

Research Progress in the Selective Adsorption of Removal of Heavy Metal Ions from Wastewater

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Abstract—Toxic heavy metals in water have been a serious hazard human beings health and eco-environment. However, these heavy metals are usually important natural resources. How separate them from polluted water and reuse them, which is a hot issue in environmental protection field. Adsorption is widely used in the removal of heavy metal ions from Wastewater due to stable, reliable, simple, low energy consumption, low secondary pollution, recycling. Selective adsorption is preparing corresponding adsorbing materials or setting certain solution conditions, according to the different characteristics of heavy metals, such as electronegativity, degree of confusion and ion bound state, so as to separate heavy metal ions from wastewater. Selective adsorption has outstanding advantages in the separation and recovery of heavy metals. Research progress in selective adsorption of heavy metals in recent years is summarized. And the research progress of ion exchange resin and ion imprinted material in selective adsorption of heavy metals is Focused on.

Keywords- *Selective Adsorption; Heavy Metal; Ion Exchange Resin; Ion Imprinting*

I. INTRODUCTION

With the continuous development of industry and agriculture, and the unreasonable emissions of wastewater, the phenomenon of heavy metal pollution in water has become more and more serious. Coming from metal smelting and processing, leather manufacturing, electroplating and electronic products processing, as well as photography, printing and dyeing, pesticide manufacturing, etc. The heavy metals were passed through the food chain with its biodegradation and enrichment, and finally the low concentration of heavy metals was enriched in humans and animals, which causing great harm. In the standard discharge based on the depth of treatment, the planning of the intensity of source pollution management, recovery and utilization and emission reduction of heavy metals were strongly

proposed by the national "heavy metal pollution comprehensive prevention and control in 12th five-year planning". It is an urgent technical problem that how to control heavy metals water pollution and recycle the mat the same time. The methods of separation and recovery of heavy metals mainly include chemical precipitation, membrane separation, solvent extraction, adsorption etc. Compared to other methods, adsorption method has less environmental pollution, good effect, less energy consumption, recyclable characteristics and many other advantages. According to the different electronegativity, randomness, ion bound of heavy metal ions in waste water, the adsorption material or specific solution conditions were used in selective adsorption method to separate the heavy metal ions, which has a prominent advantage in separation and recovery of heavy metals. Domestic and foreign scholars have carried out a lot of researches on the removal, separation and recovery of heavy metal ions by selective adsorption.

II. COMMONLY USED ADSORBENT OF HEAVY METALS IN SELECTIVE ADSORPTION METHOD

A. Ion Exchange Resin

Ion exchange resins have an active group of synthetic polymer materials and different ion affinity for different types of ion, and the ion exchange resin is divided into anion (cation) type according to the separation and recovery principles, properties and applicable conditions of different types of ions. Anion exchange resins are suitable for high concentrations of Cl^- , F^- , and the partition coefficients of the heavy metal ions have great differences and heavy metals exist in the form of complex anions within this system. Based on the feasibility and economic considerations, the application of anion exchange resin in heavy metal separation is less. Using the principle of ion exchange, the ability of separation of heavy metals of cation exchange resin depends on the size of electrostatic attraction. Cation exchange resins are suitable for separation and recovery of Cr^{3+} , Pb^{2+} and other high state and small radii of hydrated ions, while not obvious to the same valence of transition metals [1]. Chelating resin has higher adsorption capacity and selectivity for heavy metal ions, which has been researched and applied in the recovery of heavy metals in a way. Xu Chao et al. [2] prepared polymeric resin containing 6-aminonicotinic acid (ANA resin) to study the selective adsorption behaviors for $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ in single-component solution and double-component mixture solution, the results indicated that amino-pyridine resin has a good selection of adsorption for $\text{Cu}(\text{II})$. Tao Xuwen et al. [3] also have achieved good results for the adsorption of $\text{Cu}(\text{II})$ by using typical chelate resin containing nitrogen IRC747 as a selective adsorbent in high concentrations of $\text{Ni-Cu}(\text{II})$.

B. Ion Imprinted Material

With predetermination, recognition and practicability, ion imprinting technology is an important branch of molecular

imprinting technique, and widely used in water treatment, such as the removal of heavy metal ions in waste water, water sample pretreatment, trace analysis of ion concentration (Figure 1).

