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Review

Green and Sustainable Imprinting Technology for Removal of Heavy Metal Ions from Water via Selective Adsorption

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Abstract: Revolutionary technological advances have posed new challenges to humans, and modern technology needs to seek new breakthroughs. Imprinting technology, also known as template technology, is a technology based on the interdisciplinary development of polymer chemistry, biochemistry, chemical engineering, and materials science. The polymer prepared with imprinting technology, termed as imprinted polymer, has a memory effect on specific ions and can realize the selective recognition and enrichment of target species. Therefore, imprinting technology has great potential for application in water environment remediation and industrial wastewater treatment, especially for the treatment of low-concentration, toxic, and difficult-to-degrade heavy metal-containing wastewater. Herein, an overview of recent advances in imprinting technology in the field of adsorption and separation is presented, focusing on methods for the synthesis of imprinted polymers and their application to the separation and enrichment of metal ions in water. Finally, we propose several key issues that remain to be solved in the near future.

Keywords: water pollution; heavy metal; imprinting technology; memory effect

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1. Introduction

With the advancement of industrialization, a series of problems have emerged along with rapid economic development [1]. For instance, the energy crisis and environmental pollution have become increasingly prominent, which has attracted the attention of scholars. Since the third scientific and technological revolution, energy has become the most important factor in supporting national economic development. Economic development cannot be achieved without the supply of energy, which is limited on the earth [2]. Some metal resources, especially potassium ions and copper ions, are not only essential elements for crop growth but are also the main raw materials for the production of fertilizers, which is crucial for agricultural development. In recent years, the development of potassium resources in seawater has seemingly been an effective way to alleviate the resource crisis. However, this method does not solve the problem at the source and creates a vicious circle due to the high energy consumption of the extraction process and the generation of large amounts of wastewater. Alternatively, the consumption of energy generated by unsustainable industrial development could be limited. However, such changes could jeopardize economic output. Therefore, industrial operations should be promoted in such a way as to minimize energy and material consumption while maintaining social progress.

The problem of environmental pollution has arisen due to a lack of human understanding and insufficient anticipation of the negative impacts caused by industrial development. Water pollution, air pollution, solid waste, and noise pollution have brought about adverse effects on our living environment and health. Water pollution (discharging harmful compounds into water systems), in particular, threatens the growth of aquatic organisms and human health [3,4]. Water is the source of life and is closely related to our lives.

Currently, almost all countries on the planet are harbors of water pollution, even in the polar regions. If the water in our lives is damaged, it will cause immeasurable harm. Over time, water pollution caused by inorganic toxic substances such as heavy metals, arsenic, cyanide, and fluoride and organic toxic substances such as phenol, polycyclic aromatic hydrocarbons (PAHs), and organochlorine pesticides (OCPs) has been widely studied. Today, the demand for and consumption of heavy metals in various industrial processes such as metallurgical processing, electroplating and coating, the electronics industry, and the energy and chemical industries is increasing. As a result, a large number of heavy metal pollutants are inevitably generated. Heavy metal pollutants have a wide range of sources and diffusion pathways [5,6]. They can enter the atmosphere, water bodies, and soils through industrial emissions and further expand their contamination scope with the migration of environmental flows, posing a serious threat to organisms and ecological security. It can be seen that water pollution caused by heavy metal ions is a serious threat to human health and ecological safety, while heavy metals are indispensable raw materials for national economic development [7,8]. Based on the above two points, scholars at home and abroad have carried out a lot of research work with a view to effectively controlling, solving, and preventing the pollution of heavy metals and, at the same time, doing a good job in the efficient separation and enrichment of heavy metal ions. For the sustainable development of the country's economy, there is an urgent need to pay attention to the problem of energy shortages and develop new methods and technologies. It is necessary to find more effective ways to remove pollutants and return to a clean and safe water ecosystem. To date, the main water pollution treatment technologies that have been developed include physical treatment (adsorption, ion exchange, membrane separation, etc.), chemical treatment (coagulation, redox, neutralization, etc.), biological treatment (activated sludge, biofilm, bio-oxidation ponds, etc.), and the synergistic effects of the three methods. Among them, compared with other remediation methods, the adsorption method, as a very meaningful environmental remediation technology, is widely used in the treatment of heavy metals in wastewater due to the advantages of high efficiency, reusability, simple operation, and energy savings. Adsorption is a method to realize the removal of heavy metal ions by utilizing the interaction force between solid-phase adsorbent materials and adsorbates in water. It mainly utilizes the high specific surface area of the adsorbent and the special functional groups on its surface to interact (physical/chemical) with specific metal ions to realize the separation effect on metal ions [9–11]. The adsorption capacity, adsorption rate, selectivity, and adsorption regeneration performance of adsorbents are important parameters for evaluating the performance of adsorbents. Typical adsorbent materials include activated carbon, zeolite, silica gel, biosorbent materials, and so on. Activated carbon is widely used due to its large specific surface area and rich void structure. They have been frequently used as standard adsorbents for municipal wastewater treatment. For instance, Niazi et al. [12] prepared micro-mesoporous activated carbon adsorbents from chestnut shells via phosphoric acid activation followed by carbonization and adsorbed Cr(VI) from water at $pH = 2.0$ with a maximum adsorption capacity of 85.47 mg/g. In addition, Islami et al. [13] prepared activated carbon adsorbents from pistachio shells, which were modified to produce sulfonic acid-functionalized magnetic activated carbon adsorbents and used for the adsorption of heavy metal ions in aqueous solutions. The adsorption results showed that the maximum adsorption capacity of the adsorbent for Pb(II), As(III), and Cd(II) reached 147.05 mg/g, 151.51 mg/g, and 119.04 mg/g, respectively, which is a significant enhancement over the adsorption effect of unmodified activated carbon. In recent years, Dong et al. [14] synthesized a novel biochar-based iron oxide adsorbent material (FeYBC) using a one-step method using grapefruit peel and ferric chloride solution as carbon sources. The adsorption experiment shows that the adsorption capacity of FeYBC for Cr(VI) is obviously higher than that of the original biochar, and the maximum adsorption capacity for Cr(VI) can reach 24.37 mg/g. This adsorption is mainly achieved with pb ion exchange and surface complexation reduction. Based on the concept of green chemistry, Qian et al. [11] also reported research advances on the removal of heavy metals

(Cd, Pb) utilizing biochar adsorbents. Furthermore, silica gel is also a commonly used, environmentally friendly adsorbent. Xu et al. [15] utilized amino-modified attapulgite (M-ATP) for the adsorption of Cu(II) and Pb(II) in water, and the adsorption capacity of Cu(II) and Pb(II) was 87.42 mg/g and 88.19 mg/g, respectively. The adsorption process of adsorbents and metal ions can generally be detailed in three stages: external diffusion, surface diffusion, and internal absorption. For the whole adsorption separation process, the adsorbent is the core and key. Therefore, it is necessary to select and prepare suitable adsorbents and fully consider the selectivity and regeneration utilization of adsorbents.

Under the rapid development of global industry, heavy metal ions, as one of the main pollution sources, have failed to be biodegradable. They will gradually accumulate in the ecological environment or the human body, and when the concentration exceeds a certain threshold, it will cause great harm to human health. Therefore, the effective removal of heavy metal ions from the environment is an urgent task to protect human health and the sustainable development of ecosystems. At the same time, the recycling of heavy metal ions is also of great significance in solving the problem of resource crises. Therefore, the study of the selective adsorption of heavy metal ions is particularly important. Currently, heavy metal ion selective adsorption studies based on adsorption mechanisms are mainly categorized into the following four groups: hard–soft-acid–base (HSAB) theories [16], the principle of non-electrostatic interactions, self-inhibition of competing ions, and molecular imprinting. Below, we briefly describe these four adsorption mechanisms.

The HSAB reaction pattern follows that hard acids preferentially bind to hard bases and soft acids preferentially bind to soft bases [17]. According to the acidity and hardness of the target metal ions, selective adsorption can be realized by choosing the matching functional groups or functional ligands. Under acidic conditions, the amino group could be easily protonated to NH^{3+}, which in turn generates strong electrostatic interaction with the anionic state of Cr(VI). Zhang et al. [18] successfully prepared poly(dopamine) microspheres with controllable sizes, which showed good adsorption selectivity for Cr(VI). Its adsorption of Cr(VI) could reach equilibrium in 8 min at pH = 2.5–3.8. In another study, Liu et al. [19] synthesized two kinds of polypyrromethine loaded with a hydroxyl functional group (-OH) and found that the adsorption of Pb^{2+} using these two adsorption materials was not significantly affected when Cd^{2+} and Ni^{2+} existed, respectively. The selectivity mechanism of this material can be explained with the HSAB theory: Pb^{2+} is a critical acid, Cd^{2+} and Ni^{2+} are soft acids, and hydroxyl (-OH) is a hard base, so the affinity of Pb^{2+} with hydroxyl (-OH) is greater than that of Cd^{2+} and Ni^{2+}.

