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Synthesis and characterization of gadolinium doped cobalt ferrite nanoparticles with enhanced adsorption capability for Congo Red

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HIGHLIGHTS

- $CoFe_{2-x}Gd_xO_4$ nanoparticles are synthesized by an improved hydrothermal method.
- Gd^{3+} doping enhances the adsorption capacity of Co ferrite nanoparticles for CR.
- The Langmuir maximum adsorption capacity of $CoFe_{1.93}Ga_{0.07}O_4$ for CR is higher.
- The initial adsorption rate is sensitive to the BET surface area of nanoparticles.
- Gd^{3+} doping decreases M_s and H_c of Co ferrite nanoparticles.

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ABSTRACT

Nanoparticles of $CoFe_{2-x}Gd_xO_4$ ($x = 0, 0.03, 0.05, 0.07, 0.1$) are synthesized by an improved hydrothermal method. Here, the doping of Gd^{3+} ions leads to an obvious enhancement of absorption capability for Congo Red (CR) from aqueous solution onto $CoFe_{2-x}Gd_xO_4$ nanoparticles. The morphology and structure of the samples have been characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM) and Raman spectroscopy. The results indicate that the obtained samples are pure cubic spinel phase with uniform morphological structure. With increasing the doping amount of Gd^{3+} ions, the average particle size gradually reduces from 13 to 8 nm. The hysteresis loops are investigated using a vibrating sample magnetometer (VSM), where the saturation magnetization and coercivity decrease with the Gd^{3+} ions doping, further, a remarkable superparamagnetic behavior gradually exhibits. UV–vis spectrophotometer records the adsorption properties of as-synthesized nanoparticles for CR. Due to the substitution of Gd^{3+} ions, compared with undoped ferrite, the removal ability for CR increased from 131.1 to 161.1 mg g^{-1}. The absorption kinetics is described well by the pseudo-second-order model. Calculated from Langmuir isotherm model, the maximum adsorption capability of CR dye onto $CoFe_{2-x}Gd_xO_4$ is up to 263.2 mg g^{-1}, here, $x = 0.07$. This study demonstrates that the addition of rare earth (RE) ions can further enhance the adsorption capability of ferrite nanoparticles for dyes.

1. Introduction

The pollution of water resources by kinds of dyes has become a serious global environmental issue. Many organic dyestuffs are harmful to human beings and toxic to microorganisms, so, from a point of view of public health and safety, they must be removed before discharged into natural environment [1]. As a result, nowadays, the removal of dyes and other colored contaminants from wastewater is becoming an important research hotspot in the field of material science as well as environmental science. Various separation techniques have been successfully developed, such as chemical precipitation, adsorption and biological process [2–4]. Among these, adsorption based on magnetic separation is considered to be superior to other approaches because of its high efficiency, lost cost and simple operation process to wastewater treatment [5]. By exerting an external magnetic field, it is much easier to separate the magnetic adsorbents from the polluted

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water. Obviously, as to magnetic separation technique, the choice of the magnetic adsorbents is very vital during the adsorption process. Generally, three factors should be considered: (1) the high adsorption capacity for the dyes; (2) the excellent magnetic performance; and (3) the suitable preparation method of magnetic adsorbents.

A large number of adsorbents, such as porous carbon nanospheres/nanotubes [6,7], iron oxides [8], activated carbon [9], chitosan [10], core–shell nanoparticles [11], layered double hydroxide (LDH) [12], magnetic nanocomposite [13], have been applied to remove dyes from the wastewater. However, owing to high cost, difficult disposal and regeneration, some of these adsorbents cannot be widespread used. Thus, in recent years, as a typical eco-friendly adsorbent, spinel ferrite nanomaterials, because of their excellent physicochemical characteristics and larger specific surface areas, exhibit a higher removal capacity for dyes, which has become the focused research area of magnetic separation technology. For example, Mahmoodi and Rahimi reported the synthesis and dye degradation of zinc ferrite nanomaterials [14,15]; Wang et al. investigated the synthesis of $MnFe_2O_4$ ferrite and their possible application in water treatment [16]; Jia et al. prepared mesoporous rodlike $NiFe_2O_4$ and analyzed their adsorption behavior of phosphate [17]; Bao et al. presented the synthesis of MFe_2O_4 ($M = Fe^{2+}$, Mn^{2+}, Co^{2+}, Zn^{2+}) magnetic nanoparticles and their adsorptive removal of tetracyclines from water [18]. In a word, the literature review indicates that, as to spinel ferrite adsorbents, further improving the performances and finding out a facile, environmental-friendly and cost-effective synthesis route are still two research hotspots. As is known, to meet requirements of being used for the removal of dyes, magnetic spinel ferrite nanoparticles should be monodisperse with small sizes and uniform size distribution. Whereas, it is noted that nanosized magnetic particles always tend to aggregate because of their high surface energy and magnetic properties. To solve this problem, two measures are often taken, one is to control the structure and morphology of ferrite nanoparticles by different ion substitution, another is to further optimize synthesis route.

