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Facile synthesis of low-cost magnetic biosorbent from peach gum polysaccharide for selective and efficient removal of cationic dyes

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ABSTRACT

Magnetic biosorbents derived from renewable resource are emerging as a new class of adsorbing material for environmental cleanup because of their eco-friendly characteristic, easy availability and low cost. Herein, a novel magnetic peach gum bead (MPGB) biosorbent was successfully fabricated by a simple one-step reaction based on the simultaneous formation of magnetic nanoparticles and cross-linking of natural peach gum polysaccharide. Benefiting from the combined merits of peach gum and magnetic nanoparticles, the MPGB not only showed excellent adsorption performance for cationic dyes but also exhibited convenient magnetic separation capability. The influences of pH, ionic strength, initial dye concentration, contact time and temperature on the adsorption property of MPGB biosorbent were investigated by choosing methylene blue (MB) as a representative cationic dye. The Langmuir isotherm fitted the adsorption isotherm well with maximum adsorption capacity of 231.5 mg g^{-1}. Kinetic data showed good correlation with pseudo-second-order model. Thermodynamic investigation revealed that the adsorption process was spontaneous and endothermic. Moreover, the MPGB exhibits nice reusability. Considering the facile fabrication process and excellent adsorption performance, the MPGBs hold great promise for using as biosorbent for environmental cleanup.

1. Introduction

Organic dye, which is widely used in industry, has become one of the primary water pollutants because trace amounts of dye in water may cause severe toxic effects on human health [1–3]. Although several strategies have been developed for removal of dyes from water, adsorption technique has been recognized as the most effective approach for decontamination of dye pollutants due to its ease of operation, high efficiency, and wide suitability for various dyes [4–7]. Over the years, activated carbon (AC) is the most commonly employed adsorbent throughout the world [8]. However, the AC suffers from several drawbacks including high cost, complex separation process and difficult to regeneration, which restricted its usefulness in water treatment. In recent years, increasing attention was paid on the development of alternative adsorbents that can overcome the disadvantages of AC [9,10]. In this regard, adsorbents from natural renewable resources have gain significant interest because their facile availability, eco-friendly characteristic, and low cost. Numerous renewable materials, such as peanut hull, banana peel and rice husk have been investigated as biosorbents for adsorption of dyes from water [6,11]. However, most of the reported biosorbents exhibited low adsorption capacity and slow adsorption rate. Hence, exploring highly efficient biosorbents for environmental treatment is still demanded.

As a kind of renewable gum exudate, peach gum (PG) is produced from the trunk and fruit of peach tree as a result of mechanical injury or physiological process [12,13]. The PG resource is abundant in many areas of the world. The PG macromolecule is highly branched and its main composition is acidic polysaccharide, which generally consists of arabinose (36–37%), galactose (42%), uronic acid (7–20%) and xylose (7%) [14,15]. Benefiting from the presence of numerous negatively charged oxygen-containing functional groups in the macromolecular chains of PG, the PG has showed excellent adsorption performance for cationic dyes based on the strong electrostatic attraction between the dyes and PG [16]. However, it is difficult to separate PG adsorbent from water after adsorption by traditional separation methods (e.g., sedimentation and filtration) especially for large scale treatment of dye solution because the PG particles may be lost or block filters. In addition, the residual PG particles in water may cause secondary pollution. To overcome the drawbacks, a viable approach is to construct PG-based magnetic adsorbent. Because magnetic adsorbents can be

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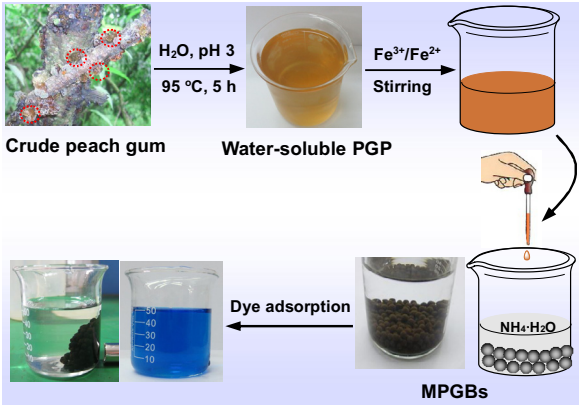

Fig. 1. Schematic illustration of the preparation of magnetic peach gum beads (MPGBs) from crude peach gum for dye adsorption.

conveniently separated from water by using an external magnetic field, a large amount of dye effluent can be purified in a short time by magnetic adsorbents using less energy and producing no extra contaminants [17–19]. Although magnetic adsorbents derived from renewable biomass such as cellulose, alginate, chitosan and corncob has been studied [20–26], PG-based magnetic adsorbent has not been reported to date.

