



Analysis of the formation process and performance of magnetic Fe₃O₄@Poly(4-vinylpyridine) absorbent prepared by in-situ synthesis



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ABSTRACT

The morphology evolution of the mesoporous magnetic composite nanospheres Fe₃O₄@Poly(4-vinylpyridine) during the formation process and its absorption property of Congo red were studied in this study. A simple solvothermal method was applied for the fabrication of Fe₃O₄@Poly(4-vinylpyridine) composites with regular structure and uniform size distribution in the presence of 4-vinylpyridine as the structure inducer. The morphology, structure and magnetism performance were characterized and the adsorption model and mechanism were discussed. The results showed that the Fe₃O₄@Poly(4-vinylpyridine) composites were efficient adsorbent for the removal of Congo red from water and it could be reused by a magnetic separation. The adsorption isotherm of Congo red on Fe₃O₄@Poly(4-vinylpyridine) composites was fitted well with the Langmuir adsorption model.

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1. Introduction

The mesoporous materials have attracted a great deal of attentions due to their unique properties, such as high surface area, tunable pore size, and narrow pore-size distribution. Up to now, much effort has been devoted to the synthesis and applications of mesoporous materials. In contrast to traditional industrial microporous materials with a pore size limited to less than 2 nm, mesoporous materials can provide large void spaces for guest species, thereby increasing the feasibility of a wide range of applications, such as in adsorption [1], separation of large molecules [2], catalysis [3], drug and DNA delivery [4], sensors [5], functional devices [6], and fuel cells [7]. Among of various mesoporous materials with different framework compositions, magnetic metal oxide is highly focused due to their inexpensive cost and facile preparation [8–11]. An appropriate selection of surfactants is a critical factor during the surfactant-mediated synthesis in a simple solvothermal method, because the surfactant can not only play a role of structure inducer, but also reduce the generation of nanoparticle agglomeration, affecting the pore formation and structural morphology. There have been many reports on the fabrication of mesoporous Fe₃O₄ nanoparticle, for example, Lin et al. [12] used hexadecylpyridinium

bromide cationic surfactant to prepare magnetic zeolites which enhanced the adsorption capacity of Congo red in aqueous solution. Xiong et al. [13] took polyvinylpyrrolidone as a surface stabilizer to prepared Fe₃O₄ nanospheres with a hierarchical hollow structure. Zou et al. [14,15] utilized PEG-2000 to synthesize a ultrathin magnetic nanoplate. Although the above surfactants have been widely used in many cases, their functionalities are single. Furthermore, the formation mechanism of mesoporous magnetic nanospheres is still rarely researched. In order to develop and make full use of the diversity of surfactant, we chose 4-vinylpyridine (abbrev. 4-VP) as the surfactant to prepare mesoporous magnetic composite nanospheres, and then studied their morphology evolution and the possible chemical reactions during the preparation process, which was of great significance to understand the formation mechanism of this kind material.

4-vinylpyridine possesses structural amphiphilicity and chemical reactivity compared with common surfactants. 4-VP can be protonated by acid, and is likely to coordinate with metal ion through nitrogen atom in the pyridine ring, which could protect the surface of crystal nucleus of iron oxides. It also has the ability to conduct thermal polymerization through double-bond during solvothermal process. Meanwhile, poly(4-vinylpyridine) is a weak polybase and exhibits chemical and morphological changes at a pH variation [16]. Therefore, in this work, we first used a simple in-situ synthesis method to prepare mesoporous Fe₃O₄@P4-VP magnetic composite nanospheres. X-ray diffraction (XRD), scanning elec-

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tron microscopy (SEM), transmission electron microscopy (TEM), infrared ray (IR) and superconducting quantum interference device (SQUID) were applied to characterize the morphology, structure and magnetism performance of the as-prepared materials. Subsequently, the effects of reaction time and the addition of 4-VP on the morphology evolution of the Fe₃O₄@P4-VP magnetic composite nanospheres and the adsorption of Congo red were investigated. Furthermore, the adsorption mechanism was discussed in the paper.

2. Experimental

2.1. Materials

FeCl₃·6H₂O, sodium acetate (NaAc), 4-vinylpyridine (4-VP), ethylene alcohol and Congo red were analytical grade and purchased from Sinopharm Chemical Reagents Company. Distilled water was used in all experiments.

2.2. Synthesis

3.7 mmol (1.00 g) FeCl₃·6H₂O and 51.8 mmol (4.25 g) NaAc were added to 25.0 mL of ethylene glycol (EG). The mixture was stirred vigorously for 60 min at room temperature to ensure a complete dissolution. 7.4 mmol 4-VP dissolved in 10.0 mL of ethylene glycol was added into the above FeCl₃·6H₂O/NaAc/EG solution with stirring for 20 min. Subsequently, the mixture was transferred to a 50 mL teflon-lined stainless-steel autoclave and sealed for heating at 190 °C for different reaction time. The precipitated black products were collected from the solution with an external magnet and washed with distilled water for several times. Finally, the black products were dried in vacuum at room temperature for 24 h. According to the previous references [17,18], the synthetic conditions for ten samples in this work were listed in Table 1.

