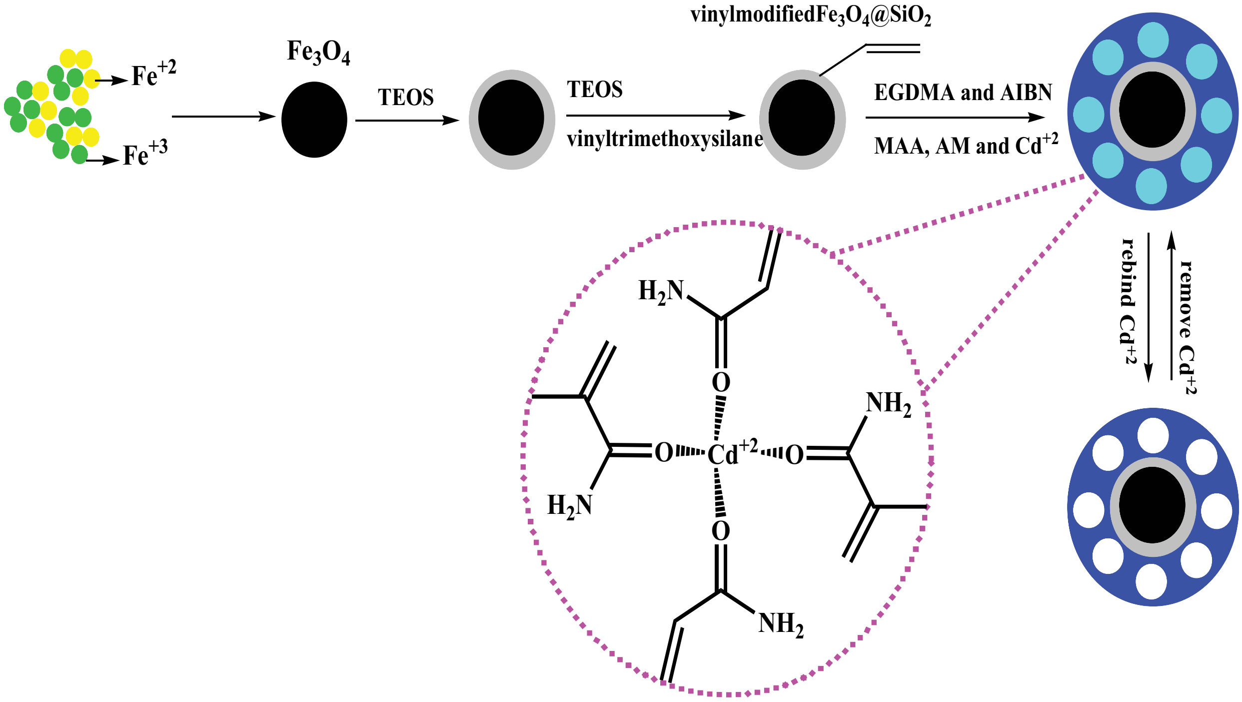


Fig. 6. Schematic representation for the synthesis of dual monomer magnetic ion imprinted polymer based on the study of Xu et al. [119].

of mercuric nitrate as template, 2-hydroxyethyl methacrylate (HEMA) and MAA as monomers. The polymerization was proceeded in the porogen solvent of methanol in the presence of EGDMA cross-linker. Solid phase extraction (SPE) method was used to determine the results of Hg(II) imprinted polymer at optimum pH 7. Hg(II) imprinted polymer surface area was measured in the 100 to 140 µm diameter size range that was 19.45 $m^2 \cdot g^{-1}$. Hg(II) imprinted adsorbent exhibited the adsorption capacity of 1.11 $mg \cdot g^{-1}$ with elimination of 87.54% Hg(II) ions [129]. In another study, Hg-IIPs were synthesized by radical polymerization of 3-mercaptopropyltrimethoxysilane ligands and Hg(II) complex, vinyltrimethoxysilane, and EGDMA as template, monomer and cross-linker, respectively with the 1:6:6 mole ratios. Hg-IIPs contained silica core to support the polymer matrix. Hg-IIPs removed the mercury ions with the adsorption capacity of 62.27 $mg \cdot g^{-1}$ at pH 4 with 1.5-h interaction time. Selectivity was also determined by comparing the adsorption performance of Hg-IIPs towards Cu(II), Cd(II), and Pb(II) ions in quaternary solutions attained the selectivity coefficient of 2.07, 16.82, and 46.92 for Hg/Pb, Hg/Cd, and Hg/Cu, respectively [130].

Carboxymethyl cellulose (CMC) is a low-cost and natural derivative material with suitable adsorption characteristics. Velempini et al. [131] reported CMC thiol imprinted polymer for Hg(II) adsorption with high selectivity. Complex was formed between the Hg(II) and ligand cysteamine and imbedded along epichlorohydrin and further crosslinked with CMC polymeric chain by an amide reaction. Isotherm and kinetic models were used to evaluate the adsorption capacity of sulfur containing IIPs (S-IIPs) corresponding the adsorption procedure tailed a P-S-O which fitted with Langmuir isotherm having 80 $mg \cdot g^{-1}$ maximum adsorption efficiency. S-IIPs showed high selectivity towards mercury ions in presence of Cd^{2+}, Pb^{2+}, Co^{2+}, Zn^{2+}, and Cu^{2+}. Furthermore, real samples of tap water, ground water, and wastewater were examined and Hg(II) recovery rate was found 99.10%, 91.88%, and 86.78%, respectively.

With extension of MIP technology, Esmali et al. [132] synthesized ion imprinted membranes (IIM) based on poly(ether sulfone) by using phase inversion and IIP were attained by acrylonitrile, acrylamide, and EGDMA radical copolymerization with bathophenanthroline (BPh) mercury ion complex. Response Surface Methodology (RSM) and Central Composite Design (CCD) were used to the the optimization of Hg(II) elimination ability. IIM mercury percentage was 98.1% with 37.5 $kg \cdot m^{-2} \cdot h$ flux under optimum parameters. IIM exhibited the maximum adsorption capacity of 432 $mg \cdot m^{-2}$ which was four time higher than NIM (105 $mg \cdot m^{-2}$).

