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Preparation of chitosan/magnetite composite beads and their application for removal of Pb(II) and Ni(II) from aqueous solution

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ABSTRACT

A simple and effective process has been proposed to prepare chitosan/magnetite nanocomposite beads with saturation magnetization value as high as uncoated Fe_3O_4 nanoparticles (*ca.* 54 emu/g). The reason was that the coating chitosan layer was so thin that it did not affect magnetic properties of these composite beads. Especially, chitosan on the surface of the magnetic Fe_3O_4 nanoparticles is available for coordinating with heavy metal ions, making those ions removed with the assistance of external magnets. Maximum adsorption capacities for Pb(II) and Ni(II), occurred at pH 6 and under room temperature were as high as 63.33 and 52.55 mg/g respectively, according to Langmuir isotherm model. These results permitted to conclude that chitosan/magnetite nanocomposite beads could serve as a promising adsorbent not only for Pb(II) and Ni(II) (pH = 4–6) but also for other heavy metal ions in wastewater treatment technology.

1. Introduction

Along with the technological progresses, toxic metal contamination becomes a serious problem threatening human health. Heavy metal ions such as Pb(II), Cd(II), Hg(II), and Ni(II) are toxic and carcinogenic at relatively low concentrations. They are not self-degradable and can accumulate in living organisms, causing severe disorders and diseases. In order to remove heavy metal ions from various environments, the techniques such as precipitation, adsorption, ion exchange, reverse osmosis, electrochemical treatments, membrane separation, evaporation, coagulation, flotation, oxidation and biosorption processes are widely used [1–10]. These conventional techniques are costly and have significant disadvantages such as generation of metal bearing sludge or wastes, incomplete metal removal, and the disposal of secondary wastes. For these reasons, there is a need for developing economic and eco-friendly methods for wastewater treatments. Adsorption is an attractive process, in view of its efficiency and the ability to treat wastewater containing heavy metals. Over the last few decades adsorption has gained importance as an effective purification and separation technique used in wastewater treatment and low cost adsorbents are becoming the focus of many investigations on the removal of heavy metals from aqueous solutions [11–15].

Chitosan has excellent properties for the adsorption of metal ions, principally due to the presence of amino groups ($-NH_2$) in the polymer matrix, which can interact with metal ions in solution by ion exchange and complexation reactions [11]. The high content of amino groups also makes possible many chemical modifications in polymer with the purpose of improving selectivity and adsorption capacity.

In this paper, chitosan/magnetite nanocomposite beads were prepared, characterized and used for removal of toxic metal ions such as Pb(II), Ni(II) in the pH range from 4 to 6. Langmuir isotherms were used to analyze the equilibrium data at different pH. These nanocomposite beads can be removed easily from water with the help of an external magnet thanks to their exceptional magnetic properties.

2. Experimental

2.1. Chemicals

All reagents were analytical grade and used as received without further purification. $FeSO_4 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$, $Pb(CH_3COO)_2$ or $NiSO_4 \cdot 7H_2O$, 4-(2-pyridylazo)rezocxin and Ni(II)-dimetyl glyoxim were purchased from Merck. NH_4OH 25 wt.%, NaOH, CH_3COOH and Br_2 were purchased from Duc Giang Chemical Company (Vietnam). Chitosan (MW = 400,000, DA = 70%) was purchased from Nha Trang Aquatic Institute (Vietnam) and re-characterized by viscometry and IR measurements at our laboratory [16].

