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Effect of modifying agents on the preparation and properties of the new adsorbents from wheat straw

Xing Xu, Baoyu Gao *, Wenyi Wang, Qinyan Yue, Yu Wang, Shouqing Ni

School of Environmental Science and Engineering, Shandong University, Jinan 250100, PR China

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ABSTRACT

Three different types of new adsorbents modified from wheat straw were synthesized after the reaction between epichlorohydrin and triethylamine by using ethylenediamine (EDA), diethylenetriamine (DETA) and triethylenetetramine (TETA) as modifying agents. The performance of the modified wheat straws (MWS) was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and elemental analysis. Results showed that the optimal dosages for the three modifying agent (EDA, DETA and TETA) were 3, 4 and 3 ml. The optimum synthesis temperature for the three MWS was 80, 85 and 95 °C, respectively. The IR spectra of the three MWS were analogical, and nitrogen contents of the MWS were found to be consistent with their adsorption capacity. The pseudo-second-order equation generated the best agreement with the experimental data for adsorption systems. In addition, the adsorption process of the three MWS reached equilibrium at 10–15 min. MWS (EDA) demonstrated the largest phosphate capacity than the other MWS.

1. Introduction

Eutrophication is a serious problem of water pollution and is caused by the nitrogen, phosphorus and other excessive nutrients for algae use. In surface freshwater systems, phosphorus is usually the limiting factor of algae growth, because in normal freshwater systems, the content of phosphorus is usually limited in comparison with that of nitrogen. As a result, the increase of phosphorus in surface freshwater systems will lead to excessive algae growth. So phosphorus removal is of great significance for the algae bloom control.

Wheat straw (WS) is regarded as an abundant and biodegradable resource available for the preparation of adsorbents that can be used for the removal of nitrate and phosphate. The idea of converting WS into an adsorbent is based on the predominant contents of cellulose (32.1%), hemicellulose (29.2%) and lignin (16.4%) in WS (Orlando et al., 2002a,b). Cellulose, hemicelluloses and lignin structures have a large amount of easily accessible hydroxyl groups that can be used for preparation of various functional polymers (Kumar et al., 2009; Reddy and Yang, 2009).

The modification reactions for the preparation of an adsorbent from WS consist of polymerization (Zhu et al., 2005), chelating (Orlando et al., 2004) and crosslinking (Sarin and Pant, 2006; Conrad and Hansen, 2007), which are commonly applied to enhance the adsorption capacity by introducing functional groups to the WS. Some adsorbents prepared from other agricultural residue have shown an excellent adsorption capacity for various ions by introducing different functional groups, including sulphonyl, amido, carboxyl, amine and other chelating functional groups (Orlando et al., 2004; Conrad and Hansen, 2007; Gong et al., 2005; Robinson et al., 2002; Biswas et al., 2008).

Adsorbents prepared from agricultural residues are considered as a low cost adsorbent and have shown significant adsorption capacity for organic pollutants and dye (Chi and Chen, 2009; Saratale et al., 2009; Memon et al., 2008; Huang et al., 2009).

The main objective of this paper is to examine the most effective preparation method that produces an adsorbent for phosphate removal. In the previous work, amine groups were introduced into other agricultural residues after reaction with the epichlorohydrin and amine in the presence of catalyst and organic medium (Orlando et al., 2002a,b; Wang et al., 2007a,b). While it was difficult to choose a suitable catalyst for the modification reaction; the effect of catalyst was to improve the synthesis of intermediate which was obtained after the reaction between cellulose and epichlorohydrin, and to provide a weak-base (pH 8–11) reaction condition to facilitate the reaction between intermediate and amine (Orlando et al., 2002a,b; Navarro et al., 1996). Several weak-base catalysts have been considered for this reaction, and only pyridine has shown an excellent catalytic effect. However, a serious secondary pollution with large mounts of odoriferous wastewater was produced after using pyridine as catalyst in the preparation of the adsorbent, and thus, a further investigation will be carried out to address this problem.

* Corresponding author. Tel.: +86 531 88364832; fax: +86 531 88364513.
E-mail address: bygao@sdu.edu.cn (B. Gao).

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In this work, a catalyst is replaced with a modifying agent. Three types of adsorbents were prepared from WS after reaction with epichlorohydrin and triethylamine by using the three modifying agents as ethylenediamine (EDA), diethylenetriamine (DETA) and triethylenetetramine (TETA), respectively. Effects of synthesis temperatures and modifying agent dosages on the preparation of MWS were considered, with phosphate removal and zeta potential as measures of treatment efficiency. Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and elemental analysis were used for the characterization of the MWS. Three kinetic models were designed to describe MWS kinetic behavior.

2. Methods

2.1. Materials

WS, obtained from Liao Cheng, Shandong, China, was washed with water, dried at 60 °C for 6 h and sieved into particles ranging from 100 to 250 μm.

2.2. Preparation of MWS

Four grams of WS were reacted with 20 ml of epichlorohydrin and 20 ml of *N*,*N*-dimethylformamide in a 250 ml three-neck round bottom flask for 60 min (Orlando et al., 2002a,b, 2003, 2004); Batch volume (1–5 ml) of different modifying agents was added and the solution was reacted for 30 min, followed by adding 20 ml of 99% triethylamine (w/w) for graft reaction. Mixture was reacted for 120 min. The synthesis temperature was controlled at 20–100 °C.