6.3. Copper

Copper is released in the environment through various anthropogenic sources and 95% of waste Cu enters in aquatic sediments and soil to accumulate toxicity by the high concentration of 50–500 $\mu g \cdot L^{-1}$ [133]. Cu reduces the chemosensory and chemoreception response of the aquatic animals that affect the prey-predator mechanism and also detection conspecifics [134]. Excess and low amount of Cu also effect and harm the human body. Excess amounts of Cu lead to fatal health effects including immunotoxicity also liver and kidney failure whereas low amount of Cu causes osteoporosis and hypochromic anemia. Therefore, Cu balance is necessary for body fluids as well as in various environments [135]. It is common knowledge, Cu is toxic for which the Cu limit for drinking water is up to 1.3 mg L^{-1} which is determined by EPA [136]. Liu et al. [137] constructed ion imprinted films (IIF) to capture low concentration of Cu by the combination of electrochemical ion switching technology with the IIP. Cu^{2+}-IIF was synthesized by using doping agent potassium ferrocyanide, pyrrole as conductor and cross liker, and template of Cu^{2+} ion. Reductions and adsorption phenomenon were combined to enhance the sensitivity of IIF and 90% of Cu^{2+} ions were eliminated at low concentration (5 ppm). Adsorbent exhibited high selectivity factor of Cu^{2+}-IIF towards Ni^{2+}, Zn^{2+}, and Cd^{2+} with 30.16, 26.52, and 49.27, respectively with 7.57 $mg \cdot g^{-1}$ adsorption capacity at 5 ppm Cu ion concentration. IIF removal capacity remained 95.13% even after 5 recycles.

In a recent study, Sun et al. fabricated surface imprinted polymer (SIP) from polyethyleneimine (PEI) imbedded with chloromethylated polystyrene (CMP) micro spherical beads for the elimination of Cu(II)-citrate (Cu(II)-CA). Cu-CA-SIP attained the imprint of Cu(II)-CA anions in their polymeric matrix with 1:1 molar ration between template and Cu-CA-SIP. Cu(II)-CA elimination rate was observed 100% at 0.5 $mmol \cdot L^{-1}$ concentration and at high concentration of Cu(II)-CA, the rate ranges 1.38 $mmol \cdot g^{-1}$ at 30°C. In Cu(II)/Cd(II)-CA, Cu(II)/Zn(II)-CA, Cu(II)/Ni(II)-CA, and Cu(II)/Fe(III)-CA systems, the Cu-CA-SIP comparative selectivity coefficients for Cu(II)-CA were 44.55, 1.40, 2.32, and 9.66, respectively. First time, the imprinting material was constructed on coordination-configuration based recognition framework for electroplating wastewater treatment [138]. With the extension in MIT, Chen et al. prepared green IIPs in in aqueous phase by the synergy of three low cost and ecofriendly functional monomers gelatin (G), 8-hydroxyquinoline (HQ) and chitosan (C), namely G-HQC IIPs. G-HQC IIPs were used for the removal of Cu(II) from aqueous solution and various adsorption affection factors were studied including tempreture, pH, and contact time. G-HQC IIPs followed the Langmuir isotherm and p-s-o kinetic models with the maximum adsorption capacity of to 111.81 mg/g at room temperature. The prepared adsorbent exhibited very high selectivity and also good reusability after ten cycles without any notable loss in adsorption capacity. Real water samples (lake, river, and sea) were also analyzed by the G-HQC IIPs and results for Cu(II) removal were satisfactory. Templates were also changed by replacing the Cu(II) with Hg(II), Pb(II), and Cd(II), respectively, the obtained three G-HQ-C IIPs performed efficiently, and this work open the door for imprinting of various heavy metal ions through multiple green functional monomers for interactions [139].

Degreasing cotton has good hydrophilic characteristics with high flexibility and a larger surface area. Cotton matrix enhances the functional ability of the surface imprinted polymers to adsorb the Cu ion from aqueous solution. In a new study, surface imprinting method was used to prepare ion-imprinted degreasing cotton (IIC) by the reaction of epichlorohydrin and degreasing cotton in presence of *N,N*-dimethylformamide and diethylenetriamine. IIC exhibited the highest adsorption capacity of 41.49 $mg \cdot g^{-1}$ at 6 pH by following kinetic model of P-S-O and Langmuir adsorption isotherm for five consecutive adsorption–desorption rotations [140]. Sensitivity of the magnetic Cu(II) IIP was enhanced by Imidazole-4,5-dicarboxylic acid and allyl chloride polymerization to synthesize Fe_3O_4@IIP-IDC. SPE optimization was performed by Box- Behnken design to attain the dual objectives of detection and adsorption of Cu(II). Adsorption capacity of 175 $mg \cdot g^{-1}$ was measured with BS isotherm model and Freundlich PSO kinetic model. The linear range was found to 10–5,000 $\mu g \cdot L^{-1}$ ($R^2 = 0.9986$), with LOQ of 4.5 $\mu g \cdot L^{-1}$ and LOD of 1.03 $\mu g \cdot L^{-1}$. Cu(II) adsorption accuracy was evaluated by recovery experiments and standard reference materials analysis in battery wastewater and food samples. Fe_3O_4@IIP-IDC adsorbent was rapid, selective and reusable (15 cycles) [141].