Additionally, the adsorption of ions in water involves non-electrostatic interactions such as affinity/hydrophobicity and hydrogen bonding. The selective adsorption effect can be achieved by optimizing the type of active groups to enhance the hydrophilic/hydrophobic and hydrogen bonding adsorption of certain inorganic ions. This principle has been applied to the development of selective adsorption materials for anions such as NO^- [20–22], $TeO_4{}^-$ [23], $C1O_4{}^-$ [24], and so on. The application of the selective ion adsorption technique based on hydrophilic/hydrophobicity is closely related to the hydration energy of the target ions, and only ions that are highly hydrophobic can be treated using this technique. As a result, this limits the range of ions to which the technique is applicable. In the future, other target ions suitable for this mechanism can be sought for selectivity-related studies.

In recent years, it has been shown that the adsorption of competitive ions with the standard resin can be effectively suppressed by optimizing the electron equivalent ratio of competitive ions and counter ions in the regeneration solution. Interestingly, the adsorption of target ions is not affected by this process. This principle has been successfully applied to the removal of NO^- and trace As(V) from groundwater. For example, Li et al. [25] optimized the electron-equivalent ratio of $SO_4{}^{2-}$ (i.e., competing ions): Cl^- or $HCO_3{}^-$ (i.e., counter ions) in the regeneration solution, and after cycling the activation/regeneration of a standard anionic resin column, highly selective removal of 110 μg/L arsenate ions from the groundwater (>80%) was achieved in 18 adsorption-regeneration cycles, and the SO_4^{2-} removal rate was less than 5%.

Finally, the focus of this paper is imprinting technology. Generally speaking, a variety of metal ions can exist in the water body at the same time, and ordinary adsorbents are unable to selectively adsorb the target metal ions in a complex system, in which case the imprinting technology came into being. Imprinting technology has unique advantages, such as simple preparation, low cost, large adsorption capacity, and highly selective recognition in the fields of separation and purification. Below, we will introduce it in detail.

2. What Is Imprinting Technique?

Imprinting technology is the artificial preparation of imprinted polymers with directed selectivity and affinity for specific substances from a bionic perspective [26]. Depending on the type of target, imprinting techniques can be categorized into two main groups: molecular imprinting techniques (MIT) and ion imprinting techniques (IIT). The concept of imprinting was first introduced in 1931. Polyakov et al. [27] discovered the adsorption properties of porous silica gel and introduced the concept of imprinting. Later, Dickey et al. [28] investigated the adsorption of dyestuffs using silica gel materials and found that the silica gel adsorbent binds to foreign molecules through van der Waals' forces, hydrogen bonding, inter-ionic attraction, and other interactions, and specifically adsorbs a certain dyestuff. However, this discovery did not attract enough attention in the academic world at that time. It is interesting to note that in 1972, Wolf and Klotz [29] in Germany first obtained molecularly imprinted polymers with a covalent method using sugar compounds as a template and investigated the process mechanism of polymerization of functional monomers containing different functional groups. Since then, the study of molecular imprinting technology is no longer limited to silicon dioxide materials. In later research, scientists successively developed the non-covalent method, the semi-covalent method, and other methods to prepare molecularly imprinted polymers, which promoted the rapid development of molecularly imprinted technology. Notably, in 1976, Nishide et al. [30] prepared an ion-imprinted polymer adsorbent using ions as templates, which made molecular imprinting technology one of the mainstream technologies to realize the research and development of selective ion-absorbent materials. Selective adsorbent materials for metal ions such as Cu(II) [31,32], Hg(II) [33,34], and Pb(II) [35,36] have been applied in a variety of fields such as the environment, chemistry, materials, and biology, and the selective removal or recovery of specific ions has been realized. In addition, Arshady et al. reported a new noncovalent imprinted self-assembly method that made significant progress in the preparation of substrate-specific polymers with noncovalent binding capabilities, such as ionic and hydrophobic, which are complementary to the guest cavities [37]. In 1993, Mosbach et al. prepared imprinted polymers by establishing a selective site identification method in polymers through the non-covalent method and realized the specific identification of theophylline molecules [38]. Later, researchers worked on developing new methods in view of the disadvantages that the commonly used functional monomers (such as acrylamide, methacrylic acid, etc.) have in terms of poor stability in forming complexes with target ions and poor selectivity of imprinted polymers in target metal ion templates. Xie et al. [39] both used metal ions and specific ligands that can form stable complexes as templates to synthesize double-imprinted polymers (that is, double-imprinting technology), which enhances the selectivity of molecular imprinting [40]. Since then, molecular imprinting technology has been gradually familiarized with and developed rapidly, becoming a hot technology for domestic and international research.

It is well known that an efficient adsorbent is the core of the adsorption process. For imprinting technology, its adsorbent is a series of polymers. Broadly, polymers prepared via imprinting technology are called imprinted polymers, which can also be divided into molecularly imprinted polymers (MIPs) and ion-imprinted polymers (IIPs). The difference between them is that the targets are different; the former are molecules, and the latter are ions. However, the preparation principle and process of the imprinted polymers are similar, taking the ion-imprinted polymer preparation process as an example. The template ions and ligands, or functional monomers, form chelates or complexes through covalent bonding, metal bonding, hydrogen bonding, and other forces and then form stable polymers under the action of cross-linking agents and initiators. Finally, the template is washed away with the relevant solvent to obtain a polymer that is complementary in size and shape to the template [41]. Different molecules have different shapes and sizes, as well as different reaction properties. They can thus be regarded as different templates. These templates combine with functional monomers in a covalent, semi-covalent, or non-covalent manner to form combinatorial units. Furthermore, polymers with template-selective recognition sites are synthesized through further polymerization or polycondensation reactions with cross-linking agents. After the formation of the polymer, some or all of the templates are removed for corresponding molecular recognition and adsorption [42,43] (as in Figure 1, using IIPs as an example). In other words, the imprinted polymer acquires a unique template "memory" that allows for fast and accurate selection of the template (target molecule or ion) from the mixture.

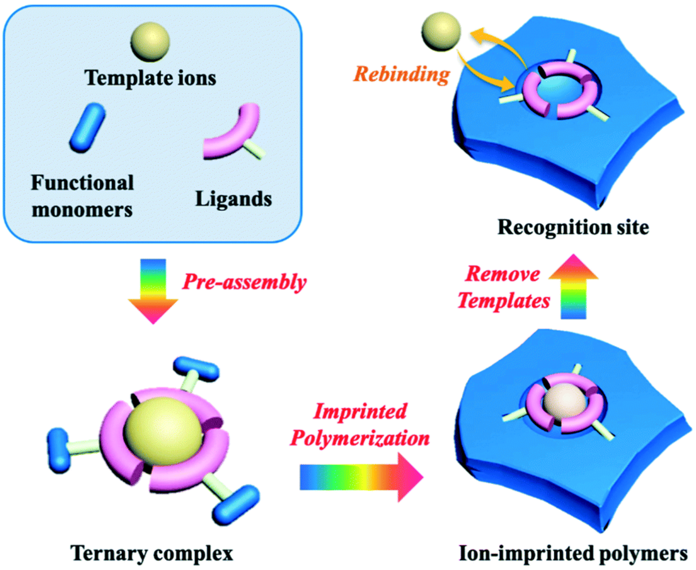

Figure 1. Schematic drawing of the preparation of imprinted polymers (in the case of ionic polymers, for example). Reprinted with permission from the Royal Society of Chemistry [43].

