Preparation of magnetic composite materials and Its Application in Heavy metal wastewater Treatment

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Abstract. The heavy discharge of industrial wastewater containing heavy metal ions has caused serious pollution to water bodies and soils. Due to the heavy toxicity and biodegradability of heavy metals, the polluted water bodies have serious consequences for humans, animals and plants. The surface of magnetic materials is easy to be functionally modified and has good magnetic sensitivity. However, some single magnetic materials have problems such as easy aggregation and difficult to disperse and separate, which limits their application. And by combining a single magnetic material with other materials, colleagues who can play their advantages can avoid the defects. The magnetic composite material changes the movement of heavy metal ions in sewage to achieve the effect of adsorption under the action of a magnetic field. It has the advantages of wide source of materials, simple preparation method, efficient adsorption, and repeated use. With a wide range of applications, the research and development of magnetic composite materials has also received widespread attention. This article gives a comprehensive overview of the structural properties of different magnetic composites and their adsorption effects on heavy metal ions, in order to provide research directions and new ideas for magnetic composites on heavy metal ion adsorption.

1. Introduction

In recent years, with the development of industry and the rapid increase in the number of factories, China's economic level has developed rapidly, but at the same time, the large-scale discharge of heavy metal-containing industrial wastewater has made China's water pollution increasingly severe. The serious pollution of the water body not only poses a threat to human life, animals and plants, but also damages the ecological environment and the food chain. In addition, the excessive use of heavy metal ions has also exacerbated the irrational use of heavy metal resources.

At present, the technical methods for treating heavy metal ions in sewage mainly include chemical precipitation method, membrane separation method, ion exchange method, adsorption method, bioremediation method, air flotation method and organic material method. Among them, the above technical methods cannot be widely used in practical problems because of the problems of harsh reaction conditions, high cost, poor enrichment effect, and easy to cause secondary pollution. In recent years, magnetic materials have actively appeared in many fields, and many researchers have shifted their research direction to the study of magnetic materials.

Magnetic material refers to a material that can react in a certain way to a magnetic field, and can be used as an adsorption material. The separation of heavy metal ions from liquid can be accelerated under
the action of an external magnetic field, and new magnetic composite materials and magnetic nanomaterials have been developed for the adsorption of heavy metal ions in industrial wastewater [1], with simple separation, high recovery rate, and large specific surface area. The characteristics of good adsorption effect and not easy to cause secondary pollution [2]. Compared with ordinary adsorption treatment methods, magnetic composite materials combine the common advantages of a single magnetic material and a carrier. The processed product is quickly separated, so that it can avoid secondary pollution to a large extent. Therefore, magnetic composite materials have received extensive attention in the removal of heavy metal ions in sewage.

Magnetic composite materials have received a lot of research and applications in the field of water pollution treatment. It involves many aspects such as the preparation of magnetic composite materials, the composite method of magnetic materials and carrier materials, the processing mechanism of magnetic composite materials and their adsorption effects. This paper systematically summarizes the mechanism and method of composite of magnetic materials and other materials. It takes a more objective look at the adsorption effect of various magnetic composite materials on different types of heavy metals in water, and provides the development of magnetic composite materials for subsequent researchers another section of your paper.

2. Preparation of magnetic composite materials

2.1 Preparation of starch-based magnetic composite materials
Starch is a common high-molecular carbohydrate, which is made by the polymerization of glucose molecules. More common in crops such as corn and potatoes. Starch-treated heavy metal ions mainly use modified starch-containing plants as raw materials. Starch-based microspheres are prepared by inverse emulsion cross-linking polymerization to obtain starch microspheres that are relatively coarse, nearly spherical, and have a large specific surface area. Add oil and water before mixing. Use its adsorption properties to adsorb heavy metal ions in water.

2.2 Preparation of a chitosan-based magnetic material composite
The composite methods of chitosan and magnetic materials mainly include inverse suspension cross-linking method and co-precipitation generation method. Inverse suspension cross-linking is to dissolve chitosan powder in acetic acid solution, then add magnetic Fe₃O₄ nanoparticles to the solution, add a small amount of surfactant to make the magnetic Fe₃O₄ nanoparticles uniformly dispersed, and then perform a crosslinking reaction to modify, the crosslinked modified chitosan derivative is directly mixed with magnetic Fe₃O₄ nanoparticles, and then dispersed uniformly, and magnetic chitosan microspheres are obtained after drying together. In the application of this method, it is necessary to focus on the dispersion of magnetic Fe₃O₄ nanoparticles. The co-precipitation method refers to the fact that chitosan is insoluble in alkaline solutions. Fe²⁺ and Fe³⁺ are added to the chitosan solution according to a certain molar ratio, and then the mixed solution is dropped into the alkaline solution dropwise, and gradually precipitated to form. Magnetic chitosan microspheres. The above two methods are more commonly used. The nano-microsphere particles formed by the inverse suspension cross-linking method have a smaller size and a larger specific surface area, which has certain advantages over the co-precipitation method.

