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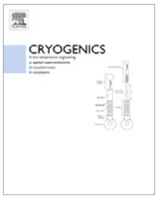

Oil-field wastewater purification by magnetic separation technique using a novel magnetic nanoparticle

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ABSTRACT

In the present work, oil-field wastewater purification through superconducting magnetic separation technique using a novel magnetic nanoparticle was investigated. The magnetic nanoparticle, which has a multi-shell structure with ferroferric oxide as core, dense nonporous silica as inter layer and mesoporous silica as outer layer, was synthesized by co-precipitation method. To functionalize the magnetic nanoparticle, plasma polymerization technique was adopted and poly methyl acrylate (PMA) was formed on the surface of the nanoparticle. The multi-shell structure of the nanoparticle was confirmed by transmission electron microscope (TEM) and the characteristic is measurable by FTIR. It is found that most of the pollutants (85% by turbidity or 84% by COD value) in the oil-field wastewater are removed through the superconducting magnetic separation technique using this novel magnetic nanoparticle.

1. Introduction

Water pollution has become a serious problem since industrial field expands astoundingly as well as the complexity of ingredients of residents' wastewater increases continuously. As a promising wastewater purification method, superconducting magnetic separation system [1] has attracted much attention. Comparing to traditional chemical and biological techniques, such as depositing, filtering, neutralizing, biological contact oxidizing, and active sludge process, this method takes advantage of low investment and operating cost, short time of processing, small space occupied, and high efficiency.

Magnetic seed plays a key role in the superconducting magnetic separation technology. Since most of the pollutants in oil-field wastewater are nonmagnetic, it is favorable that the magnetic seeds can combine with the pollutants efficiently and also be collected rapidly and thoroughly after agglomerated with pollutants due to their high ferromagnetism. In the present paper we report a novel multi-shell structured magnetic nanoparticle through coating ferroferric oxide crystal with a dense nonporous silica layer, which can prevent the magnetic core reacting with acid in low PH environment, and a mesoporous silica layer, then grafting PMA sequentially, as shown in Fig. 1.

The magnetic core makes sure that the whole magnetic particle can be collected within the superconducting magnetic separation system. The mesoporous silica layer itself is an excellent adsorbing structure. This is because the diameter distribution of the pores is in the range of 1.5–10 nm, indicating that it has huge specific surface area [2]. Moreover, the structure of the silica layer is one typical structure of all the kinds of mesoporous silica materials [3–5]. In addition, the mesoporous silica enables many special reactions such as macromolecules catalysis, adsorption and separation in the specific mesopores [6–8] so that it can be used in biology, pharmaceutics, polymer chemistry, etc. The aim of this work is to design an efficient magnetic seed in order to boost the applicability of superconducting magnetic separation for purification of wastewater.

2. Experimental methods

2.1. Synthesis of Fe_3O_4 nanoparticles

Fe_3O_4 Nanoparticles (NPs) were prepared by a co-precipitation method described in Ref. [9] with some minor modifications. In short, first mixed 5.40 g $FeCl_3{\cdot}6H_2O$ and 2.78 g $FeSO_4{\cdot}7H_2O$ into 100 mL DI water in a 500 mL flask and heated the solution to 90 °C under N_2 protection, then added 50.0 mL 1.90 mol/L NaOH dropwise and continued the reaction for 30 min. The obtained Fe_3O_4 NPs were washed with DI water several times, then scattered in sodium oleate solution using ultrasonic cleaner. After stirring for 12 h at 60 °C, the Fe_3O_4 NPs was washed with anhydrous ethanol and DI water 3 times and then dispersed in 80.0 mL DI water, forming a magnetic fluid.

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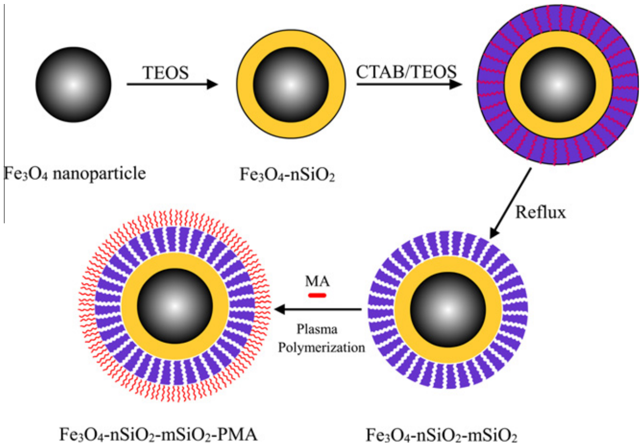

Fig. 1. Synthetic route of Fe_3O_4–$n$$SiO_2$–$m$$SiO_2$–PMA.

