



Fabrication of interpenetrating polymer network chitosan/gelatin porous materials and study on dye adsorption properties



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ABSTRACT

One kind of adsorbent based on chitosan and gelatin with interpenetrating polymer networks (IPN) and porous dual structures was prepared using genipin as the cross-linker. These dual structures were demonstrated by means of Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). Adsorptions of acid orange II dye from aqueous solution were carried out at different genipin contents, adsorption times and pH values. The results showed that this material was put up the largest adsorption capacity when the genipin content is 0.25 mmol/L, meanwhile, the lower the solution pH value the greater the adsorption capacity. The chitosan/gelatin interpenetrating polymer networks porous material displayed pH-sensitive and rapidly response in adsorption and desorption to pH altered. It is indicated that the cross-linked chitosan/gelatin interpenetrating polymer networks porous material could be used as a recyclable adsorbent in removal or separation of anionic dyes as environmental pH condition changed.

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1. Introduction

Synthetic dyes discharged from various sources, such as textile, leather, paper, rubber, etc. (Akhtar, Khan, & Husain, 2005; Gupta, Mittal, Gajbe, & Mittal, 2006) have triggered serious environment pollution. An army of the synthetic dyes are toxic and may affect water source (Chuah, Jumariah, Azni, Katayon, & Choong, 2005). Therefore, the major problem concerning environmental pollutants is removing dyes from wastewater produced in industrial activities. Numerous techniques, such as physical, chemical and biological decolorization methods, have been carried out to treat wastewater containing dyes (Robinson, McMullan, Marchant, & Nigam, 2001). For water decontamination, adsorption technology is usually regarded as an effective and economic method. Recently, activated carbon (Ahmad & Hameed, 2010), clays (Bouberka, Kacha, Kameche, Elmaleh, & Derriche, 2005; Tahir & Rauf, 2006), chitin/chitosan (Mckay, Blair, & Gardner, 1982; Yang, Bai, Xu, & Guo, 2012), polymers (Huttermann, Orikiriza, & Agaba, 2009) and agricultural wastes (Aksu & Tezer, 2000; Aksu, 2001; Saha, Chowdhury, Gupta, & Kumar, 2010) have been investigated as adsorbents.

Chitosan (CS) comprising β -(1,4)-linked N-acetyl-D-glucosamine and D-glucosamine units is obtained by the partial de-acetylation of chitin (Muzzarelli, 2011; Muzzarelli et al., 2012).

Reactive amino and hydroxyl groups on chitosan can be modified by chemical and physical method easily. Chitosan has been widely investigated as an adsorbent to capture dyes from aqueous solutions because of its low cost, easy availability, environmental friendly behavior, ready chemical modifications and remarkable adsorption capacities. However, one shortcoming for chitosan to be used as adsorbent is that chitosan readily dissolves in acidic conditions which pH is below 6 (He, Wang, Wu, Huang, & Zhang, 2011). In an attempt to overcome this problem, chitosan needs to be cross-linked. On the other hand, after adsorption dyes, it is difficult for chitosan to remove contaminants, thus materials recycling is limited. If the desorption properties of chitosan can be improved by adding anionic acid groups, then the application of chitosan in dye wastewater treatment will have broader prospects. Fortunately, a multitude of anionic acid groups (carboxyl groups) on gelatin (G) macromolecule chain exhibit negative charge in basic conditions. If blend gelatin with chitosan, negative charges on gelatin molecular chain will benefit for the anionic dyes desorption from adsorbent. At the same time, considerable hydroxyl, amino and other active groups on gelatin macromolecule chain can also adsorb reactive dyes with hydroxyl, amino, azo, sulfuric acid through ionic or hydrogen bond (Bigi, Cojazzi, Panzavolta, Roveri, & Rubini, 2002).

To improve the stability of the adsorbent as well as the biodegradability, mechanical strength and solutes diffusion in it, interpenetrating polymer networks (IPN) have been suggested by many authors for the interlocked structure in the cross-linked

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networks (Cui, Jia, Guo, Liu, & Zhu, 2014; Dragan, Perju, & Dinu, 2012; Liang, Liu, Huang, & Yam, 2009). At which one polymer chain permeates into another polymeric network at molecular level with or without chemical bonds (Ramesh Babu, Hosamani, & Aminabhavi, 2008).

Although considerable studies have been devoted to develop hydrogels based on chitosan as a bio-adsorbent, little work has been taken on the recycled chitosan/gelatin porous adsorbent. In this work, gelatin was added into chitosan to improve the desorption properties of chitosan. Genipin (Muzzarelli, 2009), a natural crosslinker, was chosen to form interpenetrating polymer networks structure. Interpenetrating polymer networks cross-linked chitosan/gelatin porous materials were prepared by freeze-drying and investigated as adsorbents for removal of anionic dye (acid orange II dye) from aqueous solutions.