Actually, the components of imprinted polymers are mainly templates, functional monomers or ligands, cross-linking agents, initiators, and porogenic agents. Functional monomers or ligands contain specific functional groups, and according to the structure of the template, the functional monomers or ligands that can produce strong effects with their functional groups are selected. Common functional monomers include methacrylic acid, 4-vinylpyridine, acrylamide, and home-made specific functional monomers. The function of cross-linking agents is to cross-link with functional monomers or ligands to form rigid polymers so that the imprinted cavities can be fixed and not damaged. Common cross-linking agents include ethylene glycol dimethacrylate, glutaraldehyde, and tetraethoxysilane. Initiators are substances that can initiate polymerization reactions under certain conditions. The most common initiator is azodiisobutyronitrile, which generally initiates the polymerization reaction at a temperature higher than room temperature. The porogenic agent is a kind of reaction solvent that can provide a polymer environment, not only as a reaction medium but also to create holes on the polymer surface. Commonly used porogens include acetonitrile, methanol, toluene, and so on. It is important to emphasize that molecular imprinting is realized using a combination of covalent and non-covalent interactions between the imprinted molecule and complementary functional monomers, and the exact combination of these interactions distinguishes the five different types (see

Figure 2) of molecular imprinting from each other. First, the imprinted functional monomer complexes (ICs) are assembled according to the chosen imprinting method. Depending on the imprinting method, complex formation either occurs prior to cross-linker incorporation or in situ during matrix polymerization. Removal of the imprinted molecule by disruption of the functional monomer–imprint interaction releases an imprinted cavity with a defined size and shape [44]. Types of molecular imprints can be categorized based on the interaction between the monomer and the imprint. Five main types of molecular imprinting were summarized through extensive research of the literature:

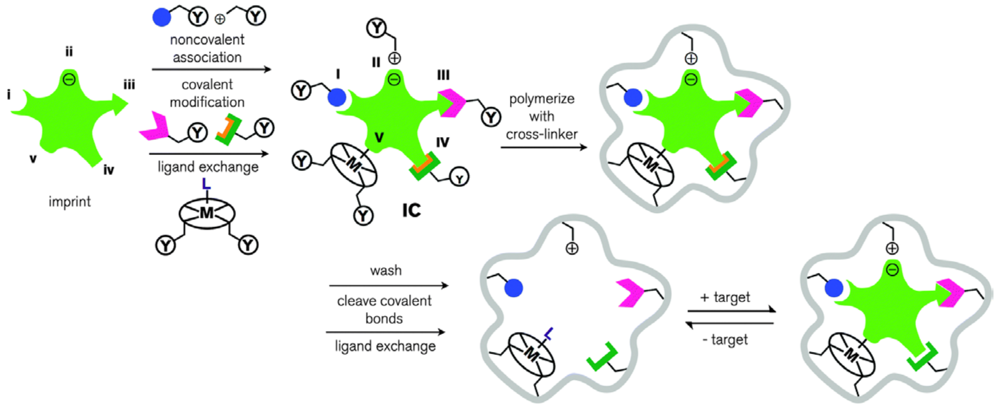

Figure 2. Five main types of molecular imprints: (i) non-covalent, (ii) electrostatic/ionic, (iii) covalent, (iv) semi-covalent, and (v) metal-centered coordination. Reprinted with permission from *Chemical Society Reviews* [44].

Non-covalent imprinting

Non-covalent imprinting was invented in the 1980s by Prof. Mosbach and his research team in Sweden [45]. Non-covalent molecular imprinting can be performed through ionic or nonionic interactions. The most common interaction is hydrogen bonding, and the main advantage of this approach is the absence of kinetic barriers associated with ic formation and bond formation recognized by the target molecule; this effect can be easily mitigated by carefully chosen system parameters. However, such weak interactions require the use of excess functional monomers because the equilibrium of the system cannot produce an imprint, and functional monomer ionic interactions (e.g., the formation of ion pairs) dominate in polar solvents and are strong enough to form stoichiometric ion channels, leading to the emergence of nonspecific binding sites in the MIP. In addition, noncovalent imprinting is not very stable. The presence of nonspecific binding sites in the matrix to which excess functional monomers bind can affect the selectivity of the MIP if excess functional monomers are present [46]. Although it is possible to cap these excess moieties in a post-polymerization step, this treatment requires great care as it can easily disrupt interactions and damage the cavity. The biggest difference between non-covalent and covalent imprinting is the different forces in the binding process between the template molecule and the functional monomer. Moreover, compared to imprinting, the specific recognition ability of non-covalent imprinting is relatively weak [47].

Covalent imprinting

Covalent interaction was created and developed by Wulff et al. The main imprinting molecules include Schiff bases, ketones, and borate esters [48–50]. Reversible covalent bonding enables the binding of highly specific blots to stable targets, which is one of the classical methods of molecular imprinting [51]. Covalent imprinting is stoichiometric and enables functional monomer residues to be present only in the imprint cavity. However, different synthesis steps are required to generate the initial imprint and functional monomer, and the bond breaking required to remove the imprint and the bond formation required to bind the target molecule are also more difficult. In addition, only a limited number of functional groups can be imprinted using the covalent method, which leads to additional kinetic barriers to covalent bond formation and slower target binding [52]. Reversible covalent reactions available for covalent interactions are limited to only a few chemical reactions, which makes the method rather limited. It can be concluded that covalent imprinting is less versatile.

Semi-covalent imprinting

Semi-covalent imprinting combines the advantages of the persistence of covalent imprinting with the rapid target selection of non-covalent imprinting. One of the main kinetic barriers is the diffusion of the target species to the imprinted site. In general, such semi-covalent imprinting uses a small sacrificial spacer fragment, such as carbon dioxide [53].

Metal-centered coordination

When metal ions become a part of the covalently bonded complex of the imprinted cavity and participate in target recognition through metal–ligand bond interaction, it is called metal-center coordination. Metal ions can exchange ligands to select target molecules. This imprinting needs to be customized according to specific requirements, in which at least one ligand with the strongest binding force must contain polymerizable molecules compatible with the cross-linking agent. In addition, the ligand exchange must be compatible with the relevant system to ensure the persistence of the ligand covalently bound to the matrix. As a result, the choice of combination depends on the imprinting and target, the substrate, synthesis conditions, and the intended application of the MIPs.

3. Synthetic Approach of Imprinted Polymer

So far, several methods have been designed and developed to synthesize imprinted polymers. The two most popular preparation methods are free radical polymerization and sol–gel methods. Among them, free radical polymerization methods specifically include several categories such as bulk polymerization, suspension polymerization, emulsion polymerization, precipitation polymerization, and surface-imprinted polymerization, which generally include three steps: initiation, propagation, and termination (see Figure 3) [54]. Table 1 shows the following common synthetic methods of imprinting polymers and their characteristics.

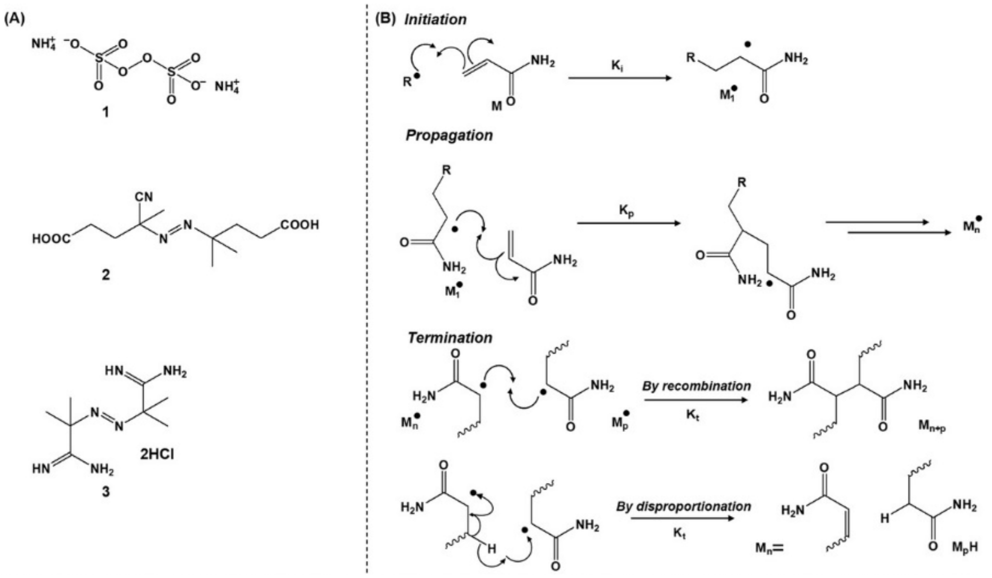

Figure 3. (**A**) Chemical structures of free radical polymerization initiators. (**B**) Schematic representation of free radical polymerization mechanism. Reprinted with permission from Wiley [54].

Table 1. Various synthetic methods of imprinted polymer.