In a remarkable study, Liu et al. combined the magnetic properties with thermosensitivity and developed thermoresponsive IIP for the removal of Cu. Cu^{2+}-IIP was synthesized by using functional monomer of *N,N*-methylene-bis-acrylamide. The complete scheme of the Cu^{2+} adsorption by IIP is described in Fig. 7. Cu^{2+} adsorption increased with temperature and maximum adsorption of 45.46 $mg \cdot g^{-1}$ was recorded at 35°C. βr was found 6.77, 7.60, and 7.14 for Cu^{2+} with respect to Cd^{2+}, Zn^{2+}, and Ni^{2+}, respectively [138]. A recent study by Chaipuang et al. [142] demonstrate the preparation of IIP based on MAA or 4-VP, ethylenediaminetetraacetic acid (EDTA), copper(II) sulfate pentahydrate, methanol, pentaerythritol triacrylate (PETA) as functional monomers, ligand, template, porogen, and cross-linker, respectively. Adsorption capacity of the prepared adsorbent was enhanced from 0.794 to 2.163 $mg \cdot g^{-1}$ within 24 h at 6 pH. The selectivity factor of Cu-IIP exhibited the progression $Mn^{2+} < Zn^{2+} < CuCl < Cu^{2+} < CuSO_4\text{-}5H_2O$ aqueous solution. This shows that Cu-IIP are the promising material to adsorb the Cu(II) from aqueous solutions.

6.4. Chromium (Cr)

Chromium is frequently used in various industries like metal cleaning, photography, and leather tanning. The release of industrial waste contains chromium metal that contaminates the aqueous environment and causes various hazards [153]. Among the two states of chromium, Cr(III) is a naturally occurring component, stable, less toxic, and an important substituent for the human body because Cr(III) functionalizes lipid metabolism but high amount lead to various health harms [154]. Cr(VI) is extremely toxic and a high amount leads to cancer. 0.1 mg L^{-1} is the highest permissible limit of Cr(VI) in surface water [155]. Therefore the removal of Cr ion is necessary from the environment and Kumar et al. [144] reported a magnetic IIP for the selective removal of Cr(VI) from aqueous media by capping Fe_2O_3 nanoparticles with silica amine derivative and MAA monomers. Dichromate $(Cr_2O_7)^{-2}$ ion, EGDMA, AIBN, and 4-VP were used as template, cross-linker, initiator, and ligand, respectively. Results followed the Langmuir isotherms and kinetic measurements were well designated through pseudo-second-order. Cr-MIIPs exhibited the maximum adsorption ability of 169.49 $mg \cdot g^{-1}$. The quantification, LOD, and RSD were found 2.7 $ug \cdot L^{-1}$ and 0.81 $\mu g \cdot L^{-1}$.

Carbon-based mesoporous materials have gained a lot attention due to large surface area, high active sites, and various functional groups to interact the analyte of interest [156]. Huang et al. [145] incorporated GO mesoporous silica (GO-MS) nanosheets with 3-propyl-trimethoxysilane monomer to increase the strengthe of imprinted polymer strength. Investigations about functional monomer amount influence,

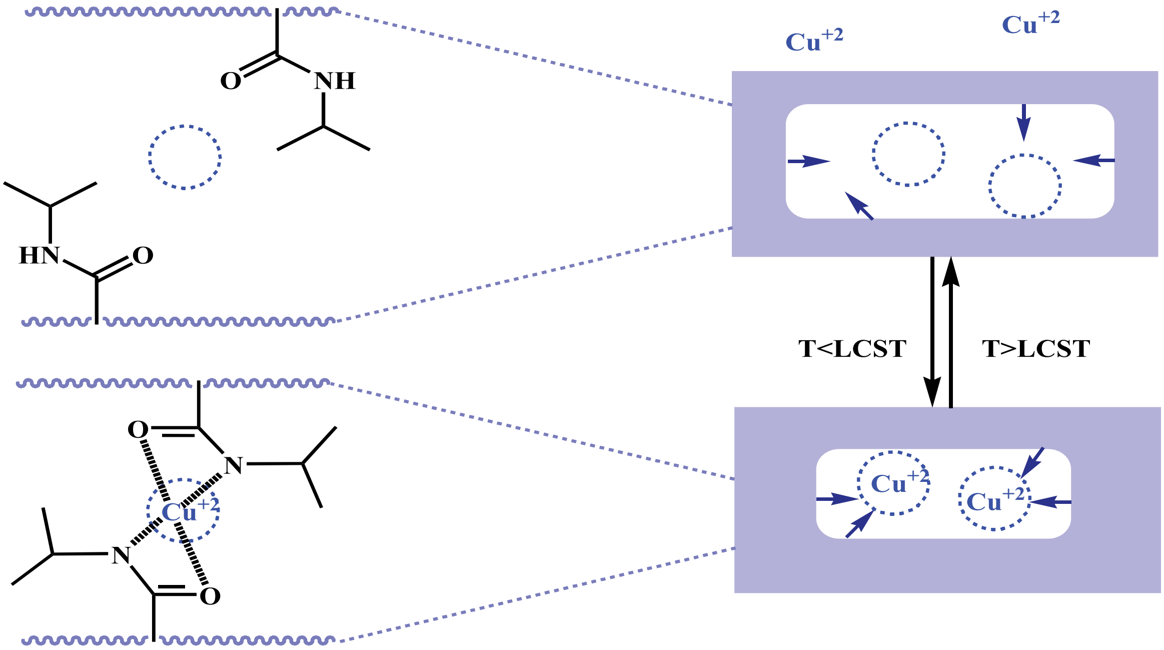


Fig. 7. Adsorption–desorption mechanism of Cu^{2+}-IIP based on the study of Liu et al. [143].

pH, tempreture, Cr(VI) concentration, and contact times were performed. High adsorption capacity of 438.1 mg·g^{-1} was achieved with in 5 min by following Freundlich and P-S-O kinetic model. The fabricated Cr(VI)-IIP exhibited high sensitivity and selectivity which made it a potential adsorbent to remove Cr(VI) from wastewater.

