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Preparation of Chitosan Metal Imprinted Resin Polymer and Application of Adsorption Properties

Xue Wang[1, 2, 3, 4, 5], Zhe Liu[1, 2, 3, 4, 5]

[1]Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi'an, Shaanxi 710075, China

[2]Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi'an, Shaanxi 710021, China

[3]The Key Laboratory of Degeneration and Unutilized Land Improvement of the Ministry of Land and Resources, Xi'an, Shaanxi 710075, China

[4]Shaanxi Engineering Research Center of Land Consolidation, Xi'an, Shaanxi 710075, China

[5]Land Engineering Technology Innovation Center, Ministry of Natural Resources, Xi'an, Shaanxi 710075, China

Abstract

Harmful heavy metals are common pollutants, which have strong carcinogenic, teratogenic and mutagenic effects on human body. With the acceleration of industrialization, the content of harmful heavy metals in the environment is increasing, which is a serious threat to human health. Therefore, it is an urgent problem to find a kind of material that can effectively adsorb the harmful heavy metals in water-soil and liquid food.

Keywords

Heavy Metal Ions; Chitosan; Adsorption.

1. Introduction

With the rapid development of global economy and society, tens of thousands of heavy metal ions, organic dyes and other pollutants are discharged into the environment in large quantities every year [1]. With the gradual improvement of people's living standards, water-soil pollution has been attached great importance by the government and relevant departments. Among them, heavy metal ions are one of the more common pollutants, which have strong toxic effects on human body and even have carcinogenic, teratogenic and mutagenic effects. As heavy metal ions are difficult to degrade and easily accumulate in organisms, they can lead to various diseases by replacing the active centers of some enzymes, vitamins and other substances, such as "Minamata disease" and "Itamata disease" in Japan, which shocked the world and seriously threatened people's health [2]. Therefore, the content of harmful heavy metals in the environment (especially in water and soil) should be strictly controlled to solve the problem of excessive harmful heavy metals from the source.

At present, many methods and materials or chemical reagents have been used to treat heavy metal pollutants in water, among which adsorption method is a high efficiency and low-cost method, which is widely used in the treatment of heavy metal pollution in water environment. Currently, among the metal adsorbents that have been developed, chitosan is widely used in the adsorption of heavy metal ions due to its advantages of non-toxic, harmless, good biocompatibility, biodegradable, and no secondary pollution. Chitosan is the only alkaline polysaccharide in nature and is the second largest renewable resource on Earth. Chitosan has been widely used in wastewater treatment, food and

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medicine, papermaking, textile and water purification. Chitosan molecules contain a large number of amino and hydroxyl groups, which is conducive to the modification of chitosan to enhance its adsorption capacity, adsorption selectivity and adaptability to the environment. Chitosan molecules contain a large number of amino and hydroxyl groups, which are easy to form N, O-carboxymethyl chitosan derivatives under alkaline conditions, which have a good adsorption effect on metal ions and organic dyes.

Wang[3] synthesized N, o-carboxymethyl chitosan, and infrared test results showed that carboxymethylation occurred simultaneously at the N and 0 positions of chitosan. The effects of substitution degree, pH, reaction temperature, adsorption time and initial dye concentration on the adsorption properties of Congo red dye were investigated. The results showed that the saturated adsorption capacity of N, O-carboxymethyl chitosan for Congo red dye was 330.62 mg/g, which was significantly higher than that of chitosan powder.

Molecular imprinting technology (MIPs), which belongs to the category of subjector-guest chemistry in supramolecular chemistry, refers to the experimental preparation technology to obtain a polymer that perfectly matches a specific target molecule (imprinted molecule, imprinted molecule or imprinted molecule) in the spatial structure and binding site. It can be vividly described as the manufacture of “artificial lock” model to recognize the “molecular key”. The technology has been widely used in the fields of efficient analysis and separation, environmental monitoring and analysis, chiral resolution, drug detection and analysis, sensors, artificial enzymes and artificial receptors, etc. MIPs has the advantages of strong recognition, high selectivity, good stability and wide application range. In recent years, increasingly extensive and in-depth research has become the focus and hot field of current research.

Chitosan metal-imprinted resin is prepared by using chitosan and metal ions to form a complex, after crosslinking polymerization to form macromolecular polymer, and then under appropriate conditions to remove imprinted metal ions, so as to form a polymer adsorption chelate resin with specific “memory” and “recognition” functions. The high selectivity and adsorption capacity of this resin mainly depend on the size of pH and temperature. In addition, the resin is relatively stable in acidic and alkaline media, and can be reused again and again, thus greatly reducing the cost of resin use.

The grafting of sulfur-containing atoms or groups on chitosan molecules can also enhance the adsorption ability of metal ions. Wang[4] used thiourea modified chitosan and Pb(II) as imprinted molecules to prepare thiourea modified chitosan Pb(II) imprinted resin for adsorption of Pb(II) in aqueous solution. The chitosan imprinted resin prepared by molecular imprinting technology achieved the purpose of selective adsorption of Pb(II).

Biju[5] prepared a MIPs using Dy(III) as imprinted molecule, which was used to adsorb Dy, Y, Lu, Nd and La in aqueous solution. The selectivity of the imprinted polymer to Dy(III) was significantly improved. The crosslinked resin can easily selectively separate Dy(III) from mixed metal ion solutions.

Huang[6] synthesized glutaraldehyde crosslinked chitosan resins using Zn2+ as imprinted molecules, and investigated their adsorption properties for transition metal ions. The results show that the resin has strong memory function for Zn^{2+}, can selectively adsorb Zn^{2+} from mixed ionic solution, and has high adsorption capacity for Cd^{2+} and Hg^{2+} of the same group. Under acidic conditions, it does not soften and dissolve, and has good reusability.

Su[7] studied the adsorption properties of nickel-imprinted chitosan crosslinked resin on heavy metal ions in crosslinked chitosan microspheres. Studies showed that the stability of chitosan resin was enhanced in acidic solution after crosslinking, and the adsorption capacity did not decrease significantly after repeated use for 10 times. The adsorption capacity of chitosan crosslinked imprinted resin for specific metal ions such as Ni^{2+}, Zn^{2+} and Cu^{2+} was more than 1 times higher than that of non-imprinted chitosan crosslinked resin. Chitosan resin could replace commercial resin. The application prospect is very broad.

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At present, molecular imprinting technology has been recognized and widely applied in many fields such as biology, chemistry and medicine, and a large number of MIPs have been prepared and used in practical production. Guo [8] prepared two kinds of chitosan imprinted resins using hemoglobin as imprinted molecules and chitosan and maleic anhydride modified chitosan as functional monomers for selective separation of hemoglobin. The results showed that the chitosan imprinted resin chromatographic column could selectively separate hemoglobin from the mixed system of hemoglobin and bovine serum albumin, indicating that the imprinted resin had higher selectivity for hemoglobin than non-imprinted resin under the same conditions.

2. Conclusion

Harmful heavy metal pollution is a worldwide problem that needs to be solved urgently. The national "Twelfth Five-Year" plan has put harmful heavy metal pollution on the agenda. Molecular imprinting technology is an emerging technology. MIPs prepared by molecular imprinting technology are one of the research topics that have attracted much attention due to their predetermination, identification and specificity in the recognition of imprinted molecules, and their relatively simple preparation process, low cost and good practicability. Although MIPs technology has many advantages and develops rapidly, there are still many challenges and opportunities in the field of practical application and industrialization in the future.

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