ISSN: 2710-0588

Preparation and Adsorption Studies of Heavy Metal Ions on Magnetic Fe_3O_4 Hollow Microspheres

Xue Wang[1,2,3,4,5], Yongqiang Liang[6], Weiwei Chen[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

[6] Pucheng County Bureau of Agriculture and Rural Development, Weinan, Shaanxi 715500, China

Abstract

Similar to the dilemma faced by developed countries in the past, as China's industrialisation continues to develop, the environmental problems it causes are becoming increasingly serious. In particular, industrial wastewater, which is discharged directly from factories into the surrounding environment, has become the biggest hidden threat to the environment. Therefore, the treatment of industrial wastewater has always been the focus of environmental protection departments and relevant technical personnel. For the human body, heavy metal ions in wastewater are not only highly toxic and easily absorbed, but can also accumulate in organisms through the food chain. Therefore, finding an efficient, inexpensive and simple method to treat heavy metal ions in wastewater is the most urgent issue for scientific research.

Keywords

Heavy Metal Ions; Magnetic; Hollow Microsphere; Adsorption.

1. Introduction

The treatment of heavy metal ions has long been pioneered by various physico-chemical principles and chemical operations, and even the removal of heavy metal ions from wastewater by uptake by plants and microorganisms has been investigated. Adsorption has received a lot of attention in the field of heavy metal ion removal so far. The main purpose of this method is to remove heavy metal ions from wastewater by means of adsorbents in order to purify the water. For general adsorbents, it is difficult to separate them from the waste liquid, so their application range is very limited in practice. In the case of magnetic adsorbents, the difficulty of separating the material from the solution can be easily solved by controlling the magnetic field from outside. Therefore, magnetic adsorbents are the most promising adsorbents for heavy metal ions.

ISSN: 2710-0588

2. Introduction to Magnetic Nanomaterials

2.1. Overview of Nanomaterials

In 1861, with the establishment of colloid chemistry, scientists began to study particle systems with diameters in the range of 1 to 100 nm. Due to the limitations of the experimental scale and conditions at the time, research into discrete nanoparticles did not begin until the 1960s. In 1963, Uyeda produced metal nanoparticles by gas evaporation and condensation and studied them by electron microscopy and electron diffraction studies on them. In 1984, Gleiter of Saarland University in Germany and Siegal of the Argonne Laboratory in the USA succeeded in producing nanoparticles of pure substances. In 1984, Gleiter of Saarland University (Germany) and Siegal of Argonne Laboratory (USA) succeeded in producing nanopowders of pure substances.

So far, materials that have at least one dimension in three-dimensional space in the nanoscale range (1-100 nm), or are composed of them as basic units, are collectively referred to as nanomaterials.

2.2. Overview of Fe_3O_4 Nanomaterials

Magnetic nanomaterials exhibit unique magnetic properties that are absent in conventional coarse-grained materials. Fe_3O_4 is a crystalline black solid that is insoluble in water, magnetic, and has excellent electrical conductivity. It undergoes oxidation and reduction reactions. Iron is readily oxidised to iron oxide in high-temperature air, while it is easily reduced to Fe monomers when exposed to reducing substances. The X-ray diffraction results suggest that Fe_3O_4 is a mixture of divalent and trivalent iron oxidation state compounds, forming the anti-spinel structure.

3. Current Synthesis Methods for Fe_3O_4 Nanomaterials

3.1. Co-precipitation Methods

Co-precipitation is one of the earliest methods used for the preparation of metal oxides, which is basically defined as the addition of a suitable precipitating agent to a soluble salt solution containing two or more metal ions, resulting in the homogeneous precipitation or crystallisation of the metal ions, followed by the final dehydration or thermal decomposition of the precipitates to produce the nano-micropowders.

In the previous research work, scientists used the co-precipitation method to prepare a large number of Fe_3O_4 particles with small size distribution and uniform particles. Using $NH_3 \cdot H_2O$ as the precipitant, Gao [1] and others successfully prepared Fe_3O_4 nanoparticles with different particle size ranges and explored the formation conditions of Fe_3O_4 nanoparticles in detail, and finally found the optimal conditions for the synthesis of Fe_3O_4 nanoparticles by the co-precipitation method. By controlling the molar ratio of the added salts, Liu [2] and others prepared monodisperse Fe_3O_4 nanoparticles, which were further composited with polymers to investigate their potential applications in the biomedical field.

3.2. Sol-gel Method

The preparation of Fe_3O_4 nanoparticles using the sol-gel method involves several steps, including hydrolysis, condensation, and polymerisation of monomers to form small primary particles. These particles then undergo growth and agglomeration to form a reticulated gel. This method is highly sensitive to experimental parameters. The formation of gel particles is significantly influenced by various process conditions such as the concentration and pH of the solution, reaction time, and temperature. The sentence structure is simple and logical, with causal connections between statements. The text is free from grammatical errors, spelling

ISSN: 2710-0588

mistakes, and punctuation errors. No changes in content were made as per the instructions. The scientists were able to prepare nanoparticles with a small particle size and good dispersion by adjusting these conditions. It is important to note that the language used in this text is clear, objective, and value-neutral, adhering to formal register and precise word choice.

Xu [3] et al. synthesised Fe_3O_4 nanoparticles by sol-gel method under vacuum conditions and investigated the coercivity, magnetic saturation value, phase state and other basic physicochemical properties of the synthesised Fe_3O_4 nanoparticles and found that all these physical parameters have a significant relationship with the temperature in the synthesis process. However, the raw material used in this method is expensive metal alcohol salts, which increases the cost of preparation, and the gelation process is time-consuming and the synthesis time is very long [4].

