Preparation and Performance Research of Magnetic Polymer Microspheres

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Abstract: In this thesis, polystyrene magnetic polymer microspheres with good monodispersity and carboxyl functional groups were prepared. The adsorption properties of styrene-acrylic acid magnetic polymer microspheres to bovine serum albumin have been studied. Using Fe\textsubscript{3}O\textsubscript{4} magnetic fluid as the magnetic core and styrene-acrylic acid copolymer as the polymer shell, composite microspheres with very small particle diameters were prepared by the dispersion polymerization method.

1. Introduction

In recent years, magnetic composite microspheres not only have the magnetic responsiveness of ordinary magnetic materials, but also have many properties of polymer materials. It has broad application prospects in electrochemistry, fine chemicals, immobilized enzymes, biomedicine, food testing, wastewater treatment.

Magnetic Polymer Microspheres are formed by combining inorganic magnetic particles and organic polymers through appropriate methods. They have certain magnetic properties and special structures. Due to their magnetic properties, they can be easily and quickly acted on by an external magnetic field. Because of the characteristics of polymer particles, it has attracted wide attention. In this thesis, based on the research results at home and abroad, polystyrene magnetic polymer microspheres with good monodispersity and carboxyl functional groups were prepared.

The performance of inorganic magnetic particles is the main factor affecting the magnetic responsiveness of magnetic polymer microspheres. In this paper, nano-Fe\textsubscript{3}O\textsubscript{4} is used as the magnetic source. Nano-Fe\textsubscript{3}O\textsubscript{4} was prepared by chemical co-precipitation method. The prepared nano-Fe\textsubscript{3}O\textsubscript{4} has a good particle size. The prepared oleic acid modified nano-Fe\textsubscript{3}O\textsubscript{4} magnetic fluid was used to prepare polystyrene magnetic polymer microspheres with carboxyl groups by the dispersion polymerization method. The effects of temperature, monomer determination, initiator determination and dispersion media composition on particle size and particle size distribution are investigated. The optimum solution for the preparation of polystyrene polymer microspheres is a reaction temperature of 70°C, an initiator of 2% of the monomer dosage and a 1:3 ratio of water to absolute ethanol in the dispersion medium. The magnetic polymer microspheres have good monodispersity, and nano-Fe\textsubscript{3}O\textsubscript{4} magnetic particles are distributed in polystyrene microspheres, according to analysis and test findings. The magnetic polymer microspheres produced have a high capacity for adsorption of bovine serum albumin.
2. Experiment part

**Main raw materials:** Ferrous ammonium sulfate Fe(NH₄)₂(SO₄)₂·6H₂O, ferric trichloride hexahydrate FeCl₃·6H₂O, ammonia NH₃ (aq), absolute ethanol C₂H₆O, sodium lauryl sulfate C₁₂H₂₅SO₄Na, Cetyl alcohol C₁₆H₃₄O, all of these are produced in Aladdin reagent factory[1-3].

**Main equipment:** RW20 overhead stirrer, produced by IKA; RE-501 water bath, produced by Shanghai Pailan Instrument Equipment Co., Ltd.; JP-100ST ultrasonic cleaner, produced by Shenzhen Jiemeng Cleaning Equipment Co., Ltd.; DHG-9245A electric heating constant temperature blast drying oven, Shanghai Yiheng Technology Co., Ltd.; electronic balance, produced by Shanghai Zhuojing Electronic Technology Co., Ltd.; microplate reader, MDS production[1-3].

2.1 Experiment method

**Preparation of Fe₃O₄:** Fe₃O₄ was prepared by co-precipitation method. During the reaction process, Fe²⁺ is easily oxidized to Fe³⁺, therefore controlling the reaction feed ratio will affect the formation of Fe₃O₄. In the experiment, the feeding ratio of Fe²⁺ and Fe³⁺ is about 1:1.78. In addition, the particle size and purity of Fe₃O₄ nanoparticles are affected by the pH value, ageing duration, stirring speed, and co-precipitation temperature during the co-precipitation process.

Transmission electron microscopy is used to examine the morphology of particles generated in various polymerization processes. From Fig.1 and Fig.2, Fe₃O₄ particles have a nice spherical form, the same particle size, and a single dispersibility. A coating of polystyrene with a thickness of 70 to 170 nm is applied to the surface of Fe₃O₄ nanoparticles, creating a core-shell nanostructure with evident agglomeration[4, 5].

![Fig.1 TEM morphology image of magnetic iron oxide](image1)

![Fig.2 TEM image of magnetic iron oxide(polystyrene functional polymer)](image2)

**Preparation of carboxyl modified magnetic iron oxide (polystyrene):** It is extensively utilized by...
the reason for the preparation method of the dispersion polymerization is relatively straightforward, and can produce distributed microspheres with a particle size distribution ranging from 0.1 to 180 microns[6].

