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Original article

Fabrication of macroporous polystyrene/graphene oxide composite monolith and its adsorption property for tetracycline

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ABSTRACT

Macroporous polystyrene microsphere/graphene oxide (PS/GO) composite monolith was first prepared using Pickering emulsion droplets as the soft template. The Pickering emulsion was stabilized by PS/GO composite particles *in-situ* formed in an acidic water phase. With the evaporation of water and the oil phase (octane), the Pickering emulsion droplets agglomerated and combined with each other, forming a three-dimensional macroporous PS/GO composite matrix with excellent mechanical strength. The size of the macrospores ranged from 4 μm to 20 μm. The macroporous PS/GO composite monolith exhibited high adsorption capacity for tetracycline (TC) in an aqueous solution at pH 4–6. The maximum adsorption capacity reached 197.9 mg g^{-1} at pH 6. The adsorption behaviour of TC fitted well with the Langmuir model and pseudo-second-order kinetic model. This work offers a simple and efficient approach to fabricate macroporous GO-based monolith with high strength and adsorption ability for organic pollutants.

1. Introduction

Tetracycline (TC), a kind of broad-spectrum antibiotics, had been widely used to treat bacterial infections in many fields during last century [1,2]. However, many undesirable adverse effects including chronic toxicity, hepatotoxicity, and impact on tooth development have been found gradually [3]. Nowadays, the pollution of TC in surface and ground water has been proved to be a serious environmental concern due to the improper use and the relatively high solubility of TC in water (~170 mg/100 g water) [4,5]. Therefore, the development on the effective removal of TC from the polluted water has become an urgent task. Until now, various materials including montmorillonite [6–8], carbon nanotube [9], and graphene oxide (GO) [10–12] have been reported as the adsorbents for TC. Among them, graphene oxide (GO) has attracted considerable attention owing to the plenty of oxygen functional groups, intercalating and ion exchange property [13,14], and the strong affinity of GO to molecules containing phenyl caused by the strong electrostatic attraction force and π–π interaction [15]. Many attempts have been made to fabricate GO-based adsorbents with different morphologies, such as sheet-like GO [16] and three-dimensional macroporous GO [17,18], to increase the amount of the active sites on GO adsorbents so as to obtain an improved adsorption performance. For example, Gao *et al.* [17] used a unidirectional freeze-drying method to prepare GO aerogels with continuous pore structure, which have an equilibrium adsorption capacity for Cu^{2+} in the aqueous solution as high as 19.1 mg g^{-1} and a fast adsorption rate. However, pure macroporous structured GO generally exhibits poor mechanical property. Meanwhile, the agglomeration of GO sheets during the fabrication process also leads to the loss of the adsorption capacity. A feasible way to solve the above mentioned problems is to make GO distribute homogeneously into a strong polymer matrix to form macroporous polymer/GO composites.

Pickering emulsion droplets can be used as good macropore templates [19]. Besides the common inorganic or polymeric particulate stabilizers, GO has also been proved to be able to act as the stabilizer for a Pickering emulsion since the GO sheets have the hydrophilic edges due to the oxygenated groups and the hydrophobic surface due to the graphene-like aromatic structure [20]. It is noted that the hydroxyl groups on the surface of the particulate stabilizers will enhance the interaction between the agglomerated Pickering emulsion droplets through the hydrogen

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bond interaction, leading to the formation of a self-stand monolith material with a matrix composed of the stabilizer particles [21–23]. It has been reported that abundant oxygenated groups including hydroxyl groups exist on the GO sheets [24]. However, there are few reports referring to prepare macroporous GO-based monolith from a Pickering emulsion system stabilized by GO sheets, taking advantage of the hydrogen bond interaction between the oxygenated groups on GO sheets.

Herein, we employed GO coated polystyrene microspheres (PS@GO) as the stabilizers to form an octane/water Pickering emulsion. During the evaporation process of water and octane, the Pickering emulsion droplets aggregated together, and combined with each other through the hydrogen bond interaction between the stabilizers. Finally, a three-dimensional macroporous PS/GO composite monolith was formed after all of the liquid components were evaporated. The macroporous PS/GO monolith showed an excellent adsorption ability for TC in aqueous solution with a maximum adsorption capacity of 197.8 mg g^{-1}. At the same time, the macroporous PS/GO composite monolith has an excellent mechanical strength, which can bear a load of 2500 times its own weight. This work provides a new way to prepare high-strength and high-efficiency macroporous GO-based monolith adsorbents for the pollutants such as organic dyes, antibiotics, and heavy metal ions.