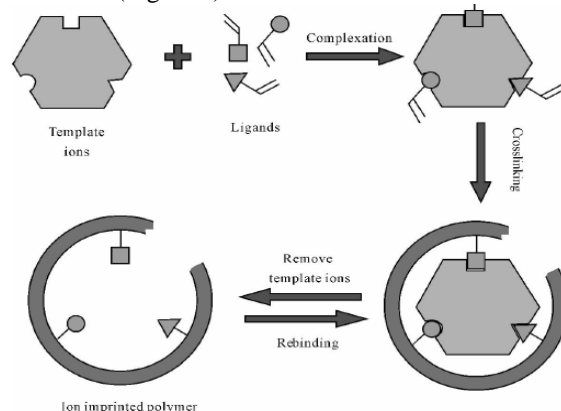


Figure 1. Schematic of ion imprinting process

When the template ion contacted with the polymer functional monomer, both of them were combined by form of by covalent or non-covalent bond. After completion of the reaction and elution, the polymer have formed the three-dimensional hole that fully match with the spatial configuration and binding site of template ions. Because of the "memory" function, imprinted polymer is highly selective for the imprinted ions [4].

Several key elements of ion-imprinted materials are the proportions of the imprinted ion, functional monomers and cross linking agent. Their main role, principle and common materials are shown in table 1.

Functional monomer is a key factor in the preparation of ion imprinted polymers, it should be able to bind with the template ion, and must be able to be linked with the crosslinking agent. Wang et al. [5] achieved selective adsorption of $\text{Cu}(\text{II})$ through nitrogen-containing groups and chelation oxygen-containing groups of a novel polyethyleneimine-functionalized ion-imprinted hydrogel ($\text{Cu}(\text{II})$ -p(PEI/HEA)) on the $\text{Cu}(\text{II})$ adsorption capacity and adsorption selectivity are good. The maximum adsorption capacity for $\text{Cu}(\text{II})$ was 40.00 mg/g, and the selectivity coefficients of ion-imprinted hydrogel for $\text{Cu}(\text{II})/\text{Pb}(\text{II})$, $\text{Cu}(\text{II})/\text{Cd}(\text{II})$ and $\text{Cu}(\text{II})/\text{Ni}(\text{II})$ were 55.09, 107.47 and 63.12, respectively, which were 3.93, 4.25 and 3.53 times greater than those of non-imprinted hydrogel, respectively. In recent years, the common natural polymers have been used as the functional monomers for the preparation of molecularly imprinted polymers, which are mostly used for water treatment, recovery of precious metals and detection of trace metals. Chen Zhijun et al. [6] prepared magnetic Fe_3O_4 -chitosan nanoparticles by using Zn^{2+} as a template, glutaraldehyde as crosslinking agent, and the adsorption capacity and selectivity of the novel hydrogel were good. The maximum adsorption capacity for $\text{Zn}(\text{II})$ was 28.9 mg/g.

TABLE I. PREPARATION FACTORS OF ION IMPRINTED POLYMERS

Preparation factors	Main effect	Selection principle	Commonly used materials
Imprinted Ion	To participate in the polymerization reaction, and easy to be removed after the reaction.		Metal ions, mainly for metal cations, including metal ions, transition metal ions, rare earth metal ions, actinide metal ions and other categories, in which transition metal ions have been studied more than others[7].
Functional monomer	Formed by covalent or non-covalent interactions with metal ions to form binding sites, and then metal imprinted polymer were formed under the action of crosslinking agent and initiator	specific recognition properties of the hole were formed between the monomer and the metal ions, various monomers containing functional groups, such as amino, hydroxyl, sulfhydryl that exhibit chelation to heavy metals.	Vinyl (4-vinyl benzene formaldehyde, divinyl benzene, 4-vinyl phenol) and acrylic acid (esters) (methyl acrylic acid, acrylic acid, methyl methacrylate vinegar), Borate compounds; PC; s heterocyclic bases etc. [8]
Cross-linkers	To make imprinted polymers become stable and improve mechanical strength, and make polymers with functional groups to form spatial structure, and make functional residues derived from functional monomer evenly distributed in a polymer network.	Generally select the Cross-linkers' activity similar to what the functional monomer have	Aldehydes (glyoxal, glutaraldehyde, formaldehyde, etc.); polyethylene glycols; crown ethers [9].
Imprinted Ion; Functional monomer; Cross-linkers	Affect the performance of Imprinted Polymer	When excessive amount of functional monomer, it is easy To occur polymerization reaction with itself, if not enough, it cannot completely work with the imprinted ion and will affect the recognition function of the imprinted polymer.	Commonly used mole ratio of 1:4:10, according to the actual situation, it can be properly adjusted

Ion imprinting technology is mainly applied to the adsorption of heavy metal cation, while few studies for anion. Li et al.[10] combined with surface ion-imprinting technology and sol-gel technology to synthesis a new Pb(II)-imprinted polymer for selective separation and enrichment of trace Pb(II) from aqueous solution. The equilibrium was achieved in approximately 4.0 h. The maximum adsorption capacity was 22.7 mg/g, and the Langmuir equation fitted the adsorption isotherm data.