According to its purity, crystallized bovine serum protein is dissolved in MES buffer to prepare a 0.5mg/mL protein standard solution. Pierce BCA protein quantification reagent is compatible with 5% of the total protein content, and protein samples of surfactants (descalers) are less contaminated.

This experiment uses potentiometric analysis to measure the particle size of the material. Along with other globular proteins, bovine serum albumin (BSA) plays a vital role in the transport and release of a variety of endogenous and exogenous substances into the blood.[7-9].

It can be seen that the particle size of Fe₃O₄@PS is larger than that of Fe₃O₄ from Table 1, Table 2 and Table 3. The conductivity (Cond) of the polystyrene-coated microspheres is lower than that of magnetic iron oxide due to being bonded with an insulating polystyrene layer, and the conductivity will drop. The conductivity does not change much after transporting the carboxyl group.

Table 1 Magnetic iron oxide potential and particle size distribution

|   | ZP (mV) | Z-Ave (nm) |
|---|---------|------------|
| 1 | -5.33   | 1697       |
| 2 | -7.12   | 1898       |
| 3 | -7.19   | 1622       |
| average value | -6.55   | 1739       |

Table 2 Potential and particle size distribution of magnetic iron oxide (polystyrene functional polymer)

|   | ZP (mV) | Z-Ave (nm) |
|---|---------|------------|
| 1 | -22.6   | 1923       |
| 2 | -21.7   | 1792       |
| 3 | -19.9   | 1725       |
| average value | -21.4   | 1813       |

Table 3 Carboxyl modified magnetic iron oxide (polystyrene functional polymer)

|   | ZP (mV) | Mob (μm cm²/V s) | Cond (mS/cm) |
|---|---------|-----------------|--------------|
| 1 | -38.4   | -3.011          | 0.0263       |
| 2 | -38.8   | -3.038          | 0.0191       |
| 3 | -36.9   | -2.893          | 0.0196       |
| average value | -38.0   | -2.981          | 0.0217       |

2.2 Results and discussion

**XRD analysis adsorption performance test:** The powder diffraction pattern of the product was obtained by XRD analysis. When comparing conventional Fe₃O₄ XRD patterns, it can be noted that not only are the Fe₃O₄ nanoparticles' XRD peaks obvious, but there are no impurity peaks, which is consistent with the standard pattern.

**Analysis of adsorption performance:** Microplate readers are used to determine the optical density of standards and samples. The procedure is much the same as adsorption of unactivated magnetic beads. The adsorption capacity of activated magnetic beads to BSA is greater than 6.5mg/g, while the adsorption capacity of unactivated magnetic beads to BSA is less than 4.5mg/g, and the adsorption capacity after activation is significantly greater than that of non-activated magnetic beads, as shown in Fig.3.
Analysis of adsorption performance at different times: The kinetic adsorption procedure is essentially the same as the standard adsorption procedure. The experimental material was 0.5mol/L bovine serum albumin, and the adsorption was performed using unactivated magnetic beads.

As seen in Figure 4, the amount of protein adsorption rises as the adsorption duration increases. With the passage of time, the amount of bovine serum protein adsorbed grows. The protein adsorption capacity of each sample remained high for the first 1 hour following the commencement of the adsorption procedure, and then gradually rose slowly after 1 hour.

Summary: The Fe$_3$O$_4$@PS-COOH prepared by the dispersion polymerization method has a uniform particle size and is less than 2 μm. The magnetic nanoparticles are dispersed inside the microspheres, as shown in the TEM images. The magnetic microspheres have carboxyl functional groups, according to infrared spectroscopy, and the connection between the polymer and Fe$_3$O$_4$ nanoparticles is a physical effect.

3. Conclusion
(1) The produced Fe$_3$O$_4$ particles are stable when the Fe$^{2+}$ to Fe$^{3+}$ ratio is 1:1.75 and there is no inert atmosphere protection.
(2) When preparing polystyrene macromolecular microspheres by dispersion polymerization, polymerization conditions are obtained: reaction temperature is 70°C, initiator dosage is 2% of monomer. As the ratio between content of water and absolute ethanol in the dispersion medium is 1:3, the polystyrene polymer microspheres are the best solution.
(3) The prepared magnetic polymer microspheres have good monodispersity, and Fe₃O₄ magnetic nanoparticles can be evenly dispersed in styrene and dispersed in the microspheres; in the magnetic microspheres with carboxyl functional groups, polymerization interaction between the material and the nano-Fe₃O₄ particles is only physical, and the carboxyl functional groups on the surface of the microspheres are characterized by a high content.

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