2.3 Preparation of magnetic bio-char composites
Magnetic biochar materials provide active sites for adsorption objects through hydrogen bonding, n-π conjugation, electrostatic adsorption, ion exchange, or other interactions. There are two main methods for preparing magnetic biochar composite materials: pretreatment of raw materials and subsequent addition of magnetic materials. Pretreatment is mainly to generate magnetic particles in situ before the pyrolysis reaction, and Fe³⁺ / Fe²⁺ is deposited on the raw materials by chemical precipitation method, and then magnetic particles are generated in situ during the pyrolysis. The advantages of the original biochar materials for the adsorption of heavy metals after compounding have not diminished. In addition,
a series of studies have confirmed that Fe$_3$O$_4$ can be perfectly dispersed in biochar in the form of nanoparticles, giving such materials high saturation magnetic strength [3].

2.4 Preparation of graphene and its derivatives with magnetic materials
Graphene is a two-dimensional carbon nanomaterial with hexagonal honeycomb lattice composed of carbon atoms with sp$^2$ hybrid orbitals. Due to its large theoretical specific surface area, high mechanical strength and rich electronic structure, graphene has become a highly efficient adsorbent Potential. In recent years, graphene derivatives (such as GO and rGO) have been widely used in the field of water treatment. The rich oxygen-containing groups on graphene oxide not only make it highly hydrophilic, but also have strong the vender Waals force and electrostatic interaction can chelate with heavy metal cations [4], and the adsorption capacity of heavy metal ions can reach about twice that of clay adsorbent, and it is regenerated using NaOH (c = 1mol / L) solution [5]. At present, there are also graphene-organic composite adsorbents [6], graphene magnetic adsorbents [7], graphene-mineral composite functional adsorbents [4], etc. for adsorbing heavy metal ions in water treatment related applications. Graphene oxide contains abundant oxygen-containing groups, which makes graphene oxide highly absorbent. Therefore, when graphene and magnetic materials are compositely prepared, graphene can be used as a catalyst to synthesize graphene by hydrothermal method. Magnetic nano photocatalytic material.

3. Application of magnetic composite materials in the adsorption of heavy metal ions
Magnetic nanoparticles are particles with a magnetic cut size between 1 and 100 nm. They mainly include pure metals, metal oxides, magnetic alloys and other magnetic compounds. When a single-component material cannot meet the requirements of adsorption, it can be optimally combined with materials of different properties to prepare a new composite material. By cross-linking and polymerizing with various surface-rich active adsorbents, magnetic materials can be loaded on it. The composite material provides more saturated magnetic strength, so that the treated product has superparamagnetism and can be better separated from the original water body, thereby improving the processing efficiency and avoiding secondary pollution. Composite carriers are mainly starch, cellulose, chitosan, biochar, graphene, activated carbon and carbon nanotubes and so on.

| Magnetic material type          | Heavy metal ion | Adsorption capacity (mg/g) | Reference number |
|--------------------------------|----------------|----------------------------|------------------|
| NZVI / corn starch             | Cr$^{2+}$      | 17.29                      | [8]              |
| Fe$_3$O$_4$@SiO$_2$-MnO$_2$     | Cu$^{2+}$      | 71.60                      | [9]              |
| Modified magnetic chitosan     | Pb$^{2+}$      | 57.98                      | [10]             |
| Fe$_3$O$_4$-GS                 | Pb$^{2+}$      | 17.29                      | [11]             |
| Montmorillonite-loaded Nano-Zerovalent Iron | U(VI) | 0.98                      | [12]             |
| Iron alginate mesoporous carbon microspheres | Sb(V) | 75.18                      | [13]             |

3.1 Adsorption of heavy metal ions by starch-based magnetic composite materials
Hou and his team used starch as a template to prepare a variety of Fe$_3$O$_4$ nanoparticles through co-precipitation and changing reaction conditions (starch-iron ratio, iron ion-sodium hydroxide ratio, reaction time, and reaction temperature). The adsorption time was 1 h, the pH was 11, and the temperature was 50°C. The adsorption effect on wastewater with Cu$^{2+}$ concentration of 0.338 mmol/mL was the best, all reaching 90%[14]. Experimental research shows that with the increase of adsorption time, the removal rate of Cu$^{2+}$ can be increased by increasing the pH value and increasing the reaction temperature. In addition, the increase of reaction time will also increase the removal rate of Cu$^{2+}$. Experimental research shows that as the adsorption time increases, one way to increase the removal rate
of Cu$^{2+}$ is to increase the pH value and one way is to increase the reaction temperature. In addition, the increase in reaction time will also increase the rate of Cu$^{2+}$ removal. The composite of starch and magnetic materials greatly improves the adsorption effect of heavy metal ions. However, the conditions for the composite reaction of starch and magnetic materials are relatively harsh, and it is currently difficult to directly use them in actual life.