Biopolymers based IIP are very promising substances with good features of selective biding and elimination of metal ions. Chitosan is also a biopolymer having amino and hydroxyl groups for metal chelate production and being used for IIP synthesis. Chitosan-derived IIP has low mechanical strength, especially in a slightly acidic medium that decreases the active sites of chitosan and decreases the adsorption efficiency [157,158]. Elsayed et al. [148] reported AZCS-IIP for Cr removal by impregnation of azo dyes with chitosan and the addition of active groups in chitosan enhanced the strength and coordination capacity of the polymer matrix. Chitosan amine group attached the azo dyes by amide linkage by using EDC/NHS coupling materials and further processed in glyoxal solution to form micro spherical beads of chitosan chains with coordinated Cr(III) ions. AZCS-IIP exhibited a selective response towards Cr(III) in presence of other metals 293 mg·g^{-1} adsorption was measured at 20 ppm concentration in presence of 1 g·L^{-1} adsorbent at pH 5 with βr of 15.15, 10.98, 9.85, 9.37, and 9.38 for Fe(III), Eu(III), Al(III), Ni(II), and Co(II), respectively.

Adsorptive composites for high selective elimination of Cr(VI) ion remained a challenge due to cross-contamination between complex co-existed ions. In a new study, Yang et al. designed a site-imprinted hollow aggregates (IIHS) with Al-gelled CMC beads, Cr(VI), and glutaraldehyde as substrate, template, as cross-linker for Cr(VI) adsorption with high affinity and fast capturing mechanism. Cr(VI)-IIHS exhibited the highest adsorption capacity of 679.13 mg·g^{-1} by reaching at equilibrium in a short time and maintained its performance by adsorbing beyond 530.91 mg·g^{-1} after six cycles [148]. Efficiency and selectivity of IIP for Cr(VI) can be enhanced by the addition of natural zeolite (NZ) in polymer matrix. IIP@NZ was synthesized by using Cr(VI), 4-Vp, acetone, EGDMA, and BPO as template, monomer, porogen, cross-linker and initiator, respectively. IIP@ANZ showed the maximum adsorption capacity of 6.48 mg·L^{-1} which was greater than for NIP@NZ (3.266 mg·L^{-1}). The adsorption process followed the Langmuir isotherm and P-S-O kinetic models and the fabricated adsorbent did not show any decrease in adsorption efficiency after five regeneration cycles [147].

6.5. Nickel (Ni)

Ni is extensively dispersed in various environments and main sources of Ni are natural and anthropogenic activities. Ni from industrial waste, solid and liquid fuel are producing environmental pollution and causing different health effects like lung and nasal cancer, allergy, kidney and cardiovascular diseases [159,160]. Liu et al. used 2D GO material to synthesize the IIP through RAFT polymerization because of excellent chemical and physical characteristics of GO over other materials. GO/SiO_2 composted was used to enhance the sensitivity, selectivity, and thermal stability of the IIP. Adsorption capacity of the fabricated RAFT-IIP was found 81.73 mg·g^{-1} with rapid adsorption kinetics as compared to NIP (30.94 mg·g^{-1}) [149].

Extension to the technology lead to the development of magnetic IIP by MAA, NH_2 functionalized Si-capped Fe_2O_3, and 4-Vp as functional monomer, core material, and complexion agent, respectively for the removal of Ni^{2+} from real aqueous solutions of waste industrial water. The maximum adsorption capacity was measured by the optimization various parameters such as adsorbent dose, shaking speed, and pH. The synthesized adsorbent showed the adsorption capacity of 158.73 mg·g^{-1} with high selectivity coefficient at 5 mg·L^{-1} concentration Ni^{2+} solution and pH 6. The percent RSD, quantification, and LOD were found 3.4%, 1.93%, and 0.58%. These results verifies the excellent performance of magnetic IIP for Ni(II) elimination from real aqueous solutions and the high porosity and active sites with good magnetic properties make it the excellent material for adsorption. Table 2 shows a comparative study of Kumar et al. with previous reported techniques [150].

6.6. Lead (Pb)

Pb is mainly found in silver, zinc, and copper ores, and also various anthropogenic sources release Pb in the environment [166]. Various industries use Pb in petroleum, pesticides, cables, and paints. Pb is a very dangerous pollutant due to its toxic and hazardous effects on human health, aquatic organisms, and the environment [167,168]. Ao and Guan reported hydrophilic IIP for the elimination of Pb(II) ions with the functional monomers of 2-(allyl sulfur) nicotinic acid through the precipitation polymerization technique as shown in Fig. 8. Adsorption capacity was found 29.67 mg·g^{-1} which was three times higher than Pb(II)-NIP by following Langmuir isotherm model. Pb(II)-IIP exhibited high selectivity towards Pb(II) ions in presence of other heavy metal ions, and also retained 97.2% removal rate for original samples of industrial waste water.

Table 2
Comparative analysis of various Ni-MIP based adsorbents

Adsorbent	pH	Equilibrium time	Adsorption capacity (mg·g^{-1})	References
Ni(II)-IIP	7	12	20.30	[161]
Ni(II)-IIP	6	6	125	[162]
Magnetic IIP	7	5	87	[163]
Microporous Ni(II)-CS-IIP	6	120	69.93	[164]
Surface Ni(II)-IIP-CS	4	60	20	[165]
Magnetic Ni(II)-IIP	6	20	158.73	[150]

In another study, MIPs were modified with hollow mesoporous silica (HMS) by grafting method for the rapid and selective detection and adsorption of Pb^{2+}. Fabricated MIP/HMS composite based adsorbent exhibited the maximum adsorption capacity of 40.52 mg·g^{-1} in the presence of Ni^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, and Cu^{2+} with high selectivity by the. β*r* over 50 and also retained its response after six cycles by recovering 100% ions in original water samples. The excellent adsorption capacity, rapid response and high selectivity made the IIP as a potential adsorbent for Pb ion elimination from aqueous samples [152]. Table 3 represents various comparative studies related to Pb adsorption.