2.3. Characterization

The surface morphology and structure of the as-prepared products were examined with a Germany LEO 1530VP field-emission scanning electron microscopy (FESEM) system, using an acceleration voltage of 15 kV. Energy-dispersive X-ray spectroscopy (EDX) analyses were taken using an EDX attachment (INCA, Oxford Instruments) on the HiTaChi SU-70 SEM instrument with a diameter of electron probe being 50–100 nm. TEM experiments were performed using a JEOL JEM2100 instrument with an accelerating voltage of 200 kV. XRD measurements were collected using a Philips X'pert Pro diffractometer with Cu K α irradiation ($\lambda = 1.5406 \text{ \AA}$) at room temperature. Magnetic measurements were carried out using an SQUID magnetometer with field up to 1.5 T. Fourier transform infrared (FT-IR) spectra scanned over the range of 400–4000 cm⁻¹ with KBr slice on a Nicolet Avatar 360 spectrometer (Nicolet Thermo, U.S.A.) were employed to examine the chemical nature of products. The nitrogen adsorption/desorption isotherms were measured by using a Micromeritics TriStar II 3020 static volumetric analyzer. The surface area was calculated using the Brunauer–Emmett–Teller (BET) equation from the adsorption isotherms. Pore diameters were determined from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) method. The samples were degassed under vacuum at 100 °C for 12 h prior to measuring at -196 °C. Thermo gravimetric analysis (TGA) was operated with a Q500 thermoanalysis instrument from TA Company. Analyses were carried out under an air flow in the range of 25–800 °C with a heating rate of 10.0 °C/min. The concentration of Congo red was detected by UV–vis, which included the

configuration of a standard absorption curve and corresponding calculations.

2.4. Removal of selected organic pollutants

Congo red (C₃₂H₂₂N₆O₆S₂Na₂), which is an azo dye commonly used in the textile industry, was selected as a model organic water pollutant in this work. Fe₃O₄ (100 mg) nanospheres were mixed with 100 mL of 150 mg L⁻¹ Congo red solutions, and then oscillated in water-bathing with constant temperature vibrator at an oscillation frequency of 120 r min⁻¹. After stirring for various time of 5, 10, 20, 40, 60, 80, 100 min, the nanospheres were separated, and the supernatant solutions were analyzed by UV–vis spectroscopy (Shimadzu, Model 2550). The residual concentration of Congo red was obtained by integrating the areas of the absorbance bands in the wavelength range of 400–600 nm using a linear calibration curve over 2–50 mg L⁻¹.

2.5. Adsorption isotherms

The specific amount of Congo red adsorbed onto Fe₃O₄ nanospheres was calculated based on the following formula:

$$Q = (C_0 - C_t)V/m \quad (1)$$

where Q (mg g⁻¹) is the adsorption capacities, C_0 (mg L⁻¹) is the initial concentration, C_t (mg L⁻¹) is the solute concentration, V (L) is the volume of the aqueous solution and m (g) is the mass of the adsorbent used. In the present study, the initial concentration of Congo red solution was 200 mg L⁻¹, pH was adjusted to 5.0–6.0, the solution volume was 100 mL, and the amount of adsorbent Fe₃O₄ nanospheres was 100 mg.

To optimize the use of adsorbents, it is important to analyze the adsorption equilibrium data. The well-known Langmuir isotherm and Freundlich isotherm [19] were applied to evaluate the adsorption behavior of probe solutes on Fe₃O₄ adsorbent.

The Langmuir model concerns monolayer adsorption onto a homogeneous surface and can be written as follows:

$$Q_e = Q_m K_L C_e / (1 + K_L C_e) \quad (2)$$

where C_e (mg L⁻¹) is the equilibrium concentration of solute, Q_e (mg g⁻¹) is the equilibrium adsorption capacity of adsorbent, Q_m (mg g⁻¹) is the saturated adsorption amount of adsorbent, and K_L (L mg⁻¹) is the Langmuir adsorption constant.

The Freundlich model assumes that multilayer adsorption occurs on a heterogeneous surface and the linearized equation can be expressed as follows:

$$\ln Q_e = \ln K_F + (1/n) \ln C_e \quad (3)$$

where K_F (L mg⁻¹) and n are Freundlich isotherm constants, which refer to the capacity and intensity of the adsorption, respectively.

2.6. Desorption experiments

Typically, 100 mg of Fe₃O₄@P4-VP absorbed Congo red mixtures were added into 30 mL ethanol solution, and then ultra-sonicated for 20 min for the desorption of Congo red. The adsorbents were collected by a magnet and washed with ethanol for three times. Finally, the regenerative magnetic materials were dried at 80 °C in vacuum for 3 h and then were used for adsorption again. The cycles of desorption–adsorption process were successively repeated at least five times.

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