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The roles of hydrochloric acid and polyethylene glycol in magnetic fluids

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Abstract

Increasing interest has been drawn to the studies of magnetic fluids due to their multiple applications from industry to medicine. However, further exploration is still required for the techniques of preparing satisfying, convenient and stable magnetic fluids. We explored characteristics of magnetic liquids prepared by employing co-precipitation techniques of hydrochloric acid (HCl) and polyethylene glycol (PEG), and the functions of HCl and PEG in the magnetic liquid. According to the improved technique, after preparing Fe_3O_4 by a co-precipitation method, hydrochloric acid and PEG2000 react with magnetic particles at a certain temperature to generate the anticipated magnetic nanoparticles. The process could be under an air atmosphere rather than a N_2 atmosphere. Compared with traditional techniques, the magnetic nanoparticles prepared by this method have smaller size, better dispersion and stability, with the average hydrodynamic diameter adjustable between 8 and 50 nm. This study revealed that reduction of nanoparticles size is not mainly due to a $[Cl^-]$ coating over the magnetic nanoparticles, but that HCl reacts with Fe_3O_4 particles after being heated. Meanwhile, PEG can stabilize or coat Fe_3O_4 nanoparticles as a dispersing and stabilizing agent.

Keywords: Magnetic fluid; Hydrochloric acid; PEG

1. Introduction

Magnetic fluid (MF) is a kind of stable colloid system composed by magnetic nanoparticles dispersed in a suitable liquid carrier. The magnetic fluid generally used today was first synthesized in early 1960s [1]. Magnetic fluids consist of colloid suspensions of nanoparticles of ferromagnetic or ferrimagnetic materials dispersed and stabilized in a carrier liquid through some suitable organic surfactant. The coated surfactant forms an entropic repulsion between particles, so that thermal agitation alone is sufficient to maintain the stable dispersion among them [2]. Because of the special properties of magnetic fluids, they are widely applied in the area of sealing, bearing, grinding, speaker, damper and so on [3–8]. Their properties, such as magnetism, heat transfer and optical properties, have already been studied thoroughly [9–13]. The most common magnetic fluids are formed by ultrafine particles with superparamagnetism through dispersion with the aid of surfactants in a liquid carrier. In general, magnetic fluids have high intensity of saturation magnetization and good stability under operating temperature. First of all, the preparation of magnetic nanoparticle is of significance [14]. As for their applications in biomedicine, the particle size, distribution of particle size, shape, and surface conditions of magnetic nanoparticles are the key factors. At present, many approaches have been developed for preparing magnetic Fe_3O_4 nanoparticles, such as polyols [15], microemulsions [16], laser pyrolysis [17], sonochemical synthesis [18], and chemical co-precipitation [19], etc. Among these reported methods, the chemical co-precipitation might be the most promising one because of its simplicity and productivity [20]. However, it is very difficult to control particle size and its distribution by this method, which leads to its disadvantage in further applications in biomedicine. Moreover, the ferromagnetic nanoparticles

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are difficult to disperse in aqueous solution. As a result, large amount of dispersing agents are required, as is reported in some researches. In this study, we have improved the co-precipitation procedure: NaOH is used to reduce the irritation caused by NH_4OH; HCl and PEG2000 are adopted to control the average particle size and the distribution of Fe_3O_4 magnetic nanoparticles. Because of their non-toxicity, high hydrophilicity and good controllability, PEG2000 and HCl are selected to prepare the water-based magnetic fluid. In the experiment, we tried to discuss the functions of HCl and PEG2000 in magnetic fluid, the adjustability of average size and its distribution of particle obtained by adjusting preparation parameters, and the magnetism of PEGylated magnetic nanoparticles.