7. MIP for adsorption of dyes

MIP has very wide applications not only in metal ions adsorption but also in the extraction of the dye. Various dyes are discharged from different anthropogenic sources and contaminate the water which generates various serious health issues because most of the dyes are toxic and

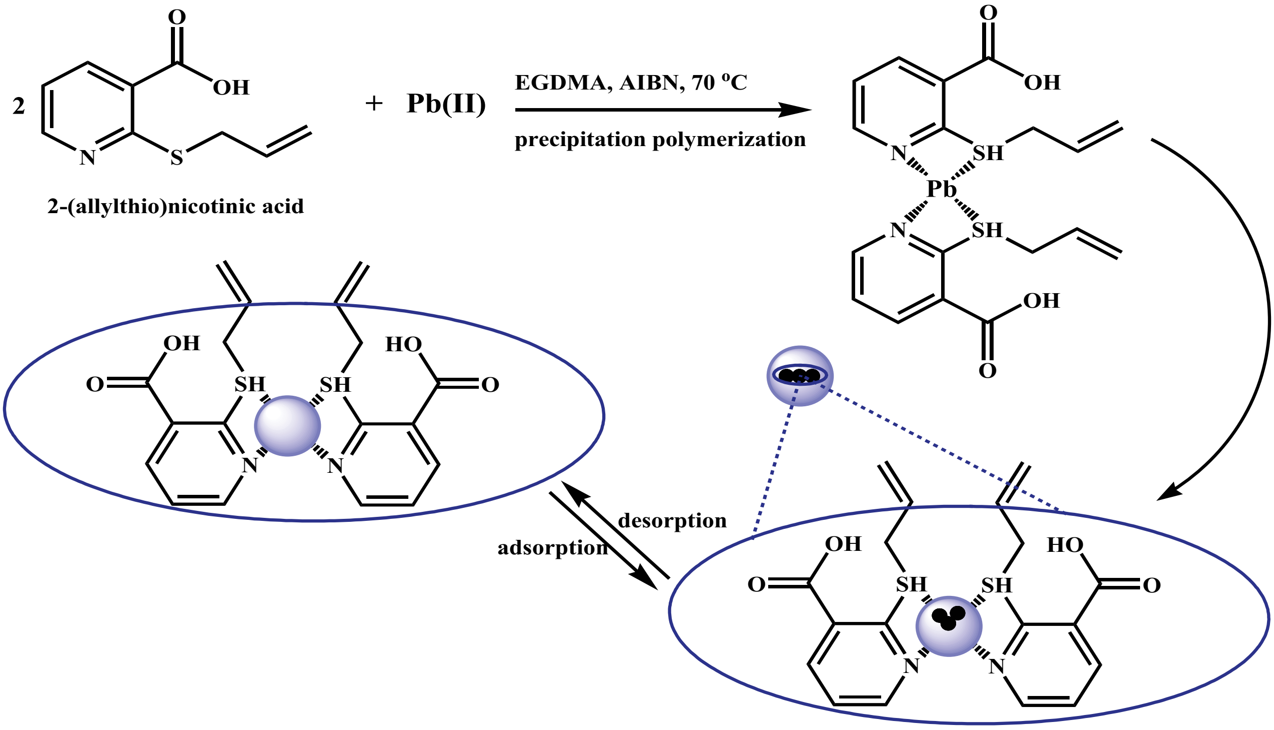


Fig. 8. Fabrication mechanism of Pb(II)-IIP based on the study of Ao and Guan [151].

carcinogenic [174–176]. In this regard, extraction of the dyes is necessary and different methods like ion exchange, biological treatment, and oxidation etc. are being used [177–179] but the most effective method of dyes removal is adsorption. This article reviews some selective studies on the adsorption of various dyes by MIP.

7.1. Congo red

Congo red is a toxic anionic dye that causes cancer and mutagen in human beings [180]. The complex structure of Congo red (CR) makes it chemically stable towards biodegradation, and obviously, adsorption is the only solution to remove the Congo red dye from the environment [181,182]. Various coloring agents are used in food to make them attractive which are not only illegal but also carcinogenic. Liu et al. [183] synthesized bifunctional MIP with monomers of [2-(methacryloyloxy) ethyl]-trimethylammonium chloride (DMC) and β-Cyclodextrin-maleic anhydride (β-CD-MA), template of CR, and cross-linker of *N,N*-methylenebisacryl amide (MBA), respectively. Fig. 9 shows the MIP synthesis using the CR matrix. SPE mechanism was used to extract

Table 3
Comparatives studies of various Pb(II)-IIP

Adsorbent	pH	Polymerization method	Adsorption capacity (mg·g^{-1})	References
Pb(II)-Si/IIP	6	Surface imprinting	3.5	[169]
Pb(II)-IIP	5	Bulk polymerization	2	[170]
Pb(II) imprinted hybrid copolymer	6.46	Bulk polymerization	7.6	[171]
Pb(II)-IIP/nano-TiO_2 matrix	5	Surface imprinting	22.7	[172]
Pb(II)-IIP (dual monomer)	7	Suspension polymerization	8.35	[173]
MIP/HMS composite	6	Surface imprinting	40.52	[152]