2.2. Synthesis of chitosan/magnetite composite beads

Chitosan/magnetite composite beads were prepared by chemical co-precipitation of Fe^{2+} and Fe^{3+} ions by NaOH in the presence of chitosan followed by hydrothermal treatment [17]. Briefly, the solution of chitosan, prepared with 0.5 g of chitosan was dissolved

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into 5 ml of CH_3COOH (99.5 wt.%, $d = 1.05$ g/ml) and 45 ml of distilled water (pH = 2–3), $FeCl_2$ and $FeCl_3$ were dissolved in 1:2 molar ratio and then the resulting solution was dropped slowly into NaOH 30 wt.% solution to obtain chitosan/magnetite beads with different mass ratios of chitosan/magnetite: 0/1 (pure Fe_3O_4); 1/2 and 4/1. The suspension was kept at room temperature for 24 h without stirring and separated by washing several times in water to remove alkaline. The particles were finally dried in vacuum at 70 °C for 24 h to obtain chitosan/magnetite composite beads as adsorbent.

2.3. Characterization methods

X-ray Diffraction (XRD) patterns were obtained at room temperature by D8 Advance, Bruker ASX, using CuKα radiation (λ = 1.5406 Å) in the range of $2\theta = 10°$–60°, and a scanning rate of 0.02 s^{-1}. Infra red (IR) spectra were recorded with Nicolet 6700 FTIR Spectrometer, using KBr pellets, in the region of 400–4000 cm^{-1}, with resolution of 4 cm^{-1}. Morphology of composites was analyzed by Field Emission Hitachi S-4500 Scanning Electron Microscope (FE-SEM) and Transmission Electron Microscope (TEM, JEOL, Voltage: 100 kV, magnification: ×200,000). Absorbance measurements were carried out on UV–vis Agilent 8453 spectrophotometer in the range of 400–800 nm. The magnetic properties were measured with homemade vibrating sample magnetometer (VSM) and evaluated in terms of saturation magnetization and coercivity. Chemical composition of samples was determined by JEOL Scanning Electron Microscope and Energy Dispersive X-ray (SEM/EDS) JSM-5410 Spectrometer.

2.4. Adsorption studies

Chitosan/magnetite nanocomposite beads were used as magnetic adsorbents for the adsorption of Ni(II) and Pb(II). The adsorption behaviors of Pb(II) and Ni(II) ions were investigated in aqueous solutions at pH 4–6 and at room temperature as follows: 0.01 g chitosan/magnetite composite beads were added to 100 ml of Pb $(CH_3COO)_2$ or $NiSO_4$ solution respectively with initial concentrations (C_0) varied from 50 to 80 mg/l for 120 min (contact time). The concentration of Pb(II) and Ni(II) ions was determined by spectrophotometric assay and the procedure is as follows: 1 ml of sample solution was mixed with 4-(2-pyridylazo)rezocxin (PAR), sodium acetate, NH_3 at pH = 10. After the formation of the Pb(II)-4-(2-pyridylazo)rezocxin complex, the concentration of Pb(II) ions was determined from the absorbance peak at 530 nm on a UV–vis spectrophotometer. To determine concentration Ni(II) ions, 1 ml of sample solution was mixed with sodium dimetyl glyoxim 1.2 wt.%, sodium hydroxide solution and Br_2 solution. After the formation of the Ni(II)-dimetyl glyoxim complex, the concentration of Ni(II) ions was determined from the absorbance at 475 nm. The amount of Pb(II) and Ni(II) uptake was calculated as % recovery = $C_0 - C_e / C_0$, where C_0 and C_e represented initial and equilibrium concentrations of metal ions in aqueous solution respectively.

3. Results and discussion

3.1. Characterization of chitosan/magnetite composite beads

3.1.1. Morphology and particles of chitosan/magnetite composite beads

Balancing between high adsorption capacity (due to chitosan) and magnetic properties (due to Fe_3O_4) various molar ratios of chitosan/Fe_3O_4 were investigated. In our study, mass ratio of CS/Fe_3O_4 of 4/1 seems to be an appropriate value (see Section 3.1.4 (Magnetic properties) and Section 3.2.1 (Isotherm adsorption study)). Fig. 1a and b shows the digital camera picture and SEM image respectively of chitosan/magnetite composite beads with CS/Fe_3O_4 ratio of 4/1. Being spherical in form, solid in structure and quite big in size, CS/Fe_3O_4 beads (microspheres) are more applicable for removal of heavy metals ion in solution with external magnets, and easily recyclable than CS-free, separated Fe_3O_4 particles.