The primary product was washed with 250 ml of distilled water to remove the residual chemicals first, then dried at 105 °C for 5 h and sieved to obtain particles of less than 250 μm. The final product was obtained after the second cycle of washing, drying and sieving and then used in all adsorption experiments.

The inter-reactive activities of triethylamine with cellulose are poor. To improve this reactivity, cellulose is reacted with crosslinking agent (epichlorohydrin) first, and produces the cellulose ether (Liu et al., 2008). Cellulose ether can be efficiently reacted with EDA after the ring opening of epoxide group in cellulose ether, and the other amido group in EDA was induced to react with triethylamine in an excess of epichlorohydrin.

2.3. Characterization of MWS

2.3.1. FTIR analysis and SEM analysis

IR spectra were recorded on Perkin–Elmer "Spectrum BX" spectrometer in 4000–400 cm^{-1} region. SEM of the sample was obtained by JEOL JSM-6480LV scanning electron microscope. The sample was coated with platinum before the SEM micrograph was obtained.

2.3.2. Nitrogen content and total exchange capacity (TEC mEq g^{-1})

The nitrogen content of MWS was measured by element analyzer (Elementar vario EL III, Germany). TEC was estimated from the nitrogen content and calculated by following equation (Orlando et al., 2002a,b; Wang et al., 2007a,b):

$$\mathrm{TEC}\ (\mathrm{mEq\ g^{-1}}) = \frac{\mathrm{N\%}}{1.4} \quad (1)$$

where TEC is the total exchange capacity (mEq g^{-1}); N% is the total nitrogen content; and 1.4 is the correction coefficient.

2.3.3. Zeta potential (mV)

The three kinds of adsorbents prepared from WS were used for the removal of anionic pollutant, so it was significant to determine the change of surface charge of MWS in comparison with WS. The zeta potential of MWS and WS were determined by electro-kinetic analyzer (JS94H Shanghai Zhongchen Digital Technical Apparatus Co., Ltd, China).

2.4. Batch adsorption

Phosphate solution with concentration of 50 mg (P) L^{-1} was prepared by solving 2.198 g KH_2PO_4 into 1000 ml of distilled water, and the solution was stocked in a 1000 ml volumetric flask.

To describe the adsorption kinetic curves of the different types of MWS, adsorption experiments were carried out by agitating 1 g of MWS with 500 ml of phosphate solutions (50 mg (P) L^{-1}), and at 20 ± 2 °C of temperature in a stirrer operating 120 rpm for 80 min. Samples (1 ml) were withdrawn at suitable time intervals and filtered to analyze for residual phosphate concentrations in solutions with an UV–visible spectrophotometer (model UV754GD, Shanghai) at an absorbance wavelength of 700 nm. The equilibrium concentration in solid phase q_e was given as:

$$q_e = \frac{(c_o - c_e)V}{m} \quad (2)$$

where q_e is the amount of phosphate sorption per gram MWS at equilibrium, c_o and c_e are the concentrations of phosphate at original and equilibrium, respectively. *V* is the volume of solution, and m is the amount of MWS (g).

3. Results and discussion

3.1. Effect of synthesis conditions on the preparation of MWS

The preparation of MWS was effected by the synthesis conditions followed as synthesis temperature and dosages of different modifying agents. Phosphate removal and zeta potential were used as the performance indicators to describe the effect of synthesis temperature and dosages of different modifying agents on the preparation of MWS.

3.1.1. Effect of synthesis temperature on the preparation of MWS

The dosages of the three modifying agents for the MWS were all designed as 2 ml in the preparation of the three MWS, and the effect of synthesis temperatures (20–100 °C) on the preparation of MWS is shown in Fig. 1.

The result shown in Fig. 1 indicates that less modification is carried out when the temperature is lower than 40 °C, and the

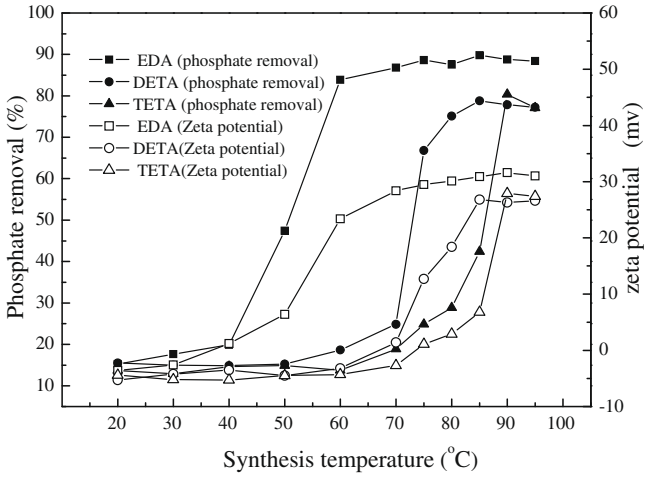

Fig. 1. Effect of synthesis temperature on the preparation of MWS.