Synthetic Methods	Strengths	Weaknesses
Bulk polymerization	Simple to operate	Irregular shape Damage-binding sites Low yield Templates are difficult to remove
Suspension polymerization	Easily adjustable in size	Poor recognition performance Low adsorption capacity
Precipitation polymerization	Effectively controls the size	High solvent consumption
Emulsion polymerization	High polymer yield High particle size uniformity	Poor adsorption capacity and low selectivity
Surface-imprinted polymerization	Rich adsorption sites High efficiency Strong recyclability Template elution is easy	Slightly poor adsorption capacity
Sol–gel method	Mild reaction conditions Simple synthesis process	Difficulty in eluting the template

3.1. Bulk Polymerization

The bulk polymerization method is one of the most common and widespread polymerization methods for the preparation of imprinted polymers. The specific preparation process is to add a certain ratio of template molecules, functional monomers or ligands, cross-linking agents, and initiators to the reaction solvent. Subsequently, nitrogen is introduced to remove the oxygen in the solution. The reaction is carried out under heating or photo-initiating conditions, resulting in block- or rod-shaped imprinted polymers. The polymer is then ground and screened to obtain granules of the desired particle size. The polymers obtained using this method are irregularly shaped, and the specific binding sites are easily destroyed during the milling process, which reduces the yield of the polymers. Only 30–40% of the polymer could be effectively utilized. In addition, some of the imprinting sites were buried deep inside the material during the preparation process, making it difficult to remove the templates. In a typical experiment, Zu and colleagues prepared MIPs with different templates using native polymerization. among them, imprinted polymers of bisphenol A and 2,4-dichlorophenoxyacetic acid with yields of 70% and 80%, respectively [55].

3.2. Suspension Polymerization

Suspension polymerization is a method where template molecules, functional monomers, cross-linking agents, and initiators dispersed in water are mechanically stirred in the presence of stabilizers or surfactants, and suspension polymerization is carried out in the form of droplets to form imprinted materials. The size of the polymer can be well-tuned by controlling the ratio of organic phase to liquid phase mixing and the rate of mechanical agitation. This method was developed on the basis of native polymerization and is widely used in the preparation of covalently and noncovalently imprinted polymers [56]. It can overcome the disadvantages of low yield and difficult control of native polymerization. However, the polymer recognition properties are poor due to the weakening of hydrogen bonding and electrostatic interactions between the template molecules and functional monomers by the aqueous phase. In addition, stabilizers or surfactants may also affect the interaction and reduce the affinity of the polymer for the template between the template molecules and functional monomers. As a result, the polymers prepared using this method had a low adsorption capacity. Takimoto and his colleagues [57] successfully synthesized monodisperse submillimeter human serum albumin-imprinted microgels via inverse suspension polymerization of water-soluble monomers with photoinitiators. In addition, the concentration and flow rate of surfactant were studied. Moreover, Alizadeh et al. [58] successfully obtained a timolol voltammetric sensor using a molecularly imprinted polymer-modified carbon paste electrode. Liu et al. [59] used 4-vinylpyridine as a functional monomer to prepare MIPs that could selectively extract p-hydroxybenzoic acid from water samples via suspension polymerization. Pan et al. [60] prepared surface-imprinted microspheres via suspension polymerization using naringin as a template molecule. The surface-imprinted microspheres were used as solid-phase extraction (SPE) adsorbents, and naringin was successfully separated and enriched in citrus extracts with a recovery of 84.4%.

3.3. Precipitation Polymerization

In the precipitation polymerization system, the growing polymer chains do not overlap or combine but continue to grow separately by trapping the newly formed oligomers and monomers, which are then separated from the solution in the form of microspheres [61]. Precipitation polymerization is the most promising method for the preparation of high-quality, homogeneous, surfactant-free spherical particles, which has unique advantages in the synthesis of stabilizers, surfactant-free spherical particles, and one-step preparation with good control of particle size. However, a large number of organic solvents are required in the polymerization process, and some of them are toxic to a certain extent. For instance, Zhou and coworkers [62] obtained molecularly imprinted polymers in the shape of monodisperse microspheres with an average diameter of 1.55 μm using methacrylic acid (MAA) as the functional monomer. Subsequently, the molecular selectivity of the imprinted polymer microspheres was evaluated by their ability to absorb nicotine and its structural analogs. In a later study, Xiao and colleagues [63] prepared aristolochic acid-imprinted polymers via aqueous-phase precipitation polymerization using aristolochic acid I (AAI) as a template molecule. The Langmuir isotherm modeling showed a good imprinting effect due to the presence of a large number of specific binding sites on MIP. The maximum adsorption of aristolochic acid I by the polymer was 1.25 mg/g. Repeatability experiments showed that the MIP could be recycled at least six times for further selective identification and separation of AAI.

3.4. Emulsion Polymerization

Emulsion polymerization is the mixing and emulsification of a polymerization mixture, water, and surfactant for emulsification [64]. The most common type of emulsion is an oil-in-water emulsion, where the monomers are dispersed in an inert liquid (e.g., water) containing a surfactant. Then, a homogeneous polymer (0.1–1 μm) is formed. Some of the other monomers are retained in the polymer, but the rest of the surfactant-free auxiliary is suspended in water, and the water-soluble initiator is dissolved in the solvent phase. Stabilized emulsions (i.e., latex particles) containing polymer microparticles in the aqueous phase are formed spontaneously during the first few minutes of the polymerization process [65]. The polymerization process then takes place within these emulsion particles. Because each particle is surrounded using a surfactant, the charge on the surfactant prevents the particles from coalescing. The advantage of emulsion polymerization is that there is no significant increase in the viscosity of the polymer, resulting in a solid content of up to 60%. This is due to the lack of interaction between water and emulsion particles. The resulting polymer has the advantages of high particle size uniformity and good regularity. For these reasons, currently, this method is used to manufacture several commercially important polymers. For example, Yang and his colleagues [66] successfully obtained regular spherical bisphenol A-imprinted polymers with diameters ranging from 30 to 60 m based on emulsion polymerization. In another similar study, Zhu et al. [67] obtained Cd(II)-imprinted polymers using conventional emulsion polymerization combined with the microwave method.

3.5. Surface-Imprinted Polymerization

With the progress of synthesis technology and the improvement of practical application requirements, imprinting technology has been further developed. New imprinting techniques, such as surface imprinting and the sol–gel method, have appeared. In the synthesis process of the above traditional polymerization method, the template is embedded deeply. There are some problems with traditional imprinting technology, such as difficult template recognition, elution difficulty, slow mass transfer rate, and low binding capacity, because its imprinting sites are distributed in the interior of the material. More seriously, these problems lead to the poor adsorption ability of the imprinted material. In recent years, surface-imprinted polymerization based on the conventional imprinted polymerization method has gradually attracted the favor of scientists, which provides opportunities for expanding new materials and new methods. Surface-imprinted polymerization disperses the adsorption sites on a solid substrate, which avoids the problems of the above methods. The biggest difference between the surface-imprinted polymerization methods and the other methods is that the polymer is loaded onto the surface of a carrier material with a high specific surface area during the polymer preparation process. The first four traditional preparation methods make it difficult to completely elute the template and have poor selectivity and few binding sites for the target molecule. The surface-imprinted polymer method can improve or overcome these problems. In general, the synthesis process of surface imprinting consists of the following three main steps: Firstly, the template and the functional monomer form a complex (e.g., covalent, noncovalent, or semi-covalent) in some way. Secondly, polymerization is carried out in the presence of an initiator and a cross-linker to form an imprinted layer containing the template on the surface of the solid substrate. Finally, the template is mechanically or chemically removed from the polymer, leaving a matching three-dimensional cavity. These imprinted cavities are specifically recognized and can be directed to recombine with the target in a large number of samples for effective adsorption. Imprinted polymers take porous materials with a high surface area as carriers, such as SiO_2, graphene, carbon-based materials, etc., and modify them by adding specific functional groups to form more structurally stable polymers. In addition, such polymers have the advantages of abundant binding sites with template molecules, a fast response rate, and strong specific recognition ability. In recent years, surface blotting technology has been widely studied and applied in different fields because of its advantages, such as easy elution of templates, high binding capacity, fast adsorption rate, and excellent selectivity. For example, Gao et al. [68] successfully obtained a core–shell imprint of bovine hemoglobin using the surface imprinting technique. After the removal of the template proteins, a thin polymer layer with specific recognition cavities for bovine hemoglobin was formed on the $Fe_3O_4@NH_2$ surface. Interestingly, Wang et al. [69] synthesized thiocyanate (SCN^-) imprinted polymers via surface-imprinted polymerization combined with the reversible addition-fragmentation chain transfer (RAFT) method using straw as a carrier. The relative selectivity factor of the polymers reached about 14.00 in the presence of interfering ions. This experiment demonstrated that the selectivity of imprinted straw for SCN^- was superior to that of non-imprinted straw, providing an application basis for the detection of trace SCN^- in various natural water samples. Coincidentally, Liu et al. [70] also successfully prepared a two-dimensional Ni(II)-imprinted polymer (GO@SiO_2-IIP) on the surface of graphene oxide/silica composites by using the RAFT technique (Figure 4). Through the combination of surface imprinting technology and two-dimensional materials, the adsorption capacity of GO@SiO_2-IIP for Ni (II) was increased to 81.73 mg/g, and the adsorption capacity of the imprinted polymer was 2.64 times higher than that of the non-imprinted polymer. Recently, Wang et al. [71] successfully obtained Pb(II) ion-imprinted nanotube adsorbents using multi-walled carbon nanotubes as carriers and chitosan, hydroxyethyl methacrylate, and N-isopropylacrylamide as functional monomers (Figure 5). The material can achieve high selective adsorption performance in a short time. In the selectivity experiments, the selectivity coefficients of Pb(II)/Cu(II), Pb(II)/Cd(II), Pb(II)/Zn(II), and Pb(II)/Ni(II) were 15.66, 59.50, 24.79 and 20.52, respectively.