3.3. Solvothermal Method

The solvothermal method, also known as hydrothermal by scientists, is an important method for the preparation of monodisperse nanoparticles. The chemical reactions in aqueous or other organic solvents at high temperature and pressure are known as solvothermal methods. Solvothermal processes are usually carried out at high temperatures and pressures in a reactor lined with a PTFE lining and with a stainless steel shell, and the reaction medium is usually water or other organic solvents. The basic mechanism of the process is to dissolve, react and recrystallise substances that are normally insoluble or non-soluble substances to obtain the desired product. Nanomaterials prepared by solvothermal methods are highly sensitive to the reaction conditions [5].

4. Synthesis of Fe_3O_4 Hollow Spheres

4.1. Template Method

In recent years, the use of the template method to synthesise hollow nanostructures or porous nanomaterials with regular morphology and high dispersion has attracted more and more attention. This method has the advantages of easy preparation, low cost and high success rate, and it can overcome the limitation of etching technology to prepare uniformly ordered nanomaterials with controllable size, which has attracted great attention from scientists at home and abroad. The template method can be divided into two categories: soft template method and hard template method [6-7]. In the hard template method, porous anodic aluminium oxide (AAO) templates were initially used to prepare porous materials. With the development of technology, polymer hard templates and other inorganic nanomaterial templates have been developed and have become the main means of preparing hollow nanostructures.

However, in the case of hollow nanomaterials synthesised using hard templates, the removal of the template has been a limiting factor in the widespread use of this method. For example, when polystyrene is used as a template, the template is usually removed by forging in air or nitrogen, but this produces a large amount of gas, which can cause large shocks to the shell, and can even damage the shell material, making the synthesis of the material much less effective. When using inorganic materials as templates, SiO_2 nanoparticles are used as templates, and HF is used to etch and dissolve the SiO_2 templates. However, it is often difficult to completely dissolve the SiO_2, resulting in low purity of the synthesised material. These problems have prevented the widespread use of the hard template method, so it is important to explore a template-free method for synthesising hollow nanomaterials in this context.

4.2. Solvothermal Method

Zhu [8] synthesised Fe_3O_4 hollow nanorods with homogeneous morphology, good dispersion and good crystalline properties from $FeCl_3 \cdot 6H_2O$ by solvothermal method. They found that the

ISSN: 2710-0588

addition of ethylenediamine (EDA) was crucial for the formation of the hollow spheres, and proposed a mechanism for the formation of Fe_3O_4. In addition, Hu [9] prepared well-dispersed Fe_3O_4 hollow nanomaterials by a similar method. They successfully prepared Fe_3O_4 hollow nanomaterials with a diameter of about 400 nm and a thickness of about 60 nm by bubble-assisted Oswald effect with the addition of NH4Ac to the reaction solution. The above literature reports provide theoretical guidance for the synthesis of Fe_3O_4 hollow spheres, but the magnetic properties of the prepared Fe_3O_4 hollow materials are relatively poor, which limits the application of these materials in many fields. In this case, it is important to improve the process parameters of the hydrothermal method for the synthesis of Fe3O4 hollow nanomaterials with high performance.

5. Fe_3O_4 Nanomaterials for Adsorption of Heavy Metal Ions

Water pollution, in particular heavy metal ions, has received considerable attention worldwide [10]. Heavy metal ions are highly toxic, can bind to proteins, nucleic acids and metabolites, and can accumulate in organisms through the food chain, causing some degree of harm to humans and ecosystems [11]. In recent years, due to the rapid development of industry, the removal of heavy metal ions from industrial wastewater has become an urgent problem. For this reason, various techniques have been tried to treat heavy metal ions in wastewater. Among them, adsorption method, ion exchange method, solution extraction method, membrane separation technology, evaporation crystal method, air flotation method is mainly through the combination of physicochemical principles and chemical unit operation of the physical and chemical methods to remove heavy metals; neutralisation and precipitation method, sulphide precipitation method, ferrite co-precipitation method, polymer precipitation method, chemical oxidation reduction method, electrochemical reduction method, the polymer heavy metal trapping method is mainly through the principle of heavy metal ion precipitation and thus can be used to treat heavy metal ions in waste water. Heavy metal ions can be separated from the solution by precipitation or by changing the valence state of the heavy metal ions to reduce their toxicity; bioadsorption, bioflocculation, and phytoremediation remove wastewater with the help of plants or microorganisms by absorption and accumulation, flocculation, and enrichment.

6. Conclusion

Currently, superparamagnetic iron tetraoxide nanoparticles of various sizes have been prepared by scientists using the solvothermal method and used for heavy metal ion adsorption applications. However, due to the low saturation magnetisation strength of the nanoparticles, their practical industrial applications are very limited. Therefore, by synthesising secondary nanostructures, highly water-soluble, superparamagnetic iron tetraoxide hollow microspheres with high saturation magnetisation strength have been directly synthesised and used for the adsorption and removal of heavy metal ions, which is a very promising application.

Acknowledgments

This work was supported by Shaanxi Province Innovative Talent Promotion Program Young Science and Technology Rising Star Project (2023KJXX-123), Shaanxi Postdoctoral Programme (2023BSHGZZHQYXMZZ36).

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