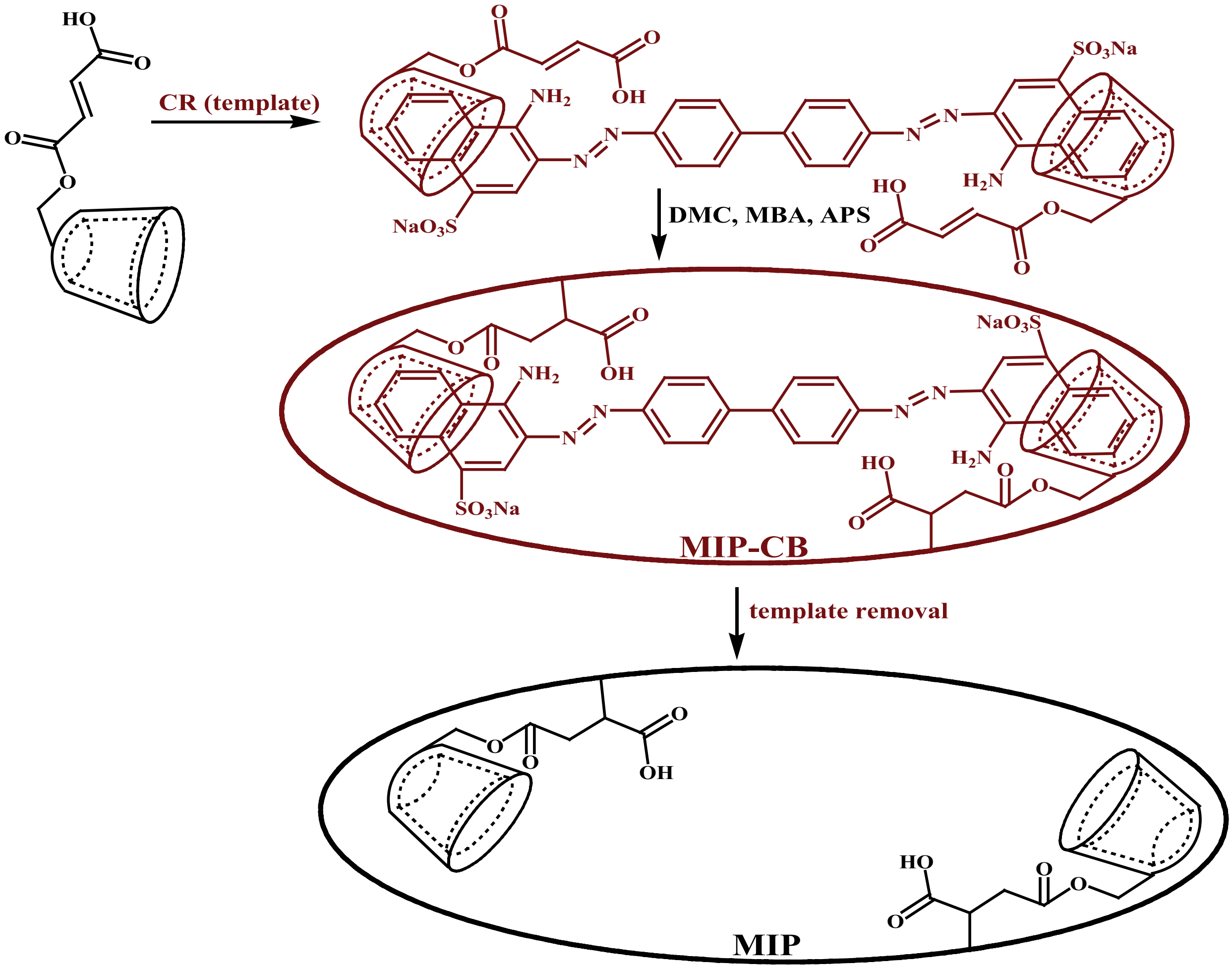


Fig. 9. Synthetic scheme of molecularly imprinted polymer for Congo red based on the study of Liu et al. [183].

Congo red from food. LOD was determined 0.07 $\mu g \cdot kg^{-1}$ with 84.2%–105.2%, percents mean recovery and RSD ≤ 1.2.

In the new study, the MIP for CR was prepared by dissolving CR in pure acetonitrile and in a DMSO mixture due to the limited solubility of the dye in a single-component system. Functional monomer MAA and cross-linker EGDMA were added in the solution and FRP was initiated by AIBN. Molar ratio of cross-linker: monomer: template for CR-MIP was 20:4:0.1, respectively. The mixture was sonicated and purged with N_2 gas to make a homogenized solution. Polymerization was processed in water bath and synthesized polymer materials were collected by vacuum filtration. CR-MIP showed high rebinding of 99.63% for 20 ppm concentration of CR with 0.5 g polymer substance at pH 7. CR was extracted by the MIP from water samples with 90% efficiency [184]. Yuan et al. described the MIP for CR by the one-step seed swelling technique, obtaining spherical MIP by rapid reaction with high monodispersity and uniform particle size. Dispersion polymerization procedure was used to prepare microspheres of polystyrene for CR template. Further reaction was proceeded by functional monomers MAA, cross-linker EGDMA, porogen acetonitrile, and initiator AIBN. Adsorption process was confirmed by P-S-O model and βr found 4.908 and 2.163 with respect to methyl orange and yellow GR. The estimation of justification data proved that the MIP has high sensitivity, selectivity and recovery for detection and adsorption of Congo red [185].

7.2. Methylene blue (MB)

Methylene blue is a cationic dye and affects the central nervous system if exposed to 1–7.5 $mg \cdot kg^{-1}$ [186] which is why the removal of MB is necessary. MB contaminates the aqueous environment and also leads to organism body by food chain [187]. Sun et al. [188] prepared an amino-functionalized TiO_2 (AT) MIP for the extraction of MB by surface MIT. MB and sodium lignosulfonate were dissolved in acetonitrile and distilled water followed by the addition of TiO_2–NH_2 and a homogenous solution formed after sonication. *N,N*-methylene bisacrylamide, and AIBN were also poured into the above solution, ATMIP was formed after polymerization. BET analysis was performed to examine the ATMIP structure which indicated that ATMIP possessed a large surface area and mesoporous structure with 2.90 eV bandgap. ATMIP attained fast adsorption equilibrium with in short time (10 min). The maximum adsorption capacity was found 40 $mg \cdot g^{-1}$ with adsorption efficiency of 66.79% after four cycles.