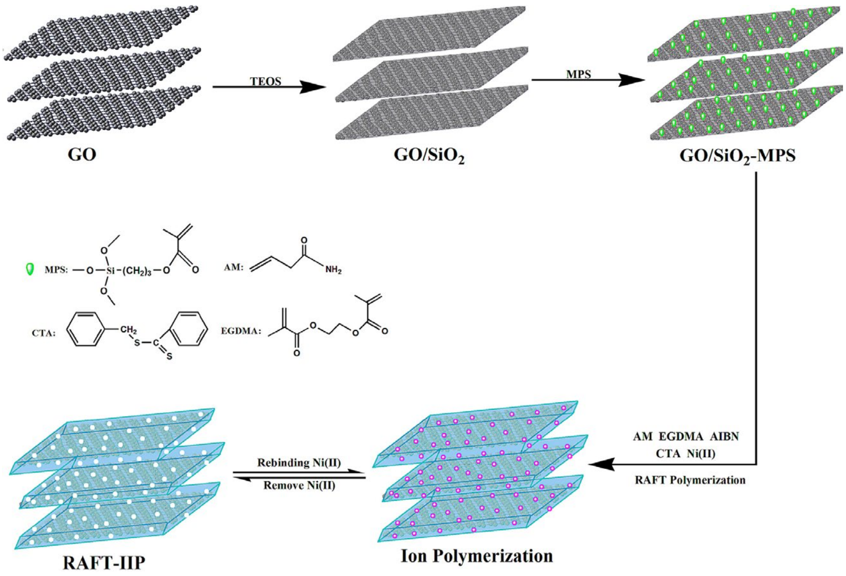

Figure 4. Schematic representation of the ion-imprinting process via RAFT polymerization. Reprinted with permission from the American Chemical Society [70].

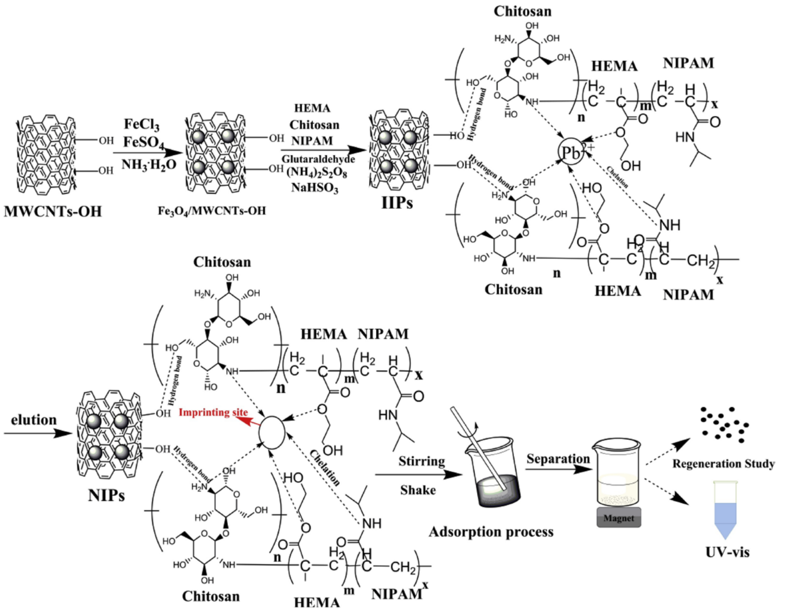

Figure 5. Schematic representation of the synthesis and application of IIPs. Reprinted with permission from Elsevier [71].

3.6. Sol–Gel Method

The sol–gel method refers to the process of forming a metal alkoxide molecular precursor, adding template ions to interact with it and immobilize it, which is then catalytically driven by acids or bases, and finally cross-linking to form an ion-imprinted polymeric network [72]. This method mostly uses a functionalized silane coupling agent as a precursor; the reaction conditions are mild, and the structural strength of the resulting imprint is high. It can play a synergistic role with the surface imprinting technique and has a wide range of applications in the field of ion-selective separation. For example, Zhou et al. [73] formed U(VI) and Cs(I) dual ion-imprinted materials (DIMS) on mesoporous silica material SBA-15 using the sol–gel method (shown in Figure 6). DIMS can selectively capture uranyl and cesium ions from water at the same time, and the adsorption equilibrium was reached at about 1.0 h. The maximal adsorption capacity of DIMS for the two ions was 221.7 mg/g and 34.5 mg/g, respectively. It is noteworthy that the adsorbent maintained a high selective recognition and capture capacity after eight adsorption/desorption regeneration cycles. In addition, Wang et al. [74] developed a new idea for the separation and enrichment of bisphenol A using the imprinting technique. Bisphenol A-imprinted microspheres with high adsorption performance were successfully obtained using silica nanoparticles as the only stabilizer in a Pickering emulsion system (Figure 7). The polymer adsorbed the target molecules at a fast rate and reached adsorption equilibrium at 30 min.

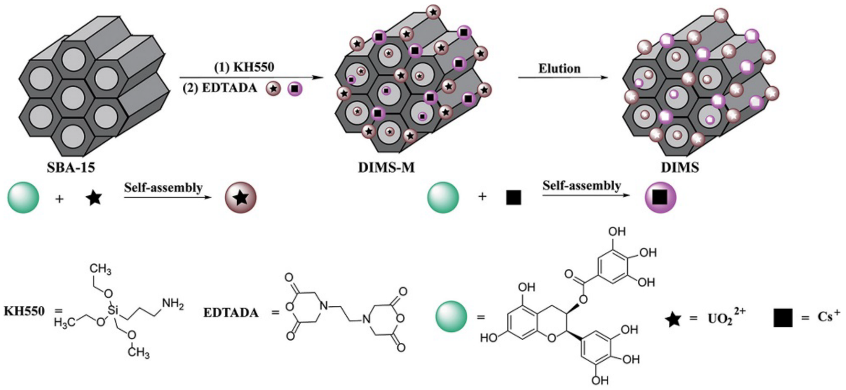

Figure 6. Schematic representation for synthesis of DIMS. Reprinted with permission from American Chemical Society [73].

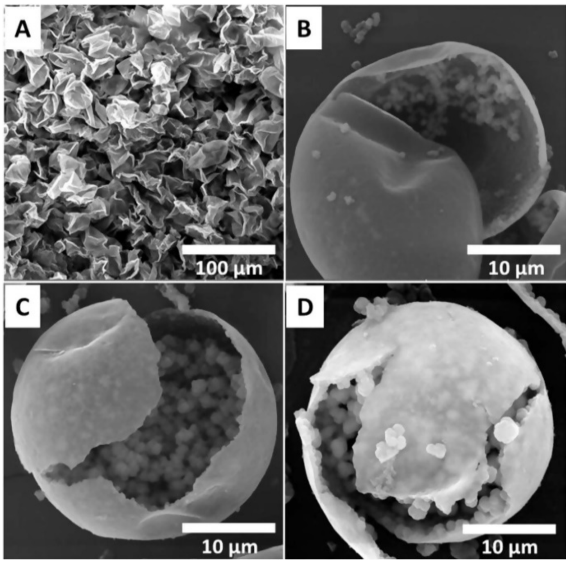

Figure 7. SEM images of the MIP over time ((**A**) sample 9: 0.5 h; (**B**) sample 10: 1.0 h; (**C**) sample 11: 2.0 h; and (**D**) sample 12: 3.0 h). Reprinted with permission from Elsevier [74].