III. RESEARCH PROGRESS OF SELECTIVE ADSORPTION OF DIFFERENT HEAVY METAL IONS

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Finally, complete content and organizational editing before formatting. Please take note of the following items when proofreading spelling and grammar:

A. Pb

Taking into account the high toxicity of lead, the content of lead in water and industrial waste water must be controlled within a reasonable range. GuJinying et al. [11] prepared the lead ion imprinted polymer microspheres by

using 1, 12- twelve alkyl O, -O⁻ two phenyl phosphoric acid (DDPA) and 4- vinyl pyridine as dual functional monomers. When pH>5, the removal rate above 95%, which has a good adsorption performance for Pb²⁺ in water, and the selectivity coefficients of ion-imprinted polymer microspheres for Zn(II) / Pb(II), Co(II)/Pb(II) and Ni(II)/Pb(II) were 86.6, 53.0 and 46.5, respectively. Fan Rongyu et al. [12] synthesized a novel Pb(II)-ion imprinted composite membranes with microporous polypropylene membrane (MPPM) as support by a modified UV-induced graft copolymerization. In the graft strategy, benzophenone was immobilized on membrane by combining physical entrapment and UV-induced covalent immobilization methods. The imprinted composite membranes exhibit good adsorption and permselectivity towards Pb(II). The maximum adsorption capacity towards Pb(II) is 2.86 and 2.75 times that Cu (II) and Zn(II), respectively.

B. Cu

As a heavy metal contaminants and an important natural resource, and it is meaningful to separation and recovery of Cu widely exist in water. Peng et al. [13] successfully synthesized the Cu(II) imprinted carbon spheres through hydrothermal method with specific molar ratio of Cu(II), glucose, four ethylene five amine (TEPA). This adsorption capacity of the amino-functionalized ion-imprinted adsorbent was found to be significantly. The experimental result indicated that the selectivity coefficients

of the imprinted material for Cu(II)/Cd(II), Cu(II)/Co(II), Cu(II)/Ni(II) and Cu(II)/Zn(II) were 31.8, 90.2, 38.6 and 36.1, respectively. Those were 10.6, 6.22, 7.11 and 39.2 times greater than that of non-imprinted material, respectively. Yuan et al.[14] demonstrate a new kind of surface imprinted smart polymer by using methacrylic acid (MAA) as function monomer, attapulgite as the support material, ethylene glycol dimethacrylate (EGDMA) as a crosslinker, and 2, 2'-azobisisobutyronitrile (AIBN) as initiator to prepare Cu(II)-imprinted microgels. The results showed that the prepared imprinted microgels have a high affinity for Cu^{2+} over Ca^{2+} and Mg^{2+} , and the adsorption equilibrium data fitted Freundlich isotherm model well. In addition, Cu(II)-imprinted smart micro-gels had pH sensitivity to control the selection recognition property.

C. Ni

High-purity nickel is an important strategic resource and raw material. It has been widely used in the field of social construction, industrial manufacturing and national defense development. High-purity nickel product strict requirements for content of cobalt and other metal impurities, therefore, removal of trace cobalt from high-purity nickel has become the key to improve the quality of high-purity nickel. The adsorption of Cu(II) achieved good result by using typical chelate resin containing nitrogen IRC747 as a selective adsorbent in high concentrations of Ni-Cu(II) [3]. Zhang et al.[15] prepared Ni(II)-imprinted m-CTS/PVA beads (Ni(II)-IMCPs). The study on the adsorptive performances of Ni(II)-IMCPs shows that the maximum adsorption capacity of Ni(II)-IMCPs for Ni(II) ions is 500.0 mg/g and have good durability and selectivity for Ni(II) ions.

