Synthesis of Fe₃O₄ composite particles by emulsion polymerization

Qingyu Huang¹*, Shuzhi Wang²
¹College of Chemical Engineering, Daqing Normal University, Daqing 163712, China
²Organic geochemical laboratory, Daqing Oilfield Company Ltd Exploration and Development Research Institute, Daqing 163712, China
5031416@163.com

Abstract. In the emulsion system containing Fe₃O₄ particles, the acrylamide monomer was polymerized and formed Fe₃O₄ composite particles. The composite particles were tested and analyzed by XRD, TEM, DLS and VSM, showing that the diameter of Fe₃O₄ composite particles was about 390nm and Fe₃O₄ composite particles had superparamagnetic properties.

1. Introduction
In recent years, ferric oxide composite particles have been used in biomedical and bioengineering applications such as cell separation and nucleic acid concentration [1] due to their relatively fast and easy magnetic separation. In addition, magnetic polymer particles have great potential in several applications such as biofluid detoxification and magnetic guidance for specific drug delivery processes. Kawaguchi et al. [2] first proposed hydrophilic magnetic emulsion synthesized from acrylamide as the main monomer. In addition, various creative methods have been studied using natural polymers and proteins as raw materials. In this field, Chatterjee et al. [3] reported various interesting papers, such as cross-linked protein magnetic microspheres and their application in the separation of red blood cells from blood. It is worth noting that all reported methods for magnetic polymer latex point to submicron particle size with considerable iron oxide content, but there are few articles on smaller hydrophilic magnetic polymer emulsions.

The objective of this paper is to present a new method for the preparation of ferric oxide composite particles by inverse emulsion polymerization and to characterize the composite particles.

2. Experiment section
2.1. Synthesis of Fe₃O₄ composite particles
According to the molar ratio Fe³⁺/Fe²⁺=2, 0.1M, 15ml FeCl₂ and 0.1M, 30ml FeCl₃ were placed in 100ml three-flask at 60°C, protected by N₂ and vigorously stirred. Excessive ammonia water was used for co-precipitation and maintained for 1 hours. Then 30ml sodium citrate aqueous solution was added and stirred for 2 hours. Magnetic nanoparticles were collected with a magnet and washed 4 times with distilled water to rinse Cl⁻. The magnetic nanoparticles were then dispersed in the water to form a magnetic fluid for further use (solid content of about 16%wt).

Then 4g AM, 0.02g MBA and an appropriate amount of OP10 were evenly mixed with the above magnetic fluid to form a 15ml mixing solution, which was slowly dropped into 20ml toluene containing an appropriate amount of Span80 after stirring vigorously for 0.5h to obtain a stable inverse
emulsion. Before polymerization, the reversed phase emulsion was placed under N₂ protection for 15min, the reaction system was heated to 60°C, and KPS was added. Polymerization was conducted at 60°C for 6h (magnetic particle content was about 5%wt). Now Fe₃O₄ composite particles were prepared.

2.2. **Analytical methods**

The photograph of Fe₃O₄ composite particles was obtained by TEM (JEOL JEM-2010, Japan). The average size and size distribution of Fe₃O₄ composite particles were determined by a laser particle size-analyzing system (ZetaPlus, Brookhaven Instruments Corporation, USA). The magnetic hysteresis loops of samples were tested by a VSM (Lake Shore 7410, USA). The XRD of Fe₃O₄/PAM SMNPs was measured by a X-ray diffractometer using Cu Kα radiation (λ=1.54056 Å) (D8 Discover, Bruker, Germany).

3. **Results and discussions**

3.1. **XRD results:**

In order to obtain the structure information of magnetic iron oxide composite particles, the crystal structure (XRD) of magnetic particles was analyzed by X-ray diffraction, as shown in Figure 1. The XRD pattern of magnetic particles is similar to that of Fe₃O₄ composite particles in ASTM. In addition, during the synthesis of products, excessive ammonia water was added and the precipitation temperature was maintained at 60°C to ensure that Fe₃O₄ was synthesized[4-5].

![XRD of magnetic composite particles.](image)

3.2. **TEM of Fe₃O₄ composite particles:**

During the experiment, a small number of uncoated Fe₃O₄ particles were produced. By magnetic separation, Fe₃O₄ coated composite particles can be obtained. Figure 2 shows TEM images of typical Fe₃O₄ composite particles. It can be seen that there are a large number of Fe₃O₄ particles in the polymer, and the magnetic composite particles are partially cross-linked with the size of 300-500nm.
3.3. Size distribution of Fe₃O₄ composite particles:
Figure 3 shows the size distribution curve of Fe₃O₄ composite particles coated by polyacrylamide. It can be seen from Figure 3 that the average particle size is 390nm. DLS analysis shows that the size of the particle ranges from 170 to 900nm, which is similar to the TEM test results.

3.4. Magnetic properties of Fe₃O₄ composite particles:
The magnetic properties of Fe₃O₄ composite particles were studied by using VSM. Figure 4 shows the magnetization curve of Fe₃O₄ composite particles. It can be seen from the curve that the superparamagnetic property is obvious, and there is no remanence when the magnetic field is zero. The saturation magnetization was 7.2emu/g. The magnetic saturation of Fe₃O₄ nanoparticles coated by polyacrylamide was significantly reduced. While the sodium citrate modified Fe₃O₄ had a magnetic saturation of 40.1emu/g.
4. Conclusions
In this paper, Fe$_3$O$_4$ composite particles with superparamagnetic properties were prepared by emulsion polymerization. The saturation magnetization was 7.2emu/g. The average particle size of Fe$_3$O$_4$ composite particles was about 390nm, and the size ranged from 170 to 920nm.

Acknowledgement
This work was supported by the < Daqing Normal University Scientific Research Fund > under Grant < number 14ZR13 >.

References
[1] Elaissari A, Rodrigue M and Meunier F 2001 J. Magn. Magn. Mater. 225 127-133.
[2] Kawaguchi H, Fujimoto K and Nakazawa Y 1996 Colloid Surf. A. 109 147-154.
[3] Chatterjee J, Haik Y and Chen C J 2001 J. Magn. Magn. Mater. 225 21-29.
[4] Zhang L, Papaefthymiou G C and Ying J Y 1997 J. Appl. Phys. 81 6892-6900.
[5] Kim D K, Zhang Y, and Voit W 2001 J. Magn. Magn. Mater. 225 30-36.