Recently, it has been noted that rapid magnetic separation can be achieved by applying a magnetic field, which has the advantages of easy operation and time and energy savings compared with traditional filtration and centrifugation. Qian et al. [75] prepared a magnetic surface ion-imprinted material (SII-MM) for the efficient adsorption of uranyl ions in an aqueous solution (Figure 8). The n-hydroxyethyl acrylamide ligand and 1-vinyl imidazole ligand first formed complexes with uranyl ions and then localized and polymerized on the surface of the vinyl-containing magnetic microspheres to form a polymer-imprinted layer. The faster kinetics, higher selectivity, and larger adsorption capacity of SII-MM for uranium suggest that SII-MM can be used as a promising adsorbent for the efficient removal of uranium from an aqueous solution.

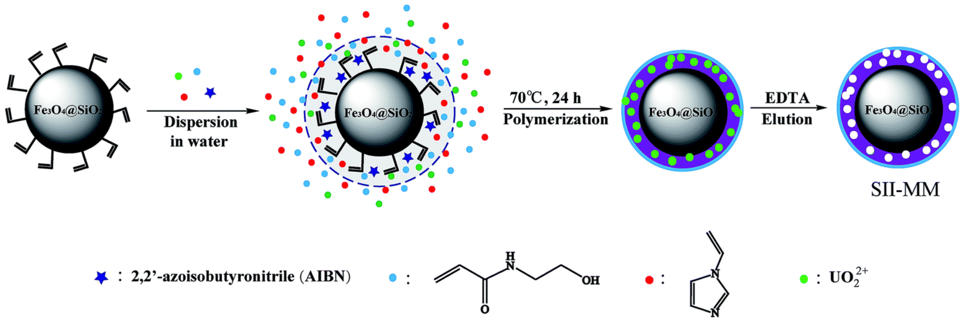

Figure 8. Schematic depiction of SII-MM by applying a magnetic field. Reprinted with permission from the Royal Society of Chemistry [75].

Temperature can also affect substance transfer and reaction processes. Ji [76] et al. synthesized a novel thermosresponsive metal-organic framework (MOF)-type adsorbent, A-MIL-121, which could effectively remove trace amounts of Cu(II) (>95%) from high salinity ($[Na^+]/[Cu^{2+}]$ = 20,000) aqueous solutions at room temperature. At high temperatures, A-MIL-121 could desorb Cu^{2+} rapidly and effectively. In view of the advantages of photoresponsivity, such as non-contact, remote controllability, and transient nature, it can be applied in the fields of adsorption and separation in conjunction with imprinting technology. Huang et al. [77] prepared photo-responsive Li(I) imprinted polymers (P-IIPs) on mesoporous carbon nitride surfaces using dibenzo-14-crown-4 as the functional monomer and azobenzene as the photosensitive monomer. The results showed that UV irradiation could release Li(I) from the imprinted cavities of P-IIPs, and the adsorption rate was promoted by visible light irradiation compared with the dark environment.

4. Applications for Water Restoration and Resource Recovery

There is a large amount of hard-to-degrade pollutants or available resources in wastewater, the vast majority of which do not exist in isolation and are mixed with other harmless or harmful substances. Traditional treatment methods, such as chemical precipitation, ion exchange, microbial degradation, etc., make it difficult to achieve the desired results. However, imprinted polymers can be applied to separate and enrich specific pollutants or available resources due to their ability to specifically recognize target substances, thus achieving the purpose of environmental purification. As such, it is necessary to apply imprinting techniques to water restoration. We investigated the prepared imprinted polymeric materials that have been used for the selective adsorption of metal ions in water bodies. Table 2 summarizes in detail the imprinted polymeric adsorbents developed in recent years for the removal and separation of various types of metal ions commonly found in waterbodies.

Pb^{2+} is a common main-group metal cation pollutant. It has neurotoxicity, and excessive content in the human body will cause metabolic disorders and irreversible harm to tissues and organs. Therefore, it is urgent to remove Pb^{2+} from water bodies. For instance, Zhang et al. [78] prepared Pb^{2+} surface-imprinted polymers with the grafting method using hollow mesoporous silica as a carrier (Figure 9). It was found that the selectivity of Pb^{2+} was very high, and the maximum adsorption capacity could reach 40.52 mg/g. The selectivity factor of Pb^{2+} was as high as 508 in a mixed solution containing Cu^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}, and Ni^{2+} at the same time. In the study by Wan and his colleagues [79], they impregnated hydrated manganese oxide (HMO) on porous polystyrene cation exchange resin(D-001) to produce composites that exhibited excellent adsorption selectivity for Pb^{2+}. This was mainly attributed to the specific intra-sphere complexation between Pb^{2+} and HMO active sites. In addition, due to the intra-sphere complexation of manganese oxides, their doping modification can also effectively enhance the adsorption selectivity of Cd^{2+} and Zn^{2+}. In addition, the modified clay limestone also showed excellent Pb^{2+} adsorption selectivity, but the mechanism of the interaction between the hydroxyl groups on the surface of iron oxides and Pb^{2+} is still unclear and needs to be further investigated in depth.

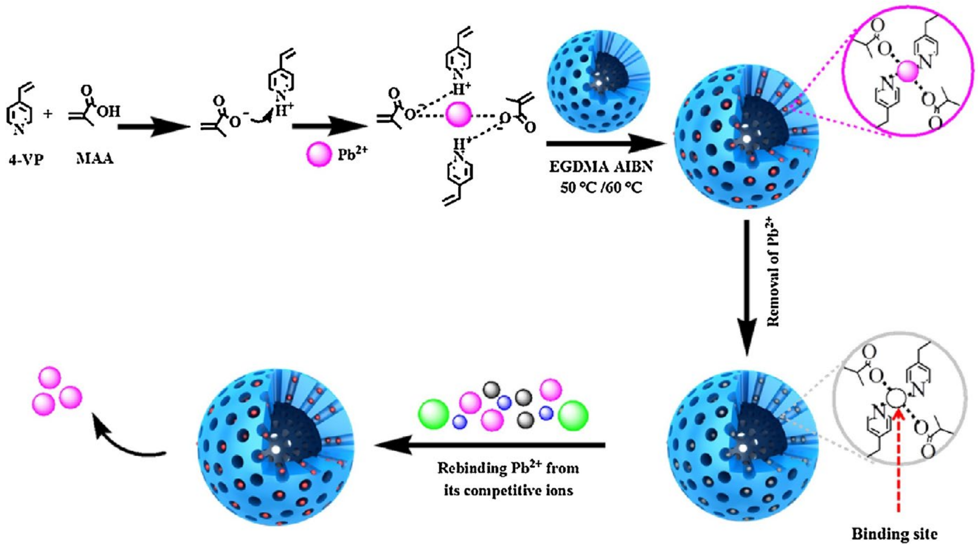

Figure 9. Schematic illustration of the experimental procedure for H-MIP preparation. Reprinted with permission from Elsevier [78].

Hg^{2+}, as a toxic heavy metal, can cause nephrotoxicity by accumulating excessively in the body. The elimination of mercury pollution has long been a hot topic of research. Hajri et al. [33] prepared an imprinted adsorbent using Hg^{2+} as a template and Schiff base-modified chitosan as a monomer, which showed much higher adsorption capacity for Hg^{2+} than other ions under the coexistence of Zn^{2+}, Cu^{2+}, Pb^{2+}, $Co^{2+,}$ and Cd^{2+}. Recently, Liu [80] invented an inexpensive and selective nanocellulose adsorbent for the separation and enrichment of heavy metal ions Hg(II) in wastewater. Magnetic mercury-ion-imprinted polymers were synthesized using the precipitation method using vinyl thymine as a functional monomer. Then, it was grafted onto modified nanocellulose, which could effectively adsorb mercury ions from wastewater. Their adsorption behavior of Hg (II) was in accordance with the secondary kinetic model and the Langmuir adsorption isotherm model. The adsorption of Hg (II)-MIP-NC on Hg (II) reached 161.31 mg/g.