2. Experiment

The magnetic Fe_3O_4 particles were synthesized by an improved chemical co-precipitation procedure. There were three stages. (1) *Primary stage*: Ferrous chloride tetrahydrate ($FeCl\cdot 4H_2O$) and ferric chloride hexa-hydrate ($FeCl_3\cdot 6H_2O$) with molar ratio of 1:1.5 were dissolved in 100 ml deionized water under vigorous stirring to prepare ferrite solution of total concentration of 0.60 M. Sodium hydroxide was then dissolved in deionized water to obtain 1 M sodium hydroxide (NaOH) as a base source. Then, through rigorous stirring, drops of 1 M sodium hydroxide were added at 50 °C until pH value of 11 was reached. It could be observed that the solution turned black due to the formation of Fe_3O_4 particles. The black mixture was then heated at 80 °C in an aqueous bath for 30 min to ripen. The sediment obtained was washed for five times with distilled water until pH value reached 7. (2) *Pre-centrifugation stage*: The volume of upper-layer of solution is kept at 100 ml. Fifty mililiters 0.5 M HCl and 1 g PEG2000 were then added at 50 °C with intensive stirring for 1 h; then the mixture was laid still for 24 h and then the upper layer of solution was dumped out and kept for later use with precipitation removed. (3) *Post-centrifugation stage*: High-speed centrifugation at $15{,}000\times g$ for 15 min was carried out for the above-mentioned upper layer solution, and precipitates were collected. It was repeated one more time; after that, distilled water was added to suspend the precipitates with ultrasonic agitation, and then the suspension was laid still for 24 h. After that, it was filtrated with 200 nm filtrator. Finally, the purified water-based magnetic fluid containing PEGylated Fe_3O_4 nanoparticles collected in the void volume had a concentration of about 10 mg Fe/ml through adjustment. The whole process above was not necessary to be in N_2 atmosphere.

The crystallinity of magnetic particles was analyzed with powder X-ray diffraction (XRD) of a Rigaku D/max2500 X-ray diffractometer by using Cu K_α radiation. The morphology of the particles and their diameters were observed by atomic force microscopy (AFM). A Nanoscope AFM (MDF-3D, AR Company, USA) operating in a contact mode in air was used to capture the images of biofilms and pits on the coupon surface. The radius of curvature of the AFM tip was ~50 nm. The scan rate varied between 1.0 and 2.0 Hz depending on the image size. The Digital Nanoscope software was used to analyze the topographic images of the coupon surface. The magnetic-particle-size distribution was investigated with Zetasizer Nano (Malvern Instrument) based on dynamic laser scattering, in which the particle size was measured by detecting the Brownian motion of the particles through probing the Doppler frequency shift of a scattered light with respect to the incident light. It was noted that the diameter detected via dynamic laser scattering was hydrodynamic diameter. The magnetization properties of the magnetic fluid were examined by a vibration sample magnetometer (VSM) with model HH-20 (Nanjing University Instrument Plant).

3. Results and discussion

3.1. The role of HCl in the preparation process of magnetic fluids

The crystalline of magnetic particles was analyzed by powder XRD. Fig. 1 shows the XRD pattern of the synthesized and dried Fe_3O_4 particles in the initial phase. It was clear that only the phase of Fe_3O_4 was detectable. There were not other phases such as $Fe(OH)_3$ or Fe_2O_3, which are usual co-products in the chemical co-precipitation procedure. The results shown in Fig. 1 reveal the high purity of the synthesized Fe_3O_4 magnetic particles. With the XRD pattern, the average core diameter of the particles can be calculated from Scherrer equation [21]:

$$L = \frac{0.94\lambda}{B(2\theta)\cos\theta}, \tag{1}$$

where L is equivalent to the average core diameter of the particles; λ is the wavelength of the incident X-ray; $B(2\theta)$ denotes the full width in radian subtended by the half maximum intensity width of the powder peak. λ is 0.15406 nm; L is obtained as about 10 nm via Eq. (1) and fit-size-only is 10.8 nm.

Fig. 2 shows the XRD pattern of the Fe_3O_4 particles synthesized with HCl but without PEG2000 and dried from magnetic fluid before centrifugation. It can be noticed that several phases including Fe_3O_4, $FeCl_2$ and FeO(OH) were detectable. The results shown in Fig. 2 reveal that the synthesized Fe_3O_4 magnetic particles reacted with HCl and were oxidized. Fig. 3 shows the XRD pattern of the Fe_3O_4 particles synthesized with both HCl and PEG2000 and dried from magnetic fluid before centrifugation. It can be noticed that several phases including Fe_3O_4, FeO(OH) and FeOCl were detectable. Fig. 4 shows the X-ray powder diffraction pattern of the dried particles from magnetic fluid by using HCl and PEG2000 after centrifugation. It can be noticed that only the phase of Fe_3O_4 was detectable. There were no other phases such as FeO(OH), FeOCl and $FeCl_2$. If HCl was added to aqueous solution containing