3.2 Adsorption of heavy metal ions by cellulose-based magnetic composite materials
Zhen used magnetic cellulose sodium and supported it with Fe$_3$O$_4$ by the emulsification method. The use of magnetic cellulose sodium has good adsorption. In the experiment of adsorbing Ni$^{2+}$ in wastewater, the removal rate of Ni$^{2+}$ can reach 86.82%, and the adsorption amount can reach 1.41mg/g. Moreover, the initial resolution of sodium magnetic cellulose after complex regeneration with a neutral EDTA solution at a concentration of 5% reached 50.17%, and the removal rate of Ni$^{2+}$ reached 65.33%[15].

Good effect for heavy metal ion treatment. However, the current research results have some limitations when applied to reality. The common feature is that the reaction conditions are too harsh, and ultraviolet rays must be used as catalytic conditions. If the ultraviolet conditions required for the reaction are changed to sunlight, the catalytic treatment can be better. The combination of cellulose and magnetic materials can more effectively use agricultural and forestry wastes, and the experimental conditions are relatively relaxed.

3.3 Adsorption of heavy metal ions by chitosan-based magnetic composite materials
Yan of Tianjin University synthesized CSB @ Fe$_3$O$_4$ and ECCSB @ Fe$_3$O$_4$ composite nanomaterials, XRD, FTIR, SEM, TEM, and VSM characterization of the two composite nanomaterials before and after adsorption of chitosan, magnetic Fe$_3$O$_4$, and Pb$^{2+}$, the adsorption behavior of CSB @ Fe$_3$O$_4$ and ECCSB @ Fe$_3$O$_4$ composite nanomaterials on Pb$^{2+}$ in water was studied. The results show that the two nanomaterials have higher adsorption capacity and better magnetic separation performance [16].

According to experiments, we can know that when the pH is low, functional groups on adsorbent surface are affected, when the pH is high, it also affects the existence of Pb$^{2+}$. The composite reaction conditions of chitosan and magnetic materials are too harsh and need to be further improved in combination with actual conditions.

3.4 Adsorption of heavy metal ions by graphene and its derived magnetic composites
Some scholars have reported that Fe$_3$O$_4$-GS with graphene oxide as the carrier has a large effect on the adsorption effect of various heavy metal ions (such as Hg$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Ni$^{2+}$). The removal rate of heavy metal ions is higher than 80% above pH 5.5 [11], according to a large amount of data, it is shown that graphene and its derivative-based magnetic composites have a good adsorption effect on various heavy metal ions at a pH of 5-7. In addition, the adsorption effect of magnetic materials does not increase with the increase in the amount of use, has a stable value. Other scholars have shown that graphene-based magnetic composites have high desorption rates, repeated use rates, and repeated use. For example, Zhang et al. used graphene as a cocatalyst to modify graphite/Fe$_3$O$_4$/ZnO magnetic nanocomposite photocatalytic material ZnO by hydrothermal method. The photocatalytic degradation test showed that the degradation rate of the composite was still more than 90% after three repeated tests [17]. The adsorption rate of other such magnetic composite materials is over 80% after repeated use for 3-5 times.

3.5 Adsorption of Heavy Metal Ions by Nanometer Magnetic Fe$_3$O$_4$
After the surface coating of ferric oxide, it can prevent its agglomeration in solution, improve its chemical stability, and have a large number of functionalizable groups on the surface [18]. Nano magnetic materials due to their large specific surface area (such as Fe$_3$O$_4$ and MgO composite materials). The adsorption rate of heavy metal ions Pb$^{2+}$ is fast, and the adsorption equilibrium state can be reached within 50 minutes. And maximum adsorption efficiency can be obtained at pH=6, its maximum adsorption capacity is 711.5 mg/g [19]. By modifying characteristic complexing groups such as amino,
mercapto, and carboxyl groups on the surface of Fe₃O₄, its can strengthen that adsorption characteristics and overcome negative effects such as agglomeration. Conducive to the dispersion and application of magnetic nanomaterials in aqueous solution. However, it is undeniable that in order to improve and expand the efficiency and applicability of magnetic Fe₃O₄ nanoparticles in the treatment of wastewater containing heavy metal pollution, there are still some deficiencies in its preparation and functionalization process [20].

4. Conclusion
With the rapid development of today's social industry and agriculture, environmental issues are becoming more and more urgent. Comrade Xi Jinping, then Secretary of the Zhejiang Provincial Party Committee, put forward the scientific conclusion that green mountains and green mountains are the golden mountains and silver mountains during an inspection in Anji, Huzhou, Zhejiang, in August 2005. However, the most important thing to solve the problem of water pollution is to solve the problem of excessive heavy metal ions in sewage. The single use of adsorptive materials is more likely to produce products that are difficult to separate in wastewater treatment and easily cause secondary pollution. Greatly limits further practical applications. Adhesive materials are combined with magnetic materials, the product can be separated quickly under the condition of external magnetic field. Materials that are compounded with magnetic materials have a wide range of sources, low cost, renewable, and environmentally friendly. Promote the sustainable development of society and have good economic, energy and environmental benefits. The composite of adsorbent materials and magnetic materials has broad application prospects in the direction of water treatment.

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