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Facile synthesis of high performance porous magnetic chitosan - polyethylenimine polymer composite for Congo red removal

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ABSTRACT

A new porous magnetic chitosan-polyethylenimine (Fe_3O_4/CS-PEI) polymer composite was synthesized by crosslinking chitosan (CS) with polyethylenimine (PEI) in the present of $FeCl_3{\cdot}6H_2O$ and $FeCl_2{\cdot}4H_2O$ in alkaline condition and applied to remove congo red (CoR) from aqueous solutions. The Fe_3O_4/CS-PEI composite was characterized by SEM, XRD, TGA and FT-IR analysis. The polymer composite owned high positive charge, large surface area, multi-level pore distribution and magnetic responsiveness. The porous magnetic Fe_3O_4/CS-PEI composite showed ultrahigh capacity (1876 mg/g) for CoR removal. It removed over 99.3% of CoR (100 mg/L) when the dosage was over 1.4 g/L. A higher temperature was benefit to CoR removal. The Fe_3O_4/CS-PEI composite was effective for CoR removal in a wide pH range (3–13). Kinetics studies suggested that the adsorption mechanism of CoR followed the pseudo-second model and it was also affected by the boundary layer diffusion. The adsorption process followed the Redlich-Peterson isotherm equation. Thermodynamic studies also demonstrated that this adsorption process was spontaneous, favorable and endothermic. The activation energy (E_a) of the adsorption process was 34.08 kJ/mol, indicating that chemisorption existed in the process. The results demonstrated that the porous magnetic Fe_3O_4/CS-PEI polymer composite is a promising adsorbent for the efficient removal of dye pollutants from aqueous solution.

1. Introduction

Dye is one of the most common pollutants in wastewater due to their strong toxicity, non-biodegradability and accumulation in plants, animals and human beings [1]. Because of the increasing diversity of industrial products, the component of dye wastewater turns increasing complicated and the treatment of which becomes an extremely difficult task. Congo red (CoR), one of the water-soluble anionic dyes, has been widely used in printing, textile, leather, cosmetic industries and biomedical laboratories [2,3]. It can severely affect the aquatic life and the food web even in a low concentration by weakening the penetration of light in water and inhibiting the photosynthesis capacity of aquatic organisms. It also can cause health problems such as difficulties in breathing, diarrhoea, vomiting and nausea to humans and animals. [4]. Therefore, it is significant and urgent to remove CoR from wastewater.

A variety of methods including membrane separation [2], adsorption [5], flocculation [6], photocatalytic chemical decomposition [7], electrolysis [8], and biological treatments [9] have been developed to remove CoR in wastewater. Among these approaches, adsorption process is regarded as an efficient alternative, due to its simplicity of design, wide adaptability, convenience and ease of operation, especially when the adsorbent is inexpensive and readily available [10,11]. Many adsorbents are applied to adsorb dyes in wastewater, including metallic oxide, activated carbon, natural materials, algae, bentonite, nanocomposite, etc. [12]. Nevertheless, these adsorbents show limitations such as low adsorption capacity, hazardous by-products, separation inconvenience, high cost or intensive energy requirements [12,13].

Chitosan (CS) is a biological polysaccharide and widespread in nature. It has desirable properties like hydrophilicity, low cost biocompatible and biodegradable [14,15]. It contains amino and hydroxyl groups that can serve as adsorptive sites for dyes. However, the low mechanical strength, poor water solubility, easily hydrolyzed under acidic conditions and other drawbacks limit its application in dyestuff wastewater treatment [16–18]. In order to overcome these limitations, the physical and chemical modifications need to be carried out on chitosan. Chemical cross-linking is an effective method to improve its mechanical strength and its chemical stability in acidic media. However, these improvements often lead to the loss of amino or hydroxyl groups and result in the decreased adsorption capacity [16]. Polyethylenimine (PEI) is an

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amorphous high performance well-known biocompatible macromolecule with abundant amino groups on its surface and widely used in drug carrier, genetic vector, flocculant etc. [19,20]. Thus, cross-linking chitosan with PEI can not only improve its mechanical strength and its chemical stability, but also increase amino groups and result in the increase of adsorption capacity. Porous materials are appealing because of their unique pore architecture, high surface area, and specific physical and chemical properties, which contribute to their excellent performance as adsorbents [13]. Compared to the long and tedious centrifugation separation process, the magnetic separation technology can be easily manipulated by an external magnetic, and can treat a large amount of wastewater in a short time. Thus, combining functionalities of magnetism and porous structures may show facile separation properties and highly efficient adsorption [21,22]. In light of these, we assumed the design of a porous magnetic chitosan-polyethylenimine crosslinking product would achieve the purpose of developing an adsorbent with superior adsorption capability and facile separation properties.

Hence, in the present work, the porous magnetic chitosan-polyethylenimine (Fe_3O_4/CS-PEI) polymer composite was prepared using a facile one-pot synthesis approach through crosslinking chitosan (CS) with polyethylenimine (PEI) in the present of epichlorohydrin as crosslinker, and $FeCl_3{\cdot}6H_2O$ and $FeCl_2{\cdot}4H_2O$ as the magnetic source. The as synthesised adsorbent not only possessed good mechanical strength, but also exhibited a super high adsorption performance for CoR removal. The designed structure provided Fe_3O_4/CS-PEI distinctive characteristics including highly positive charged, high surface area, multi-level pore distribution and magnetic responsiveness. The BET surface area of the Fe_3O_4/CS-PEI is 109.2 m^2/g with average pore width of 15.08 nm and total pore volume of 0.24 cm^3/g. The Fe_3O_4/CS-PEI showed enhanced high capacity (1876 mg/g at 40 °C) for CoR removal in aqueous solutions. The effects of dosage of Fe_3O_4/CS-PEI, initial pH and initial CoR concentration on the adsorption were studied. The thermodynamics and kinetics of the adsorption process were investigated in detail. The results showed that Fe_3O_4/CS-PEI is a high performance adsorbent with facile magnetic separation properties.