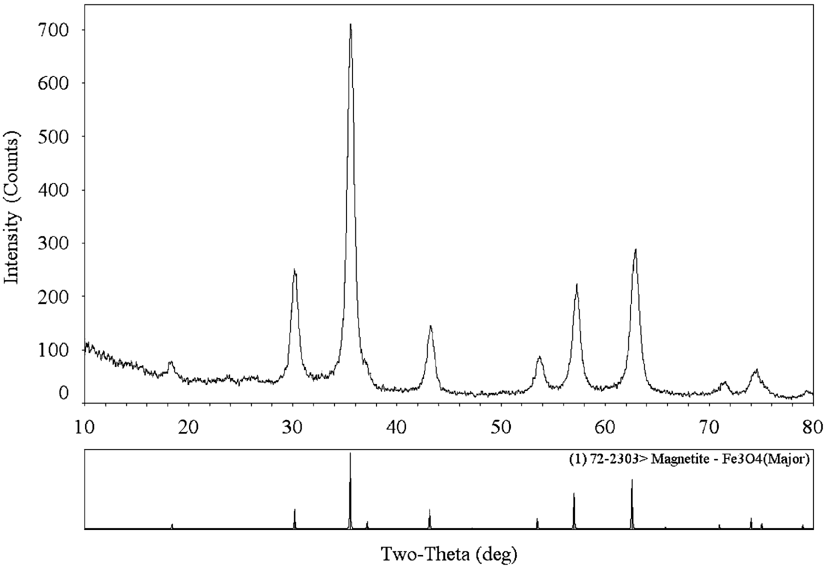

Fig. 1. X-ray powder diffraction pattern of the synthesized magnetic particles in the initial phase.

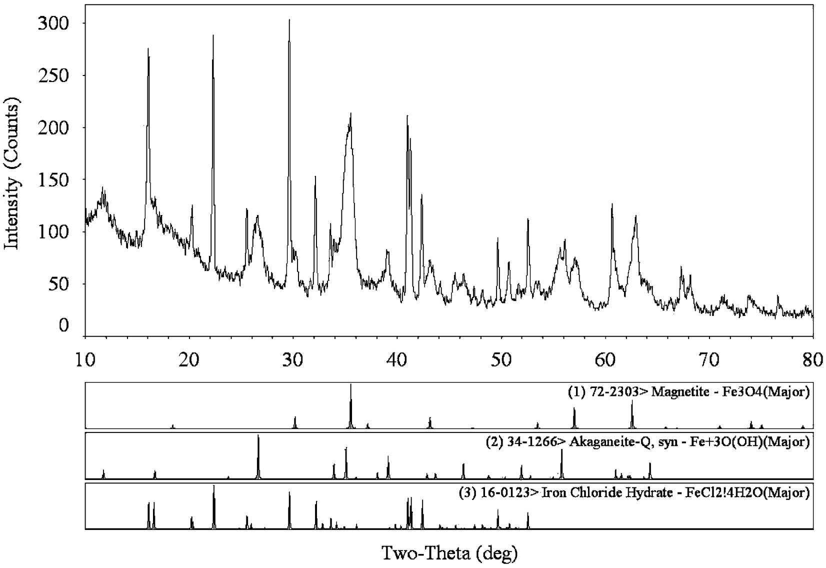

Fig. 2. X-ray powder diffraction pattern of the Fe_3O_4 particles synthesized with HCl but without PEG2000 and dried from magnetic fluid before centrifugation.

magnetic particles under heating, it would become transparent after reflux condensation, but almost lose its magnetism. Obviously, Fe_3O_4 particles reacted with HCl and then generated $FeCl_2$ and FeO(OH) after being heated; however, when HCl and PEG2000 were added simultaneously, it mainly generated Fe_3O_4 magnetic nanoparticles. It probably was because that HCl eroded some Fe_3O_4 magnetic nanoparticles and reduced their particle size, and then PEGylated surface layer was generated to prevent Fe_3O_4 nanoparticles from further eroding. So, it showed that reduction of nanoparticles size was not mainly due to a $[Cl^-]$ coating over magnetic nanoparticles but that HCl reacted with Fe_3O_4 particles after being heated. It could be further demonstrated that their particle size could not be reduced by adding sodium chloride into the suspension containing Fe_3O_4 particles. If HCl reacted excessively with Fe_3O_4 particles after being heated, they would become ferric ion or ferrous ion and almost lose their magnetism.