In another study, Hai et al. reported a magnetic MIP with the fullerene magnetic particles because fullerene enhanced the surface area and hydrophobicity increased due to delocalized π-conjugate assembly, Functional monomers were obtained through the reaction of iminodiacetic acid and methacryloyl chloride with two carboxyl groups. Magnetic MIP surface was attained with synthesized monomers, cross-linker of 2-vinylbenzene, and template of MB. The fabricated MIP-based adsorbent exhibited the maximum adsorption amount of 41.5 $mg \cdot g^{-1}$ by following Freundlich isotherm model and P-S-O equation [189].

Electrospun imprinted polymers have attained a lot of attention to adsorb various pollutants and it is interesting to associate MIT with the electrospinning technology for the adsorption of selective dyes. Sericin (SS) is a natural abundant chemical that has good adsorption properties at low cost. Rui et al. reported sericin electrospun fibers for the MB dye templates. Sericin was cross-linked with the vapors of glutaraldehyde and the mechanical strength and spinnability of the polymer matrix were improved with the addition of PVA. SS/PVA fibers exhibited a good adsorption efficiency of 58.42 $mg \cdot g^{-1}$ than the non-imprinted SS/PVA fibers with high selectivity and regeneration [190].

7.3. Rhodamine B (RhB)

Rhodamine B (RhB) is a textile cationic dye that enters in the human body with food and causes oxidative stress in nerve tissues and long exposure leads to cancer or liver dysfunction [191,192]. In a recent study, magnetic MIPs were synthesized by a composite of resorcinol-formaldehyde-melamine resin (RFMR) for the selective removal of RhB. Tea filter bag was used as a substrate and coated with polyvinylidene fluoride (PVDF). Magnetic MIP-RFMR acted as a selective filter and wild almond resin as a hydrophilic reagent. Functional monomer of resorcinol reacted with the various hydrophilic groups like $-NH_2$, –NH, and –OH in the presence of RhB template. Cross-module filtration system was processed to investigate the adsorption and filtration parameters. 0.01 g Fe_3O_4/MIRFMR of casting solution exhibited high water flux (42.5 $L \cdot m^2 h^{-1}$), removal efficiency (95.8%), flux recovery ratio (88.9%), and good wettability. Selectivity of 2.5, 2.1, 3.3, and 4.9 was measured for RhB as compared to TB, EB, MG, and AB dye. Good wettability, stability, high fouling resistance and removal efficiency make the Fe_3O_4/MIRFMR membrane as an excellent candidate to remove RhB from wastewater [193]. In an important study, Chen et al. synthesized hydrophilic molecularly imprinted nanospheres (MINs) by surface imprinting technology. Firstly, carbon spheres were obtained by the hydrothermal carbonization of glucose. MINs were prepared according green approach by the addition of 1.75 mmol of RhB, 4 mL of TEOS, 2 mL of APTES, and 400 μL of acetic acid in the mixture and polymerization was proceeded under continuous stirring for 24 h. The prepared product were washed and treated many times with 5% acetic for the complete removal of template. The experiment was designed and opted to assist the optimization conditions of matrix solid phase dispersion (MSPD) which minimizes the experimental runs. The prepared MINs exhibited the maximum adsorption capacity of 37 $mg \cdot g^{-1}$ higher than the NINs (8.8 $mg \cdot g^{-1}$) with satisfactory recoveries from 83.6% to 96.9% for RhB [194].

RhB is also added in foodstuff as a coloring agent but it is a toxic agent for human health. Zhai et al. [195] reported a chip-based column embedded with MIP-coated GO/SiO_2 for the detection and removal of trace RhB. Chip-based $MIP/GO/SiO_2$ exhibited the good adsorption capacity of 1.99 $ug \cdot mg^{-1}$ and selectivity towards RhB with the recovery rate of 88.4%, 83.7%, and 85.6% for 0.01, 0.1, and 1 $ug \cdot mL^{-1}$ analyte, respectively. Furthermore, this technique has good applications for observing potential toxic dyes in food. In another study, Bagheri and Ghaedi [196] designed an easy and green method to develop MIP for selective adsorbent for pipette-tip (PT) SPE of RhB from the samples of chili powder.

Functional bio-monomer chitosan was used in with RhB template without the consumption of organic solvent based on the green approach. RhB concentration was determined by HPLC-UV/Vis after exposing the sample to MIP/PT-SPE. Possible variables investigated and optimized with response surface methodology and Central composite design. MIP/PT-SPE showed the quantification, LOD, and linear range of 4.88 μg·kg^{-1}, 1.5 μg·kg^{-1}, and 5 μm–15 mg·kg^{-1}, respectively with 85% recovery and good repeatability at optimized conditions.

7.4. Quercetin

High amount of quercetin damages the kidney and is also harmful to pregnant women and breastfeeding babies due to its toxicity [197,198]. Hassan et al. [199] reported MIP NPs for quercetin extraction with MAA, quercetin, EGDMA, and BP as functional monomer, template, cross-linker, and initiator, respectively. MIP and NIP were synthesized by using the precipitation polymerization technique. The synthesized MIP exhibited a high binding capacity of 60 mM·g^{-1} than the NIP (10 mM·g^{-1}) with a 93% recovery rate. With technology extension, Petrova et al. fabricated MIP films by the surface imprinting with the reaction of glutathione and γ-MAPS and initiator AIBN for the template of quercetin. Two methods were used to obtain the samples, firstly, the silica particles surface was coated with the MAPS in quercetin presence and secondly, organomineral polymer was fabricated by thiol-ene click reaction in solution following alkaline or acid MAPS hydrolysis, and the obtained mixture was restrained on silica microparticles surface. Template was removed from the polymer matrix to perform the quercetin rebinding experiments. The synthesized adsorbent by the first scheme exhibited the maximum adsorption efficiency of 8 μmol g^{-1}. The samples produced from the first and second schemes showed the maximum imprinting factor value of 2–3 having quercetin: glutathione (1:6). Rebinding measurements followed the P-S-O kinetics [200]. In another study, MIP was prepared with 4-VP, DVB, AIBN, and quercetin as functional monomer, crosslinking agent, initiator, and template, respectively. MIP microspheres contained a spherical shape and diminutive diameter division of 55 mm. Synthesized adsorbent showed good adsorption efficiency of 521 μg·g^{-1} which was 4.38 times higher than the NIP. Adsorption measurement followed the Langmuir model and kinetic data fitted in P-S-O model. The adsorption efficiency was reduced by 15% after five binding-rebinding cycles. The proposed method was simple and selective to adsorb the quercetin [201].

