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A facile sol combustion and calcination process for the preparation of magnetic $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders and their adsorption behaviors of Congo red

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ABSTRACT

A facile sol combustion and calcination process for the preparation of magnetic $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders was introduced and the gel precursor and as-prepared nanopowders were characterized by TG/DSC, XRD, BET, SEM and TEM. The results have shown that the single ferrite phase of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ can be formed at 400 °C. It can be indicated that the volume of the solution is a key factor to the properties of the magnetic $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders: with the volume of absolute alcohol increasing from 10 mL to 30 mL, the average grain sizes of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powders calcined at 400 °C for 2 h with the heating rate of 3 °C/min increase from about 14.9 nm to 18.3 nm, while the saturation magnetizations increase from about 27.1 Am^2/kg to 105.2 Am^2/kg, and the specific surface area is up to maximum of 69.7 m^2/g when absolute alcohol is 15 mL. The adsorption kinetics and adsorption isotherm of Congo red (CR) onto the magnetic $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles calcined at 400 °C for 2 h with a heating rate of 3 °C/min and absolute alcohol of 15 mL were investigated at room temperature. The kinetic data related to the adsorption of CR from aqueous solutions are in good agreement with the pseudo-second-order kinetic model with a range of initial concentrations of 100–500 mg/L. Compared with Langmuir and Freundlich models for adsorption isotherm of CR, Temkin model (correlation coefficient $R^2 = 0.9937$) can be used to evaluate the CR adsorption isotherm at room temperature.

1. Introduction

In the past few decades, magnetic nanoparticles (MNPs) have attracted lots of interests. A considerable amount of researches have been carried out on the magnetic Ni–Zn ferrites owing to their large magnetic permeability, relatively low magnetic loss, high cut-off frequency, high saturation magnetization, high Curie temperature, chemical stability, low coercivity and biodegradability [1,2], as well as their wide applications in areas of biology, medicine, environment, machine, military affairs, etc.

Many approaches have been developed to synthetize nanocrystallite Ni–Zn ferrites, such as sol–gel, coprecipitation, hydrotherm, and combustion [3–7]. However, the processes of the above approaches are often complex, especially their pretreatment processes, which usually need special equipments, and most of them cost so much since they need various organic substances to disperse metal ions and form complexes. However, sol combustion and calcination technique is a novel, simple and convenient method with a unique sol combustion and calcination process [8], a short pretreatment time, homogeneous products, and easily controlled products' magnetism by the volume of solvents.

Owing to the large specific surface area and high saturation magnetization, the magnetic Ni–Zn ferrites can be used in many areas, especially the environmental area. Environmental problems related to water pollution are challenging issues in recent years, for instance, the pollution of water resources by dyes, especially the anionic azo dyes from textiles and mining industries, has become a serious concern [9]. Due to the complex aromatic structures of anionic azo dyes, the conventional biological treatment process is often ineffective, for many cases, the dyes need the chemical catalytic degradation or adsorption to be removed completely [10,11]. Congo red (CR), as one of benzidine based anionic diazo dyes, is highly resistant to microbial biodegradation and hard to be removed from water [12], so the adsorption is considered to be promising due to its simplicity in operation, high treatment efficiency without discharging any harmful by-products and easy scaling from laboratory scale to field scale [13].

In this project, we have successfully synthesized the magnetic $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders via the facile sol combustion and calcination

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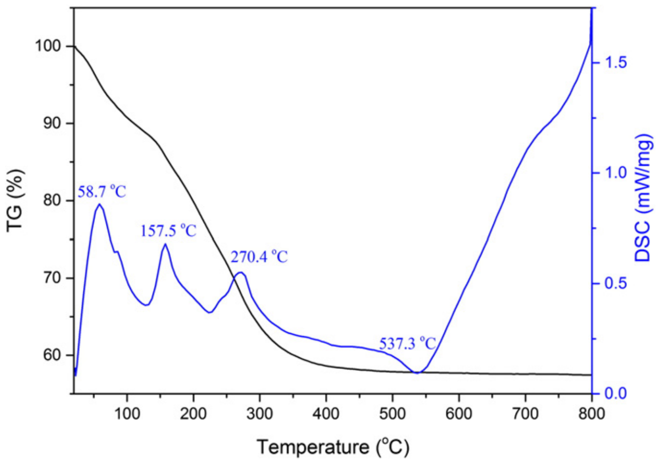

Fig. 1. TG-DSC curves of gel precursor for the magnetic $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders.

process, and their morphology, composition, structure, magnetic properties and adsorption behaviors of CR were investigated.