It is presumed generally that Fe_3O_4 particles generated under alkalinity condition are colloids with positive charge that played an important role in the stability of magnetic fluids. When Zeta electric potential is high, the particles retain distance from each other, weakening and counteracting van der Waals force to improve the stability of particles in fluids; on the contrary, when Zeta electric potential is low, the repulsion of particles decreases and

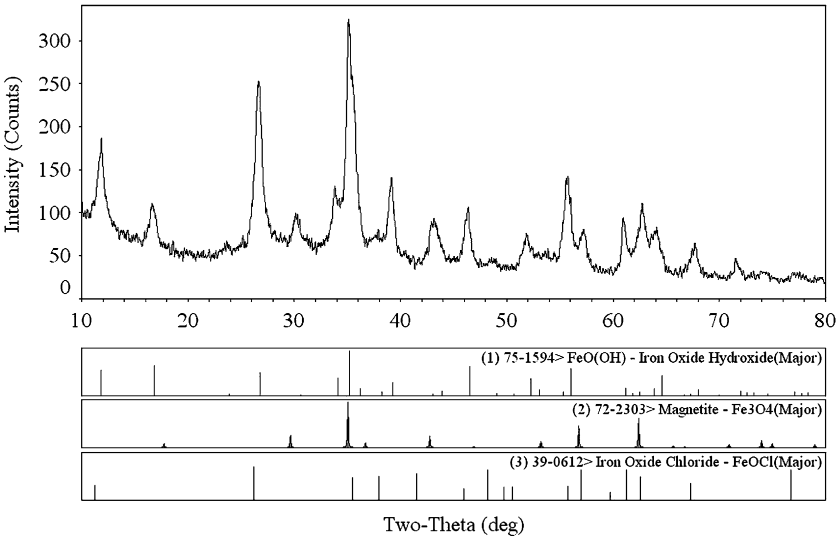

Fig. 3. X-ray powder diffraction pattern of the Fe_3O_4 particles synthesized with both HCl and PEG2000 and dried from magnetic fluid before centrifugation.

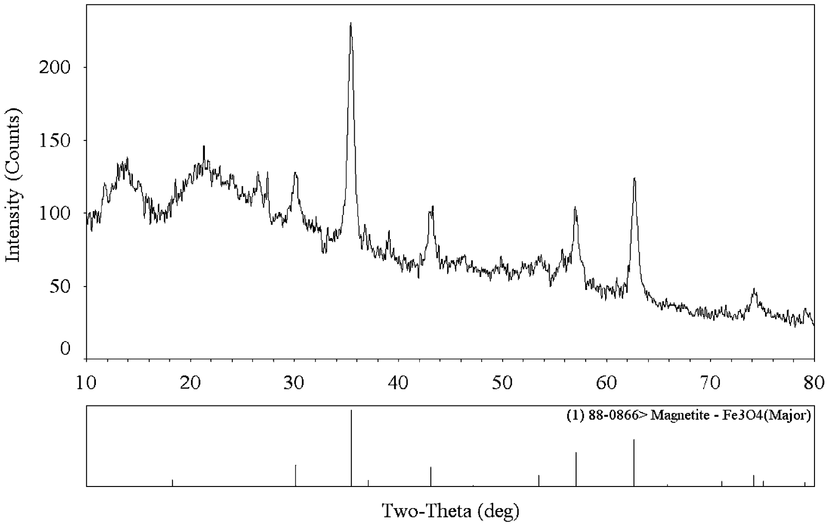

Fig. 4. X-ray powder diffraction pattern of the dried particles from magnetic fluid by using HCl and PEG2000 after centrifugation.