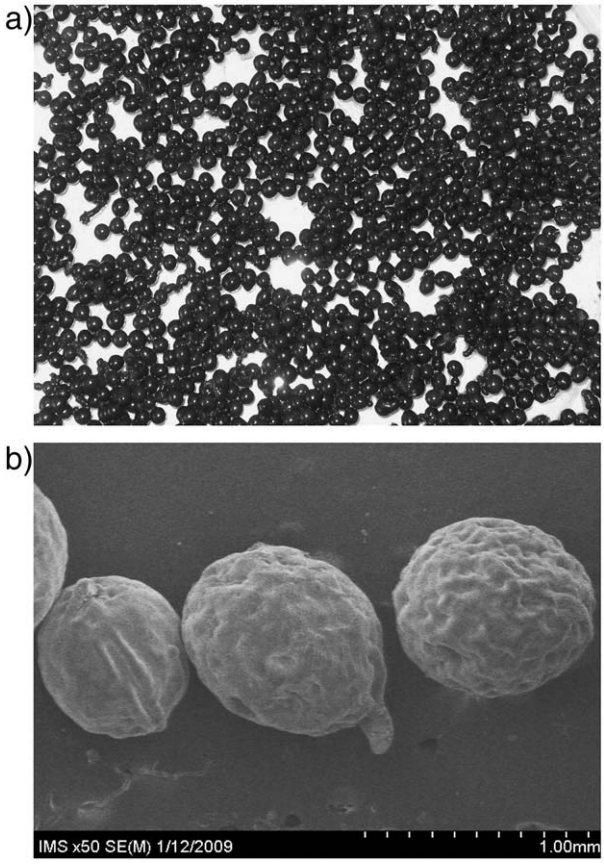

Fig. 1. a. Digital camera picture of chitosan/magnetite composite beads. b. SEM image of chitosan/magnetite composite beads (CS/Fe_3O_4 = 4/1).

3.1.2. XRD analysis

Fig. 2 showed XRD patterns of pure Fe_3O_4 (i) and chitosan/magnetite composite beads (lines (ii) and (iii)). Six characteristic peaks for Fe_3O_4 corresponding to (220), (311), (400), (422), (511) and (440) were observed in all samples (JCPDS file, PDF No. 65-3107). Quite weak diffraction lines of composite patterns indicated that

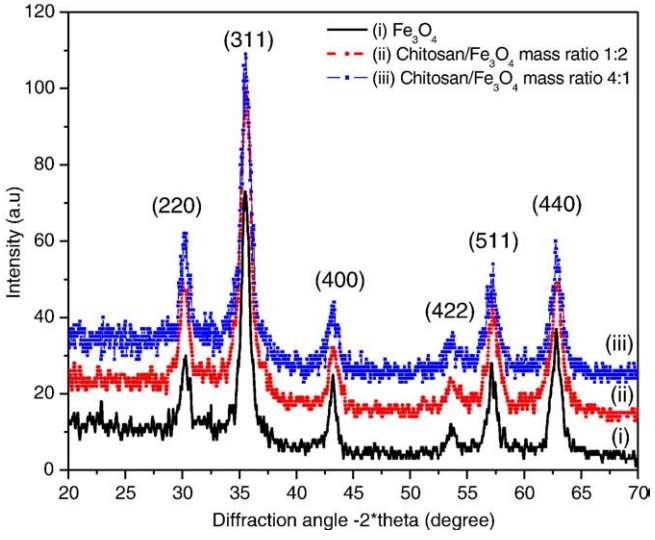

Fig. 2. XRD pattern of Fe_3O_4 and composite beads (CS/Fe_3O_4 = 1/2; 4/1).