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Adsorption isotherms, kinetics and thermodynamics of nitrate and phosphate in binary systems on a novel adsorbent derived from corn stalks

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ABSTRACT

Novel adsorbents from raw corn stalks (RCS) were synthesised after cellulose isolation followed by modification with epichlorohydrin, *N,N*-dimethylformamide, pyridine and diethylamine. The MCCS (modified cellulose from corn stalks) products were characterised by thermogravimetric analysis, elemental analysis, scanning electron microscopy–energy dispersive spectrometry (SEM-EDS) and Fourier transform infrared spectroscopy (FT-IR); moreover, the adsorption characteristics of nitrate and phosphate on MCCS were investigated in binary systems using batch adsorption procedures. The mass loss of RCS and MCCS may be divided into three stages and the modification reaction increased the stability of samples. The surface of MCCS was rougher than that of RCS and amine groups were successfully loaded onto MCCS, as shown by elemental analysis results and FT-IR spectra. The pseudo-second order kinetics equation and Langmuir isotherm could well describe the adsorption process, and the maximum adsorption capacities (298 K) of nitrate and phosphate on MCCS as calculated from the Langmuir isotherm were 13.6054 and 22.8833 mg/g, respectively. The obtained thermodynamic parameters indicated the spontaneous and exothermic nature of adsorption.

1. Introduction

With the developments in the economy and society, various human activities, such as agricultural, industrial and household, have increased wastewater with high contents of nitrate and phosphate (Rodrigues and Pinto da Silva, 2010; Bhatnagar and Sillanpaa, 2011). At present, nitrate and phosphate in wastewater are the focus of numerous investigations of contaminants, because their increasing concentration may cause eutrophication in aquatic environments. Treatment methods for wastewater contaminated with nitrates and phosphates include membrane filtration (Zularisam et al., 2006), ion exchange (Patrick et al., 2012) and biofiltration (Martin et al., 2009). Adsorption is found to be one of the most appropriate technologies owing to its low cost, ease of handling and acceptable efficiency (Gil et al., 2011; Ngah et al., 2011).

Adsorption refers to the interaction of an adsorbate and an adsorbent between the gas, solid and liquid interfaces and involves the adsorption mechanisms of Van der Waals force, complexation, hydrogen bond, ion exchange and co-precipitation (Fletcher et al., 2006; Ahmet et al., 2007). Currently, a series of novel adsorbents, including adsorbents obtained from agricultural wastes of stalk, are synthesised yearly. Stalk is an important natural biomass resource; statistically, approximately 0.7 billion tons of crop stalks are produced annually in China, with a reutilisation rate lower than 50% (Norse, 2005). Studies have showed that various kinds of stalks (corn stalk, rice stalk, wheat stalk and sorghum stalk) have been used to remove contaminants from aqueous solutions with acceptable treatment efficiencies (Robinson et al., 2002; Haque et al., 2007; Cao et al., 2011). The products of stalks after chemical modification may improve the composition structure or introduce functional groups onto the stalk surface, further benefitting the enhancement of adsorption capacity (Husseien et al., 2009).

Corn stalks (CS) are the most abundant of agricultural stalks. CS are rich in cellulose, the structure of which contains a large amount of hydroxyl groups (functional groups for pollutants removal) (Lu and Hsieh, 2012). Previous studies have shown the adsorption behaviour of nitrates, phosphates or heavy metals on CS in a single system (Chen et al., 2011a); in fact, the adsorption capacity on anions can be markedly enhanced based on adsorbent modification. This investigation aims to develop a novel adsorbent from raw CS (RCS), which have been scarcely studied. In this paper, modified cellulose from CS (MCCS) was prepared from RCS after reacting with epichlorohydrin and triethylamine in the presence of *N,N*-dimethylformamide (DMF) using

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diethylenetriamine (DETA) as a modifying agent. The reactions in the preparation of the anion adsorbent (MCCS) consisted of polymerisation, chelating and crosslinking, which may increase adsorption efficiency by introducing special functional groups to RCS (Xu et al., 2016). MCCS, together with RCS, were characterised by thermogravimetric analysis (TGA), elemental analysis, scanning electron microscopy with energy dispersive spectrometry (SEM-EDS) and Fourier transform infrared spectroscopy (FT-IR); moreover, the adsorption isotherms, adsorption kinetics and thermodynamic studies were investigated in binary systems. The achievements were of considerable importance for revealing the mechanism of nitrate and phosphate adsorption on MCCS in the future.

2. Materials and methods

2.1. Materials and chemicals

RCS samples were obtained from Xi'an, Shaanxi Province in northwestern China. After being washed with purified water thrice, RCS was smashed into fragments with the average length of 5 mm and dried at 60 °C to constant weight for future use. All reagents used were of analytical grade and provided by Kermel Chemical Reagent Co., Ltd.

2.2. Experimental methods

2.2.1. Isolation of cellulose

The isolation process of cellulose from RCS was as follows (Liu et al., 2007): first, 10 g of RCS was mixed with