particles are approaching gradually, therefore they will agglomerate through attracting each other in the range of van der Waals force. pH value of the solution decreases and its electropositivity increases after HCl is added. The larger the amount of HCl is, the higher the positive charge, the higher Zeta electric potential and the better stability will be [22]. When dealing Fe_3O_4 nanoparticles with HCl, particles agglomeration as a big particle is corroded slightly by HCl to single particles, and superficial sticky layer is generated which can prevent the decomposition and further agglomeration of nanoparticles, furthermore, the layer can remove coordinated water molecules on the surface of nanoparticles to prevent the generation of hydrogen bond among them. They suspend in aqueous solution because of thermal motion. Moreover, PEG can coat the nanoparticles or be absorbed on their surface to carry the same electric charge when HCl and PEG act together. At the same time, PEG can overcome the surface free energy of nanoparticles to prevent their agglomeration and further eroding by HCl, so the size of nanoparticles varies over a range and they suspend in the base solution without precipitation. Thus, the effect of HCl and PEG together is better than that of HCl or PEG alone. But it brings some by-products by dissolving Fe_3O_4 particles after HCl is added, so the amount of HCl has to be restricted, neither excessive nor too thick. It may increase the concentration of chloridions in the solution after adding HCl and thus affects Zeta electric potential; however, this is smaller than the $[OH^-]$'s elevation effect on electric potential. Therefore, they have to be removed after centrifugation to reduce the amount of HCl and weaken the effect of $[Cl^-]$.

3.2. The role of PEG in magnetic fluids

It is common to add surfactants in magnetic fluids when a mass of agglomeration is generated during precipitating, and standing due to that nanoparticles absorb large amount of adsorbed water, coordinated water, bridge [OH$^-$] and non-bridge [OH$^-$] and so on. For safety, stability and dispersibility, we select PEG as a surfactant. After PEG is added, it can displace H_2O, [OH$^-$] on the surface of particles, generating a sticky layer by adhering to them through coordination bond or hydrogen bond, reducing the surface free energy, preventing agglomeration from small particles to big particles, and dispersing particles stably in base solution. So PEG acts as a dispersing and stabilizing agent. The larger the amount of PEG is, the better the effect of dispersing and stabilizing of nanoparticles, the smaller their sizes, and the better the stability of magnetic fluids will be. However, when the amount of PEG is large, the effect of mutual penetration and winding should not be ignored, because it will aid in the agglomeration from small particles to big particles. When their sizes become larger and larger, their magnetism, the mutual magnetic effects among them, and the tendency of mutual aggregation increase, then the particles deposit finally [23]. It was found that the amount of PEG used together with HCl reduced tens of times than that used alone, thus it would benefit further application. Fe_3O_4 magnetic fluids generated by adding HCl and PEG are still stable after standing for several months.

3.3. The size and size distribution of magnetic fluids

In order to investigate the shape and size of magnetic particles, AFM analysis system was used. The typical shape and size of the magnetic particles are shown in Fig. 5; the PEGylated Fe_3O_4 nanoparticles are close to spherical, with average particle size of 42.53 nm. In order to investigate the size distribution of magnetic particles, a dynamic laser scattering (DLS) analysis system was used in this study. It was notable that the diameter detected by DLS system referred to a hydrodynamic diameter of particles. According to DLS results, the poly index of the size distribution of the Fe_3O_4 particles ranged from 0.159 to 0.359. The typical size distribution of the magnetic fluid is shown in Fig. 6.