2. Experimental

2.1. Materials

Analytical grade styrene (St) provided by Shanghai Chemical Reagents Co., Ltd. was purified by vacuum distillation before use. Analytical reagents including 2,2′-azobis(isobutyramidine) dihydrochloride (AIBA) (99%), phosphorus pentoxide (P_2O_5), sodium hydroxide (NaOH), potassium persulfate (KPS), octane, H_2SO_4 (98%), HCl (37%), $KMnO_4$, and H_2O_2 (30%) were all purchased from Shanghai Chemical Reagents Co., Ltd., and used as received. Polyvinylpyrrolidone (PVP) was purchased from Aladdin Reagents (Shanghai) Co., Ltd. Tetracycline hydrochloride (98%) was provided by J&K Scientific Ltd. Graphite flakes (100 mesh) were supplied by Beijing Jixing Sheng'an Industry & Trade Co., Ltd. Deionized water was used in all the experiments.

2.2. Preparation of macroporous PS/GO composite monolith

GO and PS microspheres were prepared by a modified Hummer's method and emulsion polymerization, respectively in our laboratory according to the literatures [25,26]. The detailed preparation processes were described in the Supporting information (Part I and II). The as-prepared GO was dispersed into 10 mL of water under ultrasonification at a concentration of 4 mg mL^{-1}. After the pH of the dispersion was adjusted to 2 with 1 mol L^{-1} HCl, PS microspheres were dispersed into the dispersion ultrasonically. The weight ratio of PS microspheres to GO was controlled to 1:2. Then, octane (5 mL) was added into the PS/GO dispersion to form a Pickering emulsion using a high-shear dispersion homogenizer (FJ200-SH, 15,000 rpm, 30 s). Afterwards, the emulsion was dried at 40 °C for 7 days to obtain the porous structured monolith. As a comparison, pure macroporous GO monolith was prepared according to the above same fabrication procedure without the addition of PS microspheres.

2.3. Adsorption ability of PS/GO composite monolith for TC

The adsorption kinetics of TC on PS/GO absorbent in aqueous solutions was investigated as follows: 10 mg of the sample adsorbent was dispersed into 50 mL of the aqueous solution of TC with a concentration of 29.3 mg L^{-1}. The suspension was shaken in a WHY-2 shaker (150 rpm) at 25 °C. 3 mL of the suspension was sampled at certain time intervals, and centrifuged to collect the supernatant. The UV–vis spectrum of the supernatant was recorded. The concentration of TC was determined from the absorption intensity at 357 nm. As a control, the adsorption ability of pure GO was measured under the same condition.

The adsorption capacity of PS/GO absorbent for TC in aqueous solution at different pH was also investigated. The pH of the suspension was adjusted to be 2, 4, 6, 8, and 10 using 1 mol L^{-1} HCl or 1 mol L^{-1} NaOH. 10 mg of the adsorbent and 50 mL of TC solution (29.3 mg L^{-1}) with different pH were mixed and shaken at 25 °C for 12 h to reach the adsorption equilibrium. Then 3 mL of the suspension was sampled and centrifuged to collect the supernatant. The UV–vis spectrum of the supernatant was recorded to measure the concentration of TC from the absorption intensity at 357 nm.

To obtain the adsorption isotherm of PS/GO monolith at pH 6, 50 mL of TC solution with a series of concentrations (16.4–132.7 mg L^{-1}) were adopted to the adsorption experiments. The equilibrium adsorption capacity for TC (q_e, mg g^{-1}) was calculated according to the following equation:

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

where C_0 (mg L^{-1}) is the initial concentration of TC solution. C_e (mg L^{-1}) is the TC concentration after the equilibrium adsorption of TC is reached. V (L) is the initial solution volume. m (g) is the weight of the adsorbent. When C_0 exceeded 64.6 mg L^{-1}, the obtained supernatant was diluted to triple volumes to guarantee the absorption intensity was in the range of the working curve.

2.4. Characterization

The morphologies of the samples were investigated by field-emission scanning electron microscopy (FESEM, JEOL JSM-6700F, 5 kV) and transmission electron microscopy (TEM, H-7650, 100 kV). The optical microscopy of the Pickering emulsion was observed by Leica DM 1000. X-ray photoelectron spectroscopy (XPS) was conducted on Thermo ESCALAB 250 using monochromatic Al $K\alpha$ radiation. The photos of the emulsions were taken by a digital camera. The zeta potentials of PS microspheres and GO in the aqueous solution at pH 2 were measured by dynamic light scattering analysis (DLS) on a Malvern Zetasizer NanoZS-2S90 instrument. The particle concentration in the sample solutions was 0.05 mg mL^{-1}. UV–vis spectra of the aqueous solution of TC and GO were obtained using a UV-2600. Thermo-gravimetric analysis (TGA) was operated on TGA Q5000IR in air at a heating rate of 10 °C min^{-1}. The density of the PS/GO composite monolith was also measured by weighing method, as expressed by the following equation:

$$\rho = \frac{m}{V} \quad (2)$$

where m (mg) and V (cm^3) are the weight and the volume of the sample.

3. Results and discussion

3.1. Preparation and characterization of macroporous PS/GO composite monolith

The fabrication process of a macroporous PS/GO composite monolith is illustrated in Scheme 1. First, PS microspheres were dispersed into the aqueous solution of GO to form the PS/GO composite particles, which can be used as the Pickering emulsion