2. Experimental

2.1. Materials

Chitosan (CS) with a molecular weight of 5.0×10^5 and a deacetylation degree of 95% was purchased from Yuhuan Ocean Biochemical Ltd, China. Polyetherimide (PEI) with a molecular weight of 1.0×10^4, epichlorohydrin and congo red (CoR, $C_{32}H_{22}N_6Na_2O_6S_2$) were bought from Aladdin. The chemical structure of congo red is presented in **Scheme S1** in the supporting information. Sodium hydroxide, ammonia aqueous solution (30%), hydrochloric acid (37%) and acetic acid were purchased from Shanghai Chemical Reagent Co. Ltd, China. Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) and ferrous chlorid ($FeCl_2{\cdot}4H_2O$) were purchased from Shanghai Chemical Reagents Company.

2.2. Preparation of the porous magnetic chitosan-polyethylenimine (Fe_3O_4/CS-PEI) polymer composite

The Fe_3O_4/CS-PEI polymer composite was synthesized using a one-pot synthesis approach. Typically, 1.3525 g $FeCl_3{\cdot}6H_2O$ and 0.4975 g $FeCl_2{\cdot}4H_2O$ were dissolved in 50 mL deionized water to form a homogeneous medium. 2.0 g chitosan was dissolved in 40 mL 3% acetic and the as prepared chitosan-acetic acid solution was added in to the above homogeneous medium. Subsequently, N_2 was bubbled in and the temperature was heated to 90 °C followed by addition of 40 mL ammonia aqueous solution. Then, 1.0 mL epichlorohydrin and 1.0 g PEI were added, and the mixture was reacted for 2 h. After the reaction, the obtained product was collected by magnetic separation, washed with deionized water and dried by freeze dryer.

2.3. Characterization methods and instruments

Fourier transform infrared spectra (FT-IR) were obtained on a Nicolet, Avatar 360 FT-IR spectrometer (USA). The spectrum widths were typically in the range of 4000–400 cm^{-1}. Scanning electron microscopy (SEM) was investigated using a scanning electron microscope (Nova Nano SEM 230, USA). Thermogravimetric analysis (TGA) measurements were performed in nitrogen by an STA449C thermal analyzer (Germany). Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance X-ray diffraction spectrometer (Germany) with Cu K_α radiation at $\lambda = 0.154$ nm operating at 40 kV and 40 mA. Magnetic characterization was carried out with a vibrating sample magnetometer on a Model 6000 physical property measurement system (Quantum, USA) at 300 K. Zeta potential was conducted with a zetasizer nano potential analyzer (Malvern, ZS) using He-Ne laser at a wavelength of 632.8 nm. The N_2 adsorption–desorption isotherms was carried out using a surface area analyzer (Quanta Chrome Nova1200). The specific surface area was determined by Brunauer-Emmett-Teller equation (BET) and total pore volume was defined as the maximum amount of nitrogen adsorbed at relative pressure of $P/P_0 = 0.99$.

2.4. Adsorption of CoR by Fe_3O_4/CS-PEI polymer composite

Stock solutions were prepared by dissolving congo red in deionized water to concentrations in range of 30–420 mg/L. Adsorption experiments were carried out in a constant temperature shaker. The concentration of congo red was measured by a spectrophotometer at 488 nm (the maximum absorption wavelength) after the adsorbent-adsorbate complex separated by magnet. Solution without the adsorbent was served as the control.

The adsorption capacity q_e (mg/g) was determined as flowing equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

The removal efficiency of congo red was calculated by:

$$\text{Removal efficiency} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

Where C_0 (mg/L) is the initial concentration of congo red, C_e (mg/L) is the final or equilibrium concentration of congo red, V (L) is the total volume of the solution, m (g) is the dosage of Fe_3O_4/CS-PEI and q_e (mg/g) is the amount of congo red adsorbed per unit weight of Fe_3O_4/CS-PEI. The effects of dosage of Fe_3O_4/CS-PEI, initial pH, and initial congo red concentration on removal efficiency were studied. The pH in the experiments was original pH of the congo red solutions unless mentioned specifically.

3. Results and discussion

3.1. Synthesis and characterization of Fe_3O_4/CS-PEI composite

The schematic representation for the synthesis of the Fe_3O_4/CS-PEI is displayed in Scheme 1 and the reactions happened in the process is represented in Scheme S2 in the supporting information. In the preparation process, $FeCl_3{\cdot}6H_2O$ reacted with $FeCl_2{\cdot}4H_2O$ and the magnetic Fe_3O_4 nanoparticles were generated in the present of ammonium hydroxide at 90 °C. Chitosan (CS) was crosslinked with polyethylenimine (PEI) in the present of epichlorohydrin as a crosslinker. In alkaline condition, the epoxy