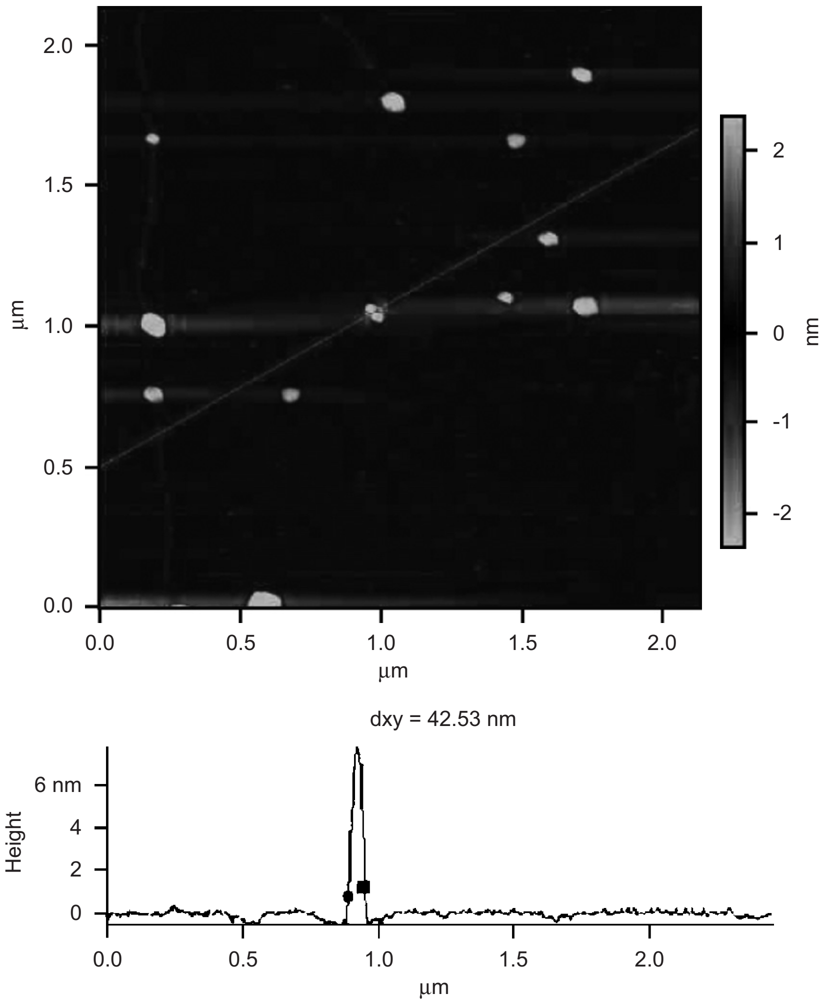

Fig. 5. AFM images of the dried particles from magnetic fluid by using both HCl and PEG2000 after centrifugation. The average size of magnetic particles is 42.53 nm.

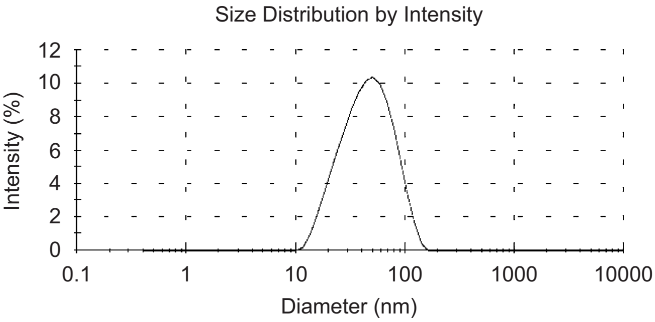

Fig. 6. Hydrodynamic diameter distribution of magnetic PEGylated Fe_3O_4 particles in magnetic fluid. The average size is 44.76 nm and the poly index is 0.359.

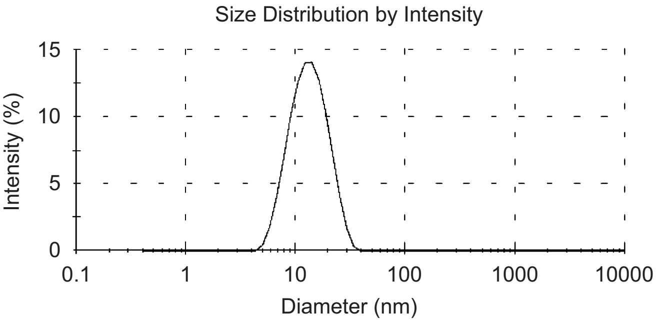

Fig. 7. Hydrodynamic diameter distribution of magnetic PEGylated Fe_3O_4 particles in magnetic fluid. The average size is 11.77 nm and the poly index is 0.159.

The average particle size is 44.76 nm for this size distribution.

In order to the reduce size distribution, Fe_3O_4 particles of various average sizes can be obtained through controlling the amount of HCl and PEG2000. Fig. 7 plots the size distribution of Fe_3O_4 particles, via greater amount of HCl and PEG2000 in the synthesis process or extending the duration at 50 °C. It shows a smaller average size (= 11.77 nm). Through the preparation procedure developed in this study, the average size of the synthesized Fe_3O_4 particles could be adjusted from 8 to 50 nm, depending on the decomposition of HCl and PEG2000 in the ferrite suspension. And it was found that after adding HCl and PEG2000, the size of the Fe_3O_4 particles as end-product was weakly related to that of the initial Fe_3O_4 particles, even if it agglomerated to micrometer particles in the initial phase, it could generate nanometer particles eventually. Thus, it facilitated the preparation of magnetic fluids.

