

Research Progress on the Adsorption Effect of Cellulose-based Modified Materials on Heavy Metals

Lulu Zhang^{1, 2, 3, 4, *} and Chao Guo^{1, 2, 3, 4}

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

²Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Natural Resources, Xi'an 710075, China

³Shaanxi Provincial Land Consolidation Engineering Technology Research Center, Xi'an 710075, China

⁴Land Engineering Technology Innovation Center, Ministry of Natural Resources, Xi'an 710075, China

Abstract

Heavy metal pollution, as an increasingly concerned environmental issue, has attracted social attention for its causes and effects. At present, heavy metals enter soil/water bodies mainly through man-made factors such as mining, metal smelting, application of pesticides and fertilizers, and natural factors such as geological erosion and weathering. Heavy metals have the characteristics of high toxicity, non-degradation, and easy bioaccumulation, which seriously threaten the survival and safety of human beings. At present, people's research on the treatment of heavy metal ions is more in-depth, and many green and efficient absorption materials have been developed, and cellulose-based biomass adsorption materials are one of them. Cellulose is one of the most abundant renewable materials in nature, and has certain adsorption properties. However, cellulose adsorption materials have a single functional group, which can be modified to enhance the adsorption performance of heavy metal ions.

Keywords

Heavy Metal; Environmental Pollution; Cellulose; Adsorption Materials.

1. Heavy Metal Definition

Heavy metals refer to metals with a specific gravity greater than 5 (generally, metals with a density greater than $4.5 \text{ g}\cdot\text{cm}^{-3}$), including gold, silver, copper, iron, lead, etc. At present, heavy metals in environmental pollution mainly refer to heavy elements with significant biological toxicity such as mercury (mercury), cadmium, lead, chromium and metalloid arsenic. Heavy metals are difficult to be biodegraded, but on the contrary, they can be enriched thousands of times under the bio-magnification of the food chain, and finally enter the human body. Heavy metals can interact strongly with proteins and enzymes in the human body, making them inactive, and may also accumulate in some organs of the human body, resulting in chronic poisoning.

2. Removal Method of Heavy Metal Ions

At present, the treatment methods for heavy metals in water mainly include flocculation precipitation method, membrane separation technology, biological method, organic material method and adsorption method [2].

2.1. Flocculation Sedimentation Method

The flocculation and precipitation method is mainly to add special flocculation materials in the water containing heavy metal ions or adjust the pH value of the water to enrich and precipitate the heavy metal ions in the water, so as to achieve the purpose of removal and separation [3]. The development of new flocculation materials and the modification of traditional flocculation materials are the hotspots in this field. In addition, researchers also developed the use of electrocoagulation technology to remove heavy metal arsenic in water through the principle of electrophoresis, which also opened up a new way for the treatment of heavy metals. However, the operating conditions of the flocculation and precipitation method are difficult to control, which is prone to secondary pollution and incomplete removal.

2.2. Membrane Separation Technology

Membrane separation technology converts heavy metal ions in water into insoluble particles of a specific size, and then removes the heavy metal ions through a filter membrane. The main methods of this technology include Electrodialysis (ED), Liquid Membrane (LM), Nanofiltration (NF), Ultra low pressure reverse osmosis (Ultra low pressure) reverse osmosis membrane, referred to as ULPROM), micelle-enhanced ultrafiltration method (Micellar-enhanced ultrafiltration, referred to as MEUF) and water-soluble polymer complex ultrafiltration method [4]. Membrane separation technology has been widely researched and explored in the field of industrial wastewater treatment as a high-tech. It has become one of the indispensable technologies for industrial wastewater treatment.

2.3. Biological Method

Removal of heavy metal ions from water by biological methods [5] is a new application field of biotechnology. The removal of heavy metals by microorganisms [6] is to use the biological properties of microorganisms to biologically remove and accumulate heavy metal ions in wastewater, and then release the metal ions from the microorganisms through a certain method to reduce the concentration of heavy metal ions. There by eliminating the pollution of heavy metal ions to the environment. The principle of microbial method is based on the fact that microbial cells can adsorb heavy metal ions in solution to the cell surface, and then transport heavy metal ions through the cell membrane to the cell body for accumulation, so as to achieve the effect of enriching and removing heavy metal ions.