8. Summary and challenges

Heavy metal ions and toxic dyes have a very serious risk to the environment and also to human health, thus enabling various extraction technologies for the removal of these toxic substances. Solvent extraction is the most common conventional technique of extraction but it required many chemical acids which makes it an unfavorable technique for the extraction of metal ions and dyes. MIT got a lot of attention is the last two decades for ion imprinting because it has several advantages over conventional extraction techniques. Target specificity is one of the main advantages of MIT for the removal of metal ions and dyes with high selectivity. Many studies have shown that MIPs are stable and resistant to temperature and organic solvents. The MIPs have also advantages in the easy fabrication process and can be used for a long time. Real water samples containing various metals have also been tested and MIP exhibited significant results over conventional studies. Reusability depends upon various factors including the material porosity, solution type, and diluent material; MIPs can withstand and reuse even after many cycles without a significant change in their adsorption capacities which makes them an attractive material for industrial applications. Some companies were made by primary exponents of the use of MIPs in separation science and have attained some achievements. The most noticeable commercial application of MIPs is that Sigma-Aldrich Company offers various MIP-based extraction materials.

Advancements in MIPs are playing a constructive role in the elimination of toxic materials from the environments which are harmful to the ecosystem and disturbing the ecological balance. The number of papers related to MIP for environmental pollutants studies is increasing and every new research is the continuity of the previous one to produce more efficient MIPs. The present studies were conducted following the analytical protocols and improvements can be seen, but the MIP use should be broadened at the commercial level by addressing these challenges.

- It is still a challenging task to produce a highly sensitive MIP for a template without functional groups [202], resulting in a template-ligand complex that makes the use of toxic substances inexorable mostly. Single-atom imprinting produces less sensitive MIP resulting insignificant results. Continuous research is required to develop novel functional monomers to resolve the single-atom imprinting issue.
- There is a need for some improvements in the MIT like the reduction of template toxicity and increasing the kinetic speed of the whole process. Template removal is still challenging in highly cross-linked MIPs. Sometimes, the template leakage also causes non-uniform binding sites in the nanostructured MIPs.
- Additionally, the available functional monomers and cross-linkers are not enough to make effective green MIPs with industrial applications.
- Continuous efforts are being made to solve these problems and in the future, the combination of nanomaterials, green chemistry, and MIP will open new doors for further effective developments. The main purpose of this review is to ensure the researchers regarding the theoretical studies of MIPs to commercialization for a clean and healthy environment.

List of abbreviations

AA — Acrylic acid
AECS — Aminoethyl chitosan
MAA — Methacrylic acid
BIBP — Bis-(1-(tert-butylperoxyl)-1-methylethyl)-benzene
[BMIM][BF$_4$] — 1-Butyl-3-methyl-imidazolium-tetrafluoroborate

BP — Benzophenone
β-CD-MA — β-cyclodextrin-maleic anhydride
CMP — Chloromethylated polystyrene
DMSO — DIMETHYL sulfoxide
DPDES — Diphenyldiethoxysilane
EGDMA — ethylene glycol dimethacrylate
HMS — Hollow mesoporous silica
HPLC — High-performance liquid chromatography
4HBA — 4-Hydroxy benzoic acid
IIC — Ion-imprinted degreasing cotton
MIT — Molecularly imprinting technology
MIP — Molecularly imprinted polymer
MBA — N,N–methylenebisacryl amide
γ-MAPS — 3-Methacryloxypropyltrimethoxysilane
NIP — Non imprinted polymer
PVA — Polyvinyl alcohol
P-S-O — Pseudo-second-order
PETA — pentaerythritol triacrylate
RAFT — Reversible addition−fragmentation chain-transfer
RhB — Rhodamine B
SS — Sericin
TAIC — Triallyl isocyanurate
TMOS — Tetramethoxysilane
4-VP — 4-Vinylpyridine
AT — Amino functionalized TiO_2
AIBN — Azobisisobutyronitrile
BPO — Benzoyl peroxide
BET — Brunauer–Emmett–Teller
[BMIM][PF_6] — 1-Butyl-3-methyl-imidazolium-hexafluorophosphate (BMIM PF_6)
BPh — Bathophenanthroline
CMC — Carboxymethyl cellulose
DMC — [2-(methacryloyloxy) ethyl]-trimethylammonium chloride
DVB — Divinylbenzene
EDTA — Ethylenediaminetetraacetic acid
FRP — Free radical polymerization
[HMIM][PF_6] — 1-Hexyl-3-methyl-imidazolium hexafluorophosphate
HEMA — 2-Hydroxyethyl methacrylate
IPTS — 3-Isocyanato- propyltriethoxysilane
IIM — Ion imprinted membranes
MMA — Methyl methacrylate
MDAA — N,N-methylenediacrylamide
MIIP — Magnetic ion imprinted polymer
[OMIM][PF_6] — 1-Methyl-3-octyl-imidazolium hexafluorophosphate
PVDF — Polyvinylidene fluoride
PEI — Polyethyleneimine
RTILs — Room temperature ionic liquids
RFMR — Resorcinol-formaldehyde-melamine resin
SPE — Solid phase extraction
SA — Salicylic acid
TMOS — Tetramethoxysilane
TEOS — Tetraethyl orthosilicate
VTMS — Vinyltrimethoxysilane

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