3.4. *The magnetism of magnetic fluids*

The magnetic properties of magnetic fluid were examined by using the VSM. Fig. 8 shows the magnetic hysteresis curve of dried particles of PEGylated Fe_3O_4 at room temperature. The magnetic hysteretic curve exhibits super-paramagnetic behavior and strong magnetism. The superparamagnetism of magnetic fluids is also observed when dispersing the PEGylated Fe_3O_4 particles into aqueous solution, as shown in Fig. 9. In our experiment, the PEGylated Fe_3O_4 particle can be stably dispersed in water without self-agglomeration.

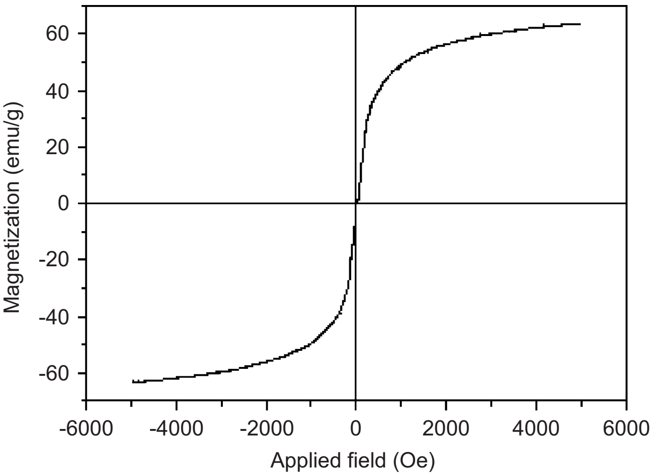

Fig. 8. The magnetic hysteretic curve of the dried PEGylated Fe_3O_4 particles at room temperature.

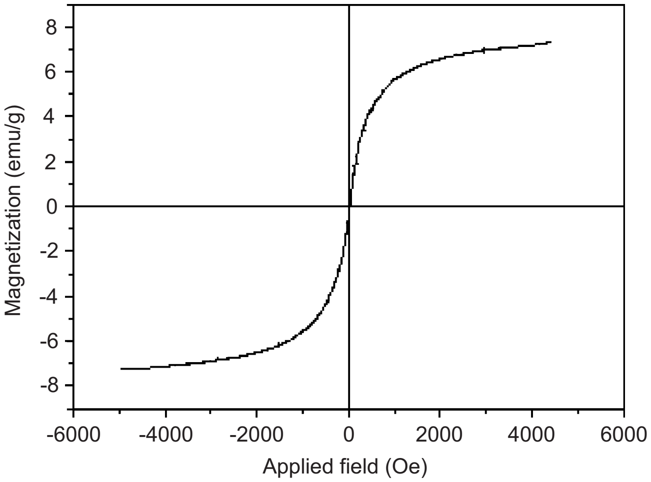

Fig. 9. The magnetic hysteretic curve of magnetic fluid at room temperature.

4. Conclusion

In this study, we have developed a route for the preparation of magnetic fluid with an improved chemical co-precipitation procedure. Compared with the traditional techniques, the PEGlyated-Fe_3O_4 particles prepared by this method have smaller size, better dispersion and stability, and need less amount of PEG. It was found that, with the addition of HCl and PEG2000 into a ferrite suspension, the average size of magnetic Fe_3O_4 nano-particles in magnetic fluid could be significantly reduced. In addition, by adjusting the amount of HCl and PEG2000, the average hydrodynamic diameter of magnetic Fe_3O_4 particles could be controlled between 8 and 50 nm. This study also revealed that reduction of nanoparticles size is not mainly due to a [Cl^-] coating over the magnetic nanoparticles, but that HCl reacts with Fe_3O_4 particles after being heated. Meanwhile, PEG can stabilize or coat the Fe_3O_4 nanoparticles as a dispersing and stabilizing agent.

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