2.4. Organic Materials Method

The development and development of new organic functional materials is also a hot spot in current water treatment research. By synthesizing polymer materials or modifying and grafting existing materials, new functions are endowed. The material can undergo ion exchange, chemical adsorption or chelation with heavy metal ions in water, thereby removing heavy metal ions. For example, Han Huaifen [7] developed a cross-linked cationic starch chelating agent for the treatment of heavy metal ions. Through experiments, the removal rate of Pb^{2+} and Cu^{2+} by the cross-linked cationic starch chelating agent can reach more than 95%. It also has a good removal effect on Cr^{3+} and Cd^{2+} . Liang Qu [8] also developed a new type of foamed plastic with interpenetrating network structure and special adsorption function for heavy metal ions.

Membrane separation technology, biological method and organic material method are the methods of adsorbing heavy metal ions that have emerged in recent years. But the technology and materials are immature, and the cost is high and the operation is complicated.

2.5. Adsorption Method

The use of adsorption methods to treat heavy metals in water is mainly through physical adsorption or chemical adsorption of heavy metal ions through the high specific surface area, loose structure, or special functional groups of the adsorption materials. The currently used

adsorption materials mainly include activated carbon, mineral materials, activated sludge, and hydrogels. Activated carbon is a porous non-polar adsorbent, which has become one of the commonly used adsorbents because of its special pore structure, huge specific surface area, more surface compounds and good mechanical strength [9]. The adsorption mechanism of activated carbon for heavy metal ions is mainly the ion exchange adsorption of metal ions on the surface of activated carbon, the chemical adsorption of oxygen-containing functional groups and the physical adsorption of surface deposition.

Among the above five methods, adsorption method is currently the main method for treating heavy metal ion wastewater. Therefore, good adsorption materials can bring better adsorption effect. With the rise of environmental awareness, cellulose, which is biodegradable, green and environmentally friendly, has a wide range of sources and low cost, has received more and more attention as an adsorbent material for adsorbing heavy metal ions.

3. Cellulose Based Adsorbent Material

Cellulose material itself is non-toxic, has good biocompatibility, stable physical and chemical properties, and is degradable, which makes cellulose widely used in many fields. Therefore, in addition to traditional industrial production, how to further effectively utilize cellulose resources and develop the application of cellulose in new technologies, new materials and new energy fields has become a research topic that scientists at home and abroad pay more and more attention to [10].

3.1. Adsorption Properties of Cellulose

Cellulose itself has a certain adsorption effect. Research workers at home and abroad have done a lot of research. The natural cellulose-containing substances are directly utilized as adsorbents, such as soybean hulls, wood chips, sawdust, rice husks, coffee grounds, tea grounds, straw straws, etc. However, the direct use of natural cellulose as the adsorbent has a small adsorption capacity and low selectivity. This is because cellulose is a straight-chain polysaccharide composed of β -1,4-glycosidic bonds. There are a large number of hydroxyl groups on this polymer structure, which makes it widely form hydrogen bonds between molecular chains and inside molecular chains. The structure covered by the hydroxyl group affects its reactivity.

3.2. Cellulose Modified Materials

Research on the modification of cellulose can increase the added value of cellulose and broaden the use of cellulose. Liu et al [11] used citric anhydride to react with cellulose by esterification to convert the hydroxyl groups on cellulose into carbonyl groups to prepare a metal ion adsorption material. The combination of carbonyl and metal ions improves the adsorption performance of cellulose to metal ions. Heinze [12] selectively oxidized cellulose by periodate, oxidized the hydroxyl groups on the C₂ and C₃ positions of cellulose to form aldehyde groups, and then used sodium hypochlorite to oxidize the obtained oxidized aldehyde groups to carboxyl groups to prepare 2,3-dicarboxycellulose adsorbent. The adsorbent has carried out adsorption experiments on Ni²⁺ and Cu²⁺ two heavy metal ions, and the results show that the adsorption of heavy metal ions by the adsorbent has been greatly improved.

4. Conclusion

Cellulosic materials have many advantages for heavy metal adsorption. In recent years, due to the shortage of resources and the deepening of the concept of sustainable development, cellulose composite materials have been widely used in wastewater treatment, and cellulose composite materials with high adsorption performance and renewability have been prepared.

The design of surface functional groups to improve the adsorption performance of cellulose has great research significance for the remediation of heavy metal pollution in water.

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