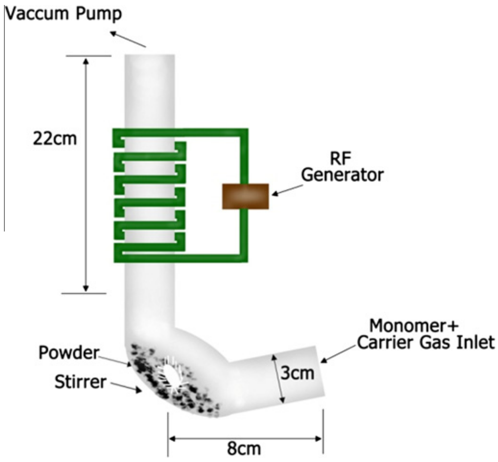

Fig. 2. Plasma polymerization system.

2.2. Synthesis of Fe_3O_4–$n$$SiO_2$–$m$$SiO_2$ NPs

Fe_3O_4–$n$$SiO_2$–$m$$SiO_2$ NPs was synthesized according to methodology described in Ref. [10] with some modifications. Briefly, 4.00 mL out of 80.0 mL magnetic fluid was treated by aqueous solution of hydrochloric acid with ultrasonication. After ultrasonic treatment for 15 min, the Fe_3O_4 NPs were collected with a permanent magnet and then scattered in the mixture of 80.0 mL DI water, 320 mL ethanol and 4.00 mL concentrated ammonia aqueous solution (25%). 1.50 mL tetraethyl orthosilicate (TEOS) was slowly introduced into the mixture with ultrasonication. After stirring at

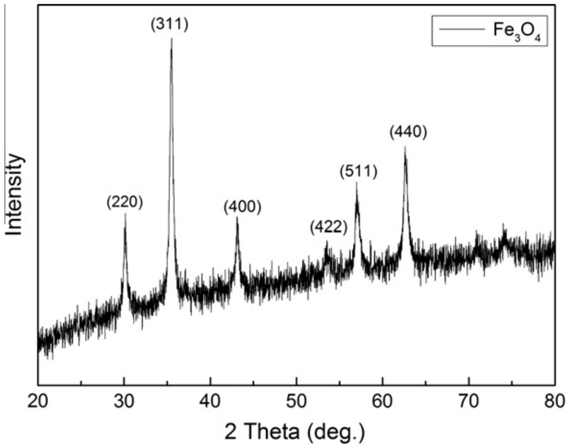

Fig. 3. XRD spectra of Fe_3O_4 NPs.

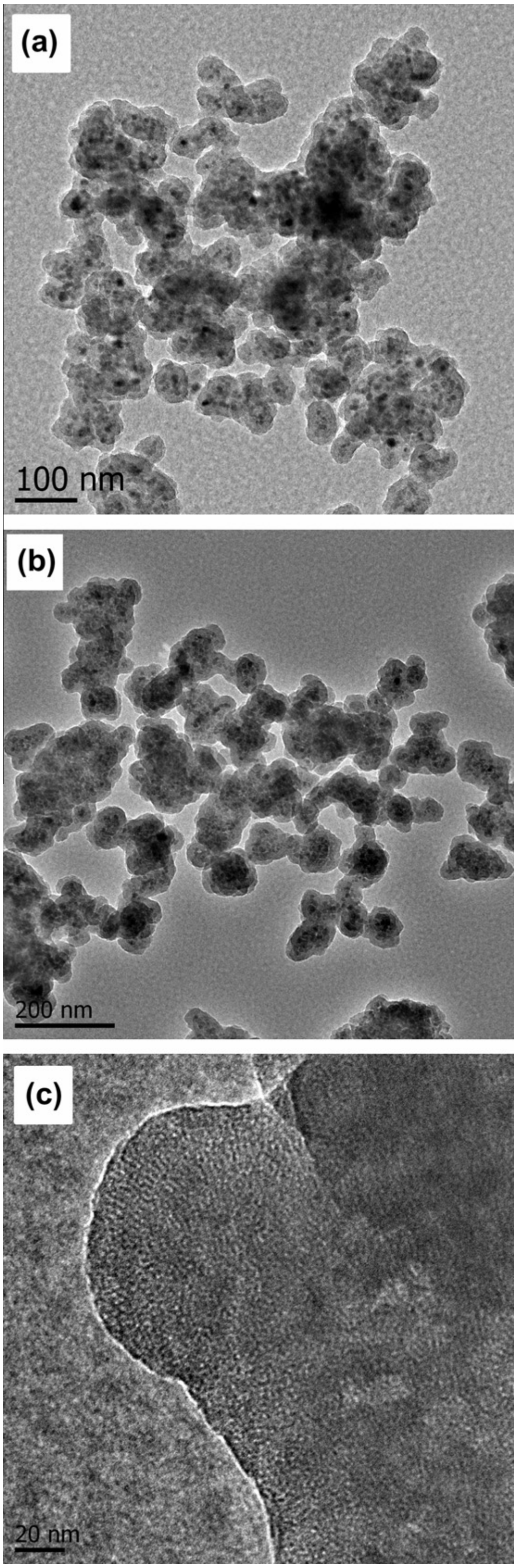

Fig. 4. Fe_3O_4–$m$$SiO_2$ NPs (a), and Fe_3O_4–$m$$SiO_2$–$n$$SiO_2$ NPs (b and c).