Recently, it is found that the electrical, magnetic and optical properties of ferrite can be tuned by introducing a relatively small amount of rare-earth ions. Correspondingly, much attention has been paid to the effect of rare-earth ion doping in different ferrites on their structural, electrical and magnetic properties. Here, it is worthy to note that the rare-earth ions doping can further decrease in particle dimension and crystallite size [19]. In fact, it is beneficial to enhance the adsorption capacity of nanoparticles for dyes. Wang et al. reported the preparation of nanocrystalline $Fe_{3-x}La_xO_4$ ferrite, where the adsorption capacity of magnetite for CR increase by adulterating a small quantity of La^{3+} ions into it. Also, they presented that the maximum adsorption capacity of the $Fe_{2.95}La_{0.05}O_4$ nanoparticles for CR was 107.64 mg g^{-1} [20]. Zhao and Nan proposed a facile and efficient solvothermal synthetic route to fabricate La^{3+} doped zinc ferrite clusters and demonstrated the good performance in removal of methyl orange from water by adsorption with La^{3+} doping [21]. However, an investigation of the literature shows that few researches have been carried out to illuminate the variation of the adsorption capacity of ferrite nanoparticles for dyes doping by other rare-earth ions.

This work aims to provide an improved hydrothermal method to synthesize Gd^{3+} ion doping cobalt ferrite nanoparticles and reveal the effect of the substitution of rare-earth Gd^{3+} ions on the magnetic property of cobalt ferrite nanoparticles and their adsorption capacity for CR dyes. Also, the corresponding adsorption mechanisms are analyzed. Here, our study further confirms that the doping of rare-earth ions into ferrite nanoparticles can enhance the adsorption capability for dyes.

2. Experimental

2.1. Chemicals

Analytical grade iron nitrate $Fe(NO_3)_3{\cdot}9H_2O$, cobalt nitrate $Co(NO_3)_2{\cdot}6H_2O$, gadolinium nitrate $Gd(NO_3)_3{\cdot}6H_2O$ and sodium borohydride $NaBH_4$ were utilized to prepare $CoFe_{2-x}Gd_xO_4$ nanoparticles without further treatment.

2.2. Synthesis of $CoFe_{2-x}Gd_xO_4$ nanoparticles

An improved hydrothermal synthesis method was introduced. The as-prepared $CoFe_{2-x}Gd_xO_4$ nanoparticles were labeled as S1 ($x = 0$), S2 ($x = 0.03$), S3 ($x = 0.05$), S4 ($x = 0.07$) and S5 ($x = 0.1$), respectively. The synthesis was divided into two steps: the reduction in metal cation to nuclei in a colloid mill and the hydrothermal oxidation. First of all, two kinds of solutions were prepared. Solution 1: $Fe(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and $Gd(NO_3)_3{\cdot}6H_2O$ were dissolved in 70 ml deionized water to give a solution with the $Co^{2+}/(Fe^{3+} + Gd^{3+})$ molar ratio of 0.5. Solution 2: sodium borohydride was dissolved in 60 ml of deionized water to obtain the solution with $[NaBH_4]/[Co^{2+} + Fe^{3+} + Gd^{3+}]$ molar ratio of 2.0. Then, solution 1 and solution 2 were synchronously added rapidly to a colloid mill with rotor speed set at around 6000 rpm and mixed for 3 min and the final slurry was obtained. Secondly, the final slurry was put into the autoclaves (150 ml) and heated at 180 °C for 24 h. Then the products was centrifuged and washed with deionized water for several times, and the obtained solid was dried at 70 °C for 12 h. Experiments were repeated three times with similar patterns. This approach contains a very rapid mixing of reducible metal cations with sodium borohydride and simultaneous nucleation of metallic cobalt, iron and gadolinium within a very short time in a colloid mill, which can involve crystal growth, agglomeration, breakage, and other process. Furthermore, nucleation and nuclei growth taking place simultaneously can be avoided in this colloid mill process, which leads to nuclei's particle size in a narrow range and further affects the physical properties of the products. The expected reaction to form $CoFe_{2-x}Gd_xO_4$ ferrites is [22]:

$$4Fe^{3+} + 3BH_4^- + 12H_2O \rightarrow 4Fe + 3B(OH)_4^- + 6H_2 + 12H^+ \tag{1}$$

$$4Gd^{3+} + 3BH_4^- + 12H_2O \rightarrow 4Gd + 3B(OH)_4^- + 6H_2 + 12H^+ \tag{2}$$

$$2Co^{2+} + 3BH_4^- + 4H_2O \rightarrow 2Co + 3B(OH)_4^- + 2H_2 + 4H^+ \tag{3}$$

$$2Co + O_2 + 2H_2O \rightarrow 2Co(OH)_2 \tag{3}$$

$$4Fe + 3O_2 + 6H_2O \rightarrow 4Fe(OH)_3 \tag{4}$$

$$4Gd + 3O_2 + 6H_2O \rightarrow 4Gd(OH)_3 \tag{5}$$

$$Co(OH)_2 + (2-x)Fe(OH)_3 + xGd(OH)_3 \rightarrow CoFe_{2-x}Gd_xO_4 + 4H_2O \tag{6}$$

2.3. Characterization

The crystallinity, crystal structure and the phase purity of the samples were described by the Power X-ray diffraction (XRD) patterns using RigakuD/max with Cu Kα radiation (λ = 1.54060 Å) (operated at 40 kV and 200 mA). Raman spectra were recorded at room temperature using a commercial Jobin–Yvon spectrometer (LabRAM ARAMIS) with a CCD detector, where an Ar ion laser (λ = 532 nm) was used as the excitation source and its power was