2. Experimental

2.1. Materials

The degree of deacetylation of the chitosan (Laizhou Hailisheng bioproduct Co. Ltd. Laizhou, China.) sample was 93%, and the molecular weight was approximately 5×10^4 . Gelatin (G) type B (from bovine skin) and Genipin (GP) were provided by Shanghai Chemical Reagent Co. (Shanghai, China) and Linchuan Biological technology Co. Ltd. (Fuzhou, China), respectively. All other chemical reagents and solvents were analytical grade.

2.2. Preparation of chitosan/gelatin porous materials

Firstly, dissolve 3 g chitosan powder in 100 mL deionized water containing 1% (v/v) acetic acid at 25 °C to obtain a 3% (w/v) solution. Dissolve gelatin in deionized water at 50 °C to obtain a 6% (w/v) solution. Then, these two solutions with a fixed chitosan-to-gelatin weight ratio 5:5 were poured together and stirred for 2 h at 50 °C. The chitosan/gelatin solutions were blended with an aqueous genipin solution in a concentration from 0.05 to 0.75 mmol and then sonicated to remove the trapped air bubbles. After thoroughly stirring, the air bubble-free solutions were poured into plastic Petri dishes and frozen in a freezer (BCD-216KD, Qingdao Haier Limited Co., Ltd., China) at -30 °C for 5 h. The frozen constructs were lyophilized in a freeze-dryer (LGJ-10, Changsha Xiangyi centrifuge instrument Co., Ltd., China) for 12 h with the atmospheric pressure for 10 Pa and a freeze-drying temperature at 30 °C. Finally, the cross-linked porous chitosan/gelatin materials were neutralized with an aqueous NaOH solution, rinsed several times in deionized water until pH was neutral and then dried in air.

2.3. Fourier transform infrared (FTIR) study

The FT-IR spectra of the samples were performed using a Perkin-Elmer (USA) 6000 FT-IR spectrometer in the wave number range of 400–4000 cm^{-1} . Samples used for the FT-IR spectroscopic analysis were prepared by grinding the dry blends with KBr and compressing the mixtures to form sheet.

2.4. Thermogravimetric (TGA) analysis

Thermogravimetric analysis was performed under 50 ml/min flowing air on a PerkinElmer (USA) TGA 7 at a heating rate of 20 °C/min. About 5 mg of samples placed in a TGA pan were heated from 30 to 700 °C.

2.5. Scanning electron microscope (SEM) observation

Freezing dried samples were carefully sectioned and fixed to a metal holder using a double-sided adhesive tape and sputtered with gold. The cross-section morphology of the sample was observed by using a scanning electron microscope (JSM-5510LV, JEOL, Japan) at an accelerated voltage of 10–20 kV at room temperature.

2.6. Adsorption studies

Dried porous materials (50 mg) were immersed in 100 mL 350 mg/L of acid orange II dye solutions (ionic strength = 0.01 mol/L) at 30 °C. If no special instructions, the pH value was 3.0. At intervals of time, the residual dye concentrations in the system were measured by a Shanghai (China) Jingke 722 model UV-Vis spectrophotometer. The amount of the dye adsorption at time t , Q_t (mg/g dried material), was calculated according to the following equation:

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where V is the volume of the solution (mL), m is the weight of the dried samples (g), C_0 is the initial dye concentration (mg/L), and C_t is the residual dye concentration at the indicated time t (mg/L).

2.7. Adsorption kinetics

The pseudo first-order and pseudo second-order kinetic rate models were used to test the dye adsorption behaviors of the porous materials. The pseudo first-order rate expression is as follows (Ho & Mckay, 1998):

$$\lg(Q_e - Q_t) = \lg Q_e - \frac{k_1 t}{2.303} \quad (2)$$

The pseudo second-order model is expressed as below (Weber & Morris, 1963):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (3)$$

where Q_e (mg/g) and Q_t (mg/g) are the amounts of adsorbed dyes by the material at equilibrium and at time t , respectively, and k_1 is the pseudo first-order adsorption rate constant (min^{-1}), k_2 denotes the second-order adsorption rate constant ($\text{g}/(\text{mg min})$).

2.8. Recycle

Dried 50 mg porous materials (0.25 mmol/L genipin) were immersed in 100 mL 350 mg/L of acid orange II dye solutions (ionic strength = 0.01 mol/L) at 30 °C. Keep shaking for 24 h. Equilibrium adsorption capacities were calculated according to Eq. (1). Centrifugal separate porous materials and dry for 24 h. Put these materials into 100 mL solutions with a fixed ionic strength 0.01 mol/L and pH 10 at 30 °C for 24 h. Repeated this absorption and desorption experiments by using the same sample for 7 times.

3. Results and discussion

3.1. Fourier transform infrared analysis

Fig. 1 illustrates the typical FT-IR spectra of series chitosan/gelatin samples. Several characteristic absorption bands of chitosan were located at 3445 cm^{-1} corresponding to the partially overlapped of amine and hydroxyl group stretching vibrations, 1576 cm^{-1} corresponding to protonated amino stretching, 1629 cm^{-1} corresponding to amide stretching, 926 cm^{-1} and

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