In this contribution, we present a facile approach for fabrication of magnetic PG bead (MPGB) biosorbent based on the simultaneous cross-linking of PG and formation of iron oxide nanoparticles (Fig. 1). Compared with other magnetic biosorbents that usually require multi-step reactions, toxic raw materials, and rigorous conditions, the MPGB biosorbent can be readily produced in one batch [27–30], which makes it attractive for practical applications. The influences of adsorption parameters such as pH, ionic strength, initial dye concentration, contact time and temperature on the adsorption performance of MPGB were examined in detail. In addition, the adsorption mechanism and regeneration property of the MPGB biosorbent were also investigated.

2. Materials and methods

2.1. Materials

Crude peach gum (CPG) was collected from peach tree at Zizhou park (Guilin, China). Ammonia solution (25 wt%), iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), iron (II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), sodium hydroxide (NaOH), methylene blue (MB, λ_{max} = 662 nm), methyl violet (MV, λ_{max} = 583 nm), Cong red (CR, λ_{max} = 496 nm), and methyl orange (MO, λ_{max} = 463 nm) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China) and used as received. Double distilled water was used throughout the experiments.

2.2. Characterization

Powder X-ray diffraction (XRD) spectra were taken on a Holland PANalytical X-Pert PRO X-ray diffractometer with Cu-Kα radiation. Fourier transform infrared (FTIR) spectra were recorded using a PE Paragon 1000 spectrometer (KBr disk). The zeta potential values of the sample at various pH values were measured with a zeta potential analyzer (Zetasizer Nano ZS90, Malvern). Scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDX) spectra were determined using a FEI SIRION 200 field-emission microscope. The magnetic moment was recorded at 300 K on a MPMS XL-7 vibrating-sample magnetometer (VSM). Absorption spectra were recorded on a UV-3600 UV-vis-NIR spectrophotometer (Shimadzu).

2.3. Preparation of MPGB biosorbent

The hydrolysis of picked CPG to afford water-soluble PG was conducted according to our previous report [13]. In a typical procedure, CPG (1 g) was soaked and agitated overnight in water (100 mL) to give a dispersion containing swelling gum. The pH of gum suspension was adjusted to 3 by adding 0.5 M HCl before stirring at 95 °C for 5 h. After reaction, the final mixture was filtrated, dialyzed and freeze-dried to give water-soluble PG. To prepare MPGB biosorbent, typically, water-soluble PG (500 mg), $FeCl_3{\cdot}6H_2O$ (405 mg, 1.5 mmol) and $FeSO_4{\cdot}7H_2O$ (209 mg, 0.75 mmol) were dissolved in 10 mL of water. The mixture was stirred at room temperature for 15 min to form a homogeneous solution. Then, the mixture was dropwise added into 20 mL of ammonia solution (25 wt%) and black MPGBs were formed immediately. After repeated washing by water, the resulting MPGBs were freeze-dried.

2.4. Adsorption experiments

Batch adsorption experiments were conducted using the following procedure. Typically, 50 mg of MPGB was added into 100 mL of dye solution of known concentration and the mixture was agitated at certain temperature (20, 40, and 60 °C). The solution pH was adjusted with NaOH (0.5 M) or HCl (0.5 M). The ionic strength of solution was adjusted with NaCl. The absorbance of dye solution was measured at specific time interval until adsorption equilibrium was reached. The MPGB was separated from water by a magnet. All adsorption experiments were carried out in triplicate, and the mean value was used to minimize random error. Dye concentration was determined by UV–vis spectrophotometer. Calibration curves were plotted between absorbance and concentration of the standard dye solutions. It should be pointed that the wavelength of absorption peaks of MB solution at high pH (e.g., 9) or low pH (e.g. 3–4) are slightly changed as compared with those of solutions in the pH range 5–8. The amount of dye adsorbed at equilibrium (Q_e) (mg g^{-1}) or at time t (Q_t) (mg g^{-1}) was calculated from the following equations:

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

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_0, C_t, and C_e (mg L^{-1}) are the initial, at time t (min), and equilibrium concentration of dye in the solution, respectively, V is the volume of the solution (L), and m (g) is the mass of MPGB used. In addition, the removal efficiency of MPGB biosorbent after reaching adsorption equilibrium was calculated as follows:

$$\text{removal efficiency} = (C_0 - C_e) \times 100\%/C_e \quad (3)$$

The selective adsorption experiments were performed in the mixture of MB and MO. 50 mg of MPGB was added to 30 mL of dye mixture. The initial concentration of MB and MO are both 0.1 mM. After stirring at 100 rpm/min for 30 min at 20 °C, the MPGB biosorbent was separated by a magnet. The residual dye concentration in the solution was measured by UV–vis spectrophotometer.

2.5. Regeneration study

In a typical procedure, 50 mg of MB-adsorbed MPGB was immersed into 100 mL of ethanol. The suspension was treated by ultrasonic at 100 W for 30 min. Subsequently, the MPGB biosorbent

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