Chromium (Cr) is one of the toxic metal ions that cause environmental pollution and affect human health. Chromium in the environment is mainly present in the form of Cr(III) and Cr(VI) ions. Both of them, especially Cr(VI), pose a risk of toxicity and carcinogenicity to human health. Gao et al. [81] prepared a chromate ion surface imprinted material, IIP-PVI/SiO_2, to selectively remove chromate from water. The experimental results demonstrated that IIP-PVI/SiO_2 has excellent affinity as well as strong recognition selectivity for chromate anions. In the presence of phosphate ions, the adsorption capacity of this adsorbent for chromate ions was much greater than that of phosphate as compared to the non-imprinted material. Huang et al. [82] prepared a Cr(VI) ion-imprinted polymer, Cr(VI)-IIP, with the surface ion-imprinting technique using 3-(2-amino ethyl amino) propyl trimethoxy silane (AAPTS) as a functional monomer and graphene oxide mesoporous silica (GO-MS) nanosheets as a carrier. The adsorbent has high selectivity for Cr(VI) ions in water. The adsorption experiments showed that the adsorption amount was as high as 438.1 mg/g within 5 min. Moreover, Cr(VI)-IIP showed high selective adsorption performance in five cycle tests. In addition, the effect of solution pH on adsorption was examined (Figure 10). The adsorption of Cr(VI) showed a trend of increasing and then decreasing when the pH was decreased from 8.0 to 1.0. The maximum adsorption of Cr(VI) was observed when the pH was 2.0.

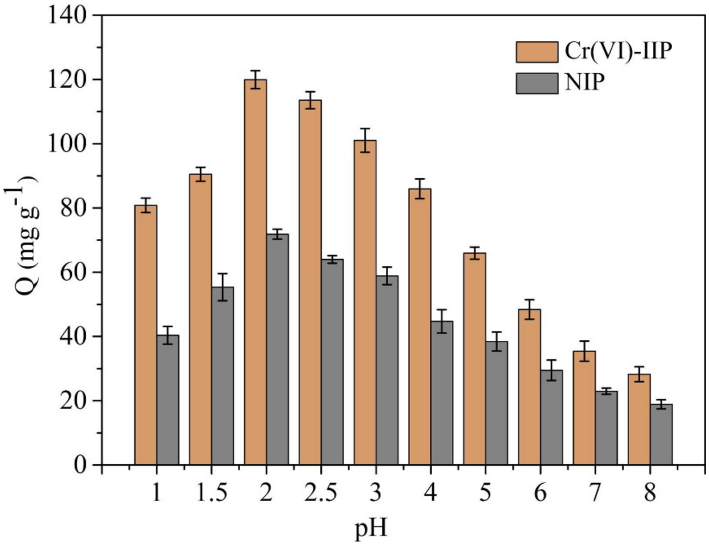

Figure 10. Influence of pH on Cr(VI) adsorption onto Cr(VI)—IIP. Reprinted with permission from Elsevier [82].

Certainly, in addition to the heavy metal ions mentioned above, there are other heavy metal ions such as Cd(II), Ni(II), As(V), etc., which can also be effectively removed using imprinting technology. Table 2 summarizes the imprinted polymer adsorbents developed in recent years. It can be seen that the imprinted adsorbents presented many merits, including high selectivity, efficiency, and adsorption capacity. In general, imprinting technology has been widely studied and applied in the field of ion-selective removal, especially the removal of specific cations. Excellent selectivity makes it one of the selective treatment methods widely used now.

Table 2. Adsorbents and their selective adsorption performance for removal of heavy metal ions.

Absorbents	Target	Adsorption Capacity (mg/g)	Coexisting Ions	Ref.
Cd-IIPs	Cd(II)	65.5	Zn(I), Ni(II), Cu(II), Co(II)	[83]
AAMA	Cd(II)	175	Pb(II), Hg(II), Cu(II), Co(II), Zn(II)	[84]
Cd(II)-IIP	Cd(II)	83.89	Ni(II), Cu(II), Zn(II)	[85]
Fe_3O_4@SiO_2@IIP	Cd(II)	29.82	Zn(II), Ni(II), Co(II)	[86]
Cd(II)-IICM	Cd(II)	509.93	Co(II), Ni(II), Cu(II)	[87]
Cd-IIMs	Cd(II)	162.44	Zn(II), Pb(II), Ni(II) Fe(III), Na(I), K(I), Ca(II), Mg(II)	[88]
Cd(II)-IIP	Cd(II)	64.74	Pb(II), Mn(II), Ni(II), Cu(II), Hg(II)	[89]
QAPs	Cr(VI)	211.8	SO_4^{2-}, NO_3^-, PO_4^{3-}	[90]
PAH-ASGO	Cr(VI)	373.1	Mg(II), Ca(II)	[91]
Cr(VI)-IIP	Cr(VI)	96.32	Cr(III)	[92]

Table 2. *Cont.*

Absorbents	Target	Adsorption Capacity (mg/g)	Coexisting Ions	Ref.
Cr(VI)-IICM	Cr(VI)	4.07	Cd(II), Cu(II), Ni(II)	[93]
Gel/CS/PPy	Cr(VI)	106.8	NO_3^-, Cl^-, SO_4^{2-}	[94]
IIP	Cr(VI)	103	Cr(III), Cu(II), SO_4^{2-},	[95]
MIP	Pb(II), As(V)	81.97, 625	Na(I), K(I), Ca(II), Mg(II), Cu(II)	[96]
DMHIIPs	Pb(II)	135.2	Cu(II), Cd(II) Ni(II)	[97]
DE/Pb(II)IIP	Pb(II)	79.38	Cd(II), Ni(II), Co(II), Cu(II), Mn(II)	[98]
MTCI-SBA-15	Pb(II)	283	Cd(II), Zn(II), Co(II), Ni(II)	[99]
IIP-MMT	Pb(II)	201.84	Zn(II), Cd(II), Cu(II), Sn(IV), Mn(II)	[100]
MA/MIIP	Cu(II)	131.47	Pb(II), Cd(II), Zn(II)	[101]
Hg-PMTF	Hg(II)	360.5	Pb(II), Cd(II), Cu (II), Ni(II)	[102]
IIM	Hg(II)	21.6	Zn(II), Pb(II), Cu(II), Cd(II), Co(II), Cr(II)	[103]
IIPs	Ni(II)	19.86	Pb(II), Cu(II)	[104]
IICFMPSs	Ni(II)	41.95	Zn(II), Cd(II), Cu(II)	[105]
Fe_3O_4@void@ IIP-Ni(II)	Ni(II)	44.64	Co(II), Cu(II), Pb(II) Zn(II),	[106]
IIC	As(V)	55.0	SO_4^{2-}, NO_3^-, $H_2PO_4^-$	[107]
M-IIP	As(V)	78.74	SO_4^{2-}, NO_3^-, $H_2PO_4^-$	[108]

In addition, imprinting technology has great application prospects in the field of metal resource recovery. Zhao et al. [109] utilized electrostatic self-assembly to realize the composite of graphene oxide and carbon-coated Fe_3O_4. The equilibrium extraction capacity on Li^+ of the magnetically imprinted material was up to 17.06 mg/g, which showed high selective extractability with selection factors of 14.31, 12.05, and 10.09, compared with those of Na^+, $K^{+,}$ and Mg^{2+}, respectively (see Figure 11). Moreover, due to its magnetic characteristics, the regenerated adsorbent can realize solid–liquid separation quickly. Even after several cycles, 91% of the initial extraction capacity could be maintained. In the preparation of lithium-ion imprinted polymers, the disadvantage of acid elution is usually unavoidable, and the extraction performance will be drastically degraded after meeting the strong acid environment. In view of this, Zhang et al. [110] first synthesized an ion-imprinted graphene-based hybrid aerogel (LIIP@N-CMS/GA) using the liquid-phase reduction self-assembly technique. The composite aerogel possesses a rich pore structure, a large specific surface area, good electrochemical activity, and high mechanical strength, so more effective lithium-ion imprinting sites can be constructed on the surface of the composite aerogel using the electron-controlled ion-imprinting technique. Combined with the electric field effect, the carboxyl functional group on the surface of the matrix, and the specific complex recognition of crown ether, the obtained 3D graphene aerogel-based lithium-imprinted membranes were able to maintain a high selective extraction and separation performance, including a high adsorption capacity of 41.05 mg/g, an extraction capacity retention of 91.7%, and an electrophilic ion removal of 95.7%, even in a strongly acidic environment (pH = 1.5). Moreover, the selective separation factors for the interfering ions, such as Na^+, K^+, Mg^{2+}, and Al^{3+}, were 51.99, 19.66, 14.37, and 12.40, respectively, showing high selectivity (see Figure 12).