2. Experimental

2.1. Preparation and characteristics of magnetic $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders

The magnetic $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders were prepared via the sol combustion and calcination process, and absolute alcohol was used as fuel. Analytical grade nickel nitrate, zinc nitrate and iron nitrate were used and the molar ratio of Ni, Zn and Fe was 1:1:4. 1.57 g $Ni(NO_3)_2 \cdot 6H_2O$, 1.59 g $Zn(NO_3)_2 \cdot 6H_2O$ and 8.64 g $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in absolute alcohol, and then the mixture was magnetically stirred for 2–4 h at room temperature to form a homogeneous sol. Later, the sol was moved into a copple and was ignited. When the fire went out, the as-burnt intermediate along with the copple was calcined at 400 °C for 2 h with the heat rate of 3 °C/min in the air to form loose nanopowders. Other conditions were invariant, the volume of absolute alcohol was changed to investigate its effect on the properties of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders.

The phase identification of the nanopowders was characterized by Rigaku D/max 2500 PC X-ray diffraction (XRD) with Cu-Kα radiation, the morphology and composition analyses were investigated with a scanning electron microscopy (SEM) and the transmission electron microscopy (TEM), the magnetic measurement was taken on an ADE DMS-HF-4 vibrating sample magnetometer (VSM), and the specific surface area was measured by the Brunauer–Emmette–Teller (BET) method with the instrument of NOVA 2000e.

2.2. Adsorption behaviors of CR onto the magnetic $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders

The initial and final concentrations of CR solutions were determined by absorbance at 500 nm with visible spectroscopy (UV-2550) [14]. 4–40 mg/L of CR standard solutions were prepared, and the absorbances of the standard solutions were examined at room temperature. And then the relation of the absorbances and the concentrations of CR standard solutions could be established, so the concentration of any solution could be calculated by the determined absorbance. The adsorption kinetic experiments were carried out by constantly stirring 20 mL of CR aqueous solution with 0.05 g of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders with various concentrations of 100–500 mg/L in a series of 50 mL flasks at room temperature. Then, the flasks were taken out at some intervals within 10 min and the adsorbents were separated by the magnetic field, and then the residual CR concentration in the aqueous solution was measured. The adsorption capacity of CR onto the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders can be calculated by the following equation [15]:

$$I = \frac{m_{CR}\left(A_{CR} - A_{mag}\right)}{m_{mag}A_{CR}}, \tag{1}$$

where I refers to the adsorbed CR amount of the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders (mg/g), m_{CR} is the total weight of CR (mg), m_{mag} is the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowder weight (g), A_{CR} is the UV absorbance value of blank CR solution, and A_{mag} is the UV absorbance value of CR solution after adsorption.

It is meaningful to predict the contamination removal rate from aqueous solution in order to design an adsorption treatment plant. To explore the adsorption mechanism for the adsorption of CR dye from aqueous solution onto the magnetic $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders calcined at 400 °C for 2 h with absolute alcohol of 15 mL and the heat rate of 3 °C/min, the pseudo-first-order model, pseudo-second-order model and intraparticle diffusion model were used to evaluate the CR adsorption data.

The pseudo-first-order formula is given as Eqs. (2) and (3) [16]:

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{2}$$

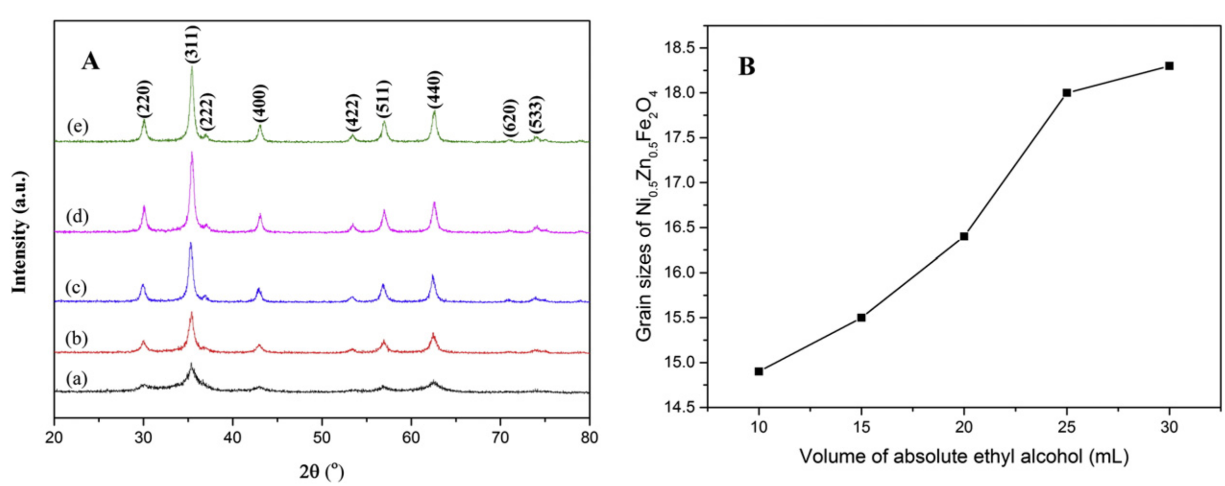

Fig. 2. XRD patterns (A) and average grain sizes (B) of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders with absolute alcohol of (a) 10 mL, (b) 15 mL, (c) 20 mL, (d) 25 mL and (e) 30 mL.