D. Cd

Cadmium was concentrated in organisms, and then will be converted into more toxic metal organic compounds such as ethyl cadmium. In Japan, itai-itai disease caused by cadmium poisoning has made a great concern. Wang Xiaoji et al. [16] prepared a kind of magnetic and molecular imprinting chitosan spheres which were able to selectively absorb Cd^{2+} ions. Cd^{2+} ions were used as templates to fabricate the molecular imprinting chitosan spheres, magnetic Fe_3O_4 nanoparticles were embedded into the chitosan spheres to endow the spheres magnetism. The result shows that, firstly, the absorption ability of such chitosan spheres to Cd^{2+} was high, which was two times that of Cu^{2+} , and was about three times that of Zn^{2+} ; secondly, such chitosan spheres were able to be separated from the aqueous solutions conveniently and very quickly under the external magnetic field, and thus to remove and concentrate the heavy metal ions, and more than 90% absorption capacity remaining after five times recycling. Buhani et al.[17] synthesized a Cd(II) imprinted mercapto - functionalized silica gel sorbent via a surface imprinting technique for selective adsorbent of Cd(II) ion in aqueous. The adsorbent of Cd (II) ion-imprinted ionic polymer (Cd(II)-IIP) has higher capacity and selectivity than the non-imprinted polymer (NIP) adsorbent. Adsorption capacity of Cd(II)-IIP and NIP are 83.89 and 35.91 mg/g, respectively. The largest

selectivity coefficients (α) of the Cd(II)-IIP sorbent for Cd(II) in the presence of Ni(II), Cu(II) and Zn(II) are 99.798, 93.045, and 86.617 respectively.

E. Sr

Strontium belongs to the low-level radioactive metal, which has a half-life of 27.7 years. Sr was often accumulated in the bones and muscles when it enters the human body. It is not easy to be eliminated in the body metabolism. Chronic radiation sickness caused by Sr poisoning, which seriously affects the survival of mankind and the next generation. Li Chunxiang et al. [18] prepared Sr(II) ion-imprinting polymer by surface molecular imprinting technique and sol-gel process with Sr(II) as the template, chitosan as the functional monomer, attapulgite as the support, and glycidoxypolytrimethoxysilane as the coupling agent. Under the optimum conditions, the ion-imprinted polymer has fast kinetics for the adsorption of Sr (II), and its maximum adsorption capacity is 3.71 times as that of attapulgite. Its selectivity is more than 3.0 times as that of attapulgite. A model for selective removal of target radio elements can be set up according to the results.

F. Cr

The water contaminated by chromium has made a great concern, because the metal is widely used in electroplating, tanning, metal processing, nuclear power plant, textile industry and the preparation of chromium liquid. Cr(III) and Cr(VI) are the most common form of Cr, and the toxicity of Cr(VI) more than 500 times that of Cr(III) [19]. Cr(VI) is toxic for micro-organism, plants, animals and humans, such as lung cancer, kidney, liver and stomach damage [20] (the United States Department of health and human services, 1991). The traditional heavy metal ion pollution is generally the cation, and the Cr(VI) is in the presence of the anion group. Medhat investigated adsorption and preconcentration of chromate species from water and wastewater using carminic acid modified anion exchanger (IRA 900). After modification, the IRA 900 resin possessed a large number of hydroxyl groups so that it has a function of selectively adsorbing Cr(VI) anion. This gave rise to the selective removal of Cr(VI) species even in the presence of higher concentrations of other competitive anionic species by adjusting the solution environment (pH 4.3) [21].

IV. CONCLUSION AND OUTLOOK

Selective adsorption has the advantages of high efficiency, low pollution, recycling and strong recognition in the separation and recycling of heavy metals. Compared with other adsorbent, chelating resin and ion imprinted materials have high adsorption capacity and adsorption selectivity, and have a broad application prospects, but also have some problems: (1) The actual water quality is complex, so the adsorbent should be selected according to the water quality, and the adsorption behavior and optimum adsorption conditions of different heavy metals should be researched in the actual water quality, In order to apply the selective adsorption to engineering practice.(2) At present, research object of ion imprinting technology are cations, while few

studies on anions because of some factors that limit its application in the removal of metal anion. (3) In the preparation of ion imprinted material, most polymeric organic compounds, such as functional monomer, initiator, cross-linkers are toxic. Those compounds will bring new pollution when it is used to heavy metal wastewater treatment. (4) The studies on the adsorption mechanism of heavy metal ion-imprinted materials are not enough. Therefore, it is time to increase the adsorption of heavy metal ions on the ion imprinted materials, expand the scope of application of imprinted technology, and explore new functional monomer, initiator and crosslinking agent to avoid secondary pollution.

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TABLE II.