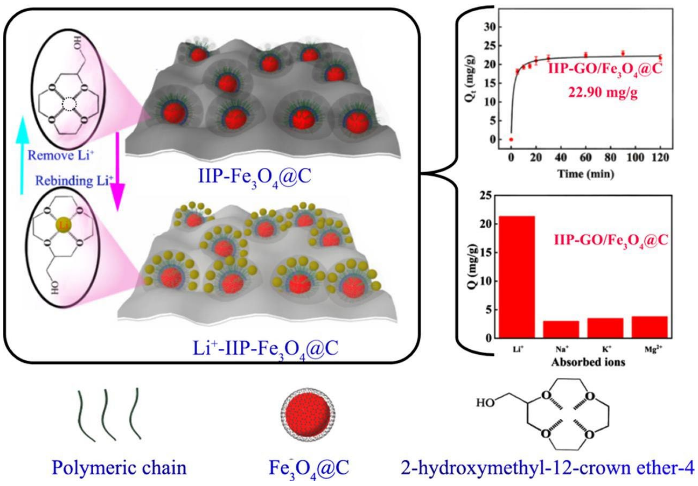

Figure 11. Adsorption selectivity of IIP-GO/Fe_3O_4@C and NIP-GO/Fe_3O_4@C. Reprinted with permission from Elsevier [109].

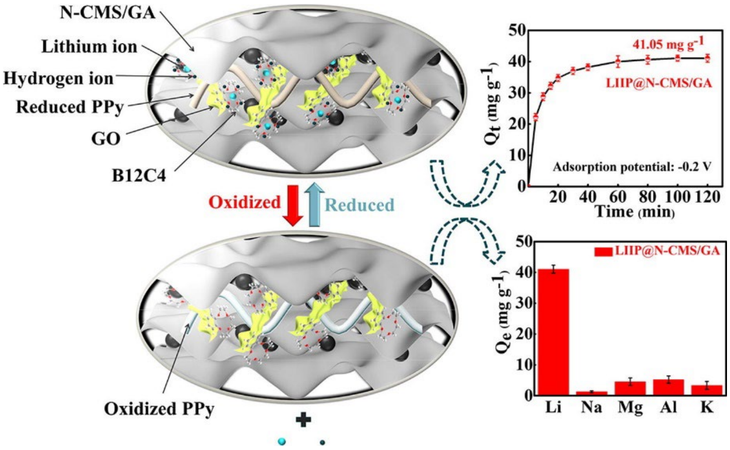

Figure 12. Mechanism and performance of the obtained LIIP@N—CMS/GA. Reprinted with permission from Elsevier [110].

Elemental Cu is also an important class of metal resources with potential industrial properties. Wastewater containing the heavy metal copper is an important asset that can be recycled. Yu et al. [111] successfully synthesized a novel Cu (II) ion imprint using sugarcane bagasse for the collection of copper ions from sludge leachate. The results showed that the adsorption capacity of the imprinted bagasse was 32.0 mg/g, which was higher than that of the unimprinted bagasse (22.9 mg/g). The recycling experiment proved that the imprinted bagasse has reusability. The competitive adsorption results showed that the adsorption affinity of the imprinted bagasse for Cu(II) was stronger than that for the co-ions such as Ca(II), Zn(II), Mg(II), Cd(II), and Pb(II), and this environmentally friendly and green imprinted biosorbent has a promising future in the recycling of Cu(II) ions in wastewater.

In recent years, studies have shown that selective identification, enrichment, and removal of metal ions, especially rare and precious metal ions, are of great significance for environmental sustainability, economic development, and resource recycling. For instance, Zhang et al. [112] synthesized ITG-OCMC microspheres with excellent selective adsorption of Ag(I) in an aqueous solution using a new technique combining surface imprinting and polymer cross-linking. Under certain conditions, the maximum amount of Ag(I) absorbed could reach 156.32 mg/g. Another report is the recovery of Au (III). Gao et al. [113] prepared thiourea-modified chitosan imprinted resin (IM-TUCS) and explored its adsorption behavior for Au(III). The adsorption equilibrium was reached within 4 h, and the maximum adsorption amount was as high as 933.2 mg/g. Notably, IM-TUCS could be reused four times with a gold recovery of about 93%. With its good mass transfer performance, large adsorption capacity, fast adsorption rate, and high reutilization rate, imprinting technology has a broad development prospect in the field of metal ion recovery. As can be seen in Table 3, we have summarized the application of imprinting technology in metal resource recovery. It is obvious that the imprinting technology also has the advantages of high efficiency, high adsorption, specificity, and a high recovery rate in the field of metal resource recovery.

Table 3. Imprinting technology in the recovery of metal resources.

Adsorbents	Metal Resources	Adsorption Capacity (mg/g)	Time (min)	Ref.
MCTS@GO@DIIP	Cd(II), Ni(II)	39.35, 33.91	30	[114]
Li^+-IIP-Fe_3O_4@C	Li(I)	22.26	40	[115]
Li-IIMs	Li(I)	23.0	60	[116]
IBCN-Cu	Cu(II)	152.2	150	[117]
MIIP	Rb(I)	186	60	[118]
Pt(IV)-IIM	Pt(IV)	79.68	40	[119]
IIMCD	Cu(II)	78.1	--	[120]
MOF-IIP	Co(II)	132.8	120	[121]
PVDF/RTIL	Eu^{3+}	22.37	180	[122]
IUA	Au(III)	184.82	360	[123]
Cs(I)-MIIP	Cs(I)	36.15	180	[124]
RAFT-IIP	Sr(II)	145.77	60	[125]
MS-C-D	Ag(I)	39.8	120	[126]

5. Conclusions

Overall, imprinted polymers have received extensive attention from researchers in wastewater treatment due to the advantages of simple preparation, low cost, large adsorption capacity, high recovery, and selective recognition. The imprinting technology based on imprinted polymers is important for the selective removal of specific ions, especially metal ions, from water bodies. Its unique functional selectivity makes it one of the most widely used selective treatment methods nowadays. Selective adsorption of heavy metal ions in wastewater with imprinting technology can not only alleviate the current water pollution issues but also effectively recycle and utilize the metal resources, which is a win–win strategy for economic development and environmental protection. In this paper, the current research status of the preparation methods and applications of imprinted polymers is summarized. We expect that it will provide guidance and inspiration for solving some of the longstanding problems in imprinting technology.

6. Future Perspective

While imprinting technologies possess the ability to selectively identify target ions and maximize the selective separation of specific metal ions, there are still several disadvantages. For example, a few imprinted polymers have been reported for anion-selective recognition. IIPs have fewer kinds of functional monomers that can be used for synthesis, less saturated adsorption, poor thermal stability, and a small industrial application range. Moreover, the design of interactions between templates and functional monomers or ligands is mainly qualitative, making it difficult to realize the precise construction of imprinted polymers. More importantly, some of the carriers used for the preparation of IIP adsorbents are mostly synthetic inorganic porous materials, and most of the functional monomers are toxic, which invariably increases the operating cost and may lead to secondary pollution of the environment. The current research related to molecular imprinting technology mainly focuses on the preparation and application of molecularly imprinted polymers, and relatively little research has been conducted on the binding mechanism. Therefore, future research can be carried out on the development of new functional monomers and the reusability of molecularly imprinted materials. Based on the current research status, it is mainly necessary to break through the following several items to improve the performance of imprinted polymers:

i. Vigorously develop imprinted materials for anion recognition;
ii. Design new non-toxic and highly selective functional monomers and continue to promote green recycling technology;
ii. Combine imprinting technology with other new technologies and methods to prepare new types of highly selective adsorbents, improve the structure model of IIPs, and deeply analyze the microscopic mechanism of IIPs for the selective recognition of heavy metal ions;
iv. Improve the adsorption capacity of imprinted polymers, especially in the case of controllable preparation of bifunctional molecular/ionic recognition materials and low concentrations of target ions, which is of great significance for the enrichment, detection, and recovery of heavy metals in water bodies;
v. Optimize the kinetic adsorption performance and shorten the adsorption time to meet the needs of rapid identification and capture;
vi. Enhance the efficiency of separation and utilization and further strengthen the recognition ability, especially for improving the specific recognition effect on targets close to the size.

It is foreseeable that with the sustainable development of new adsorption materials and the continuous promotion of industrial applications, imprinting technology will certainly make more achievements in the field of separating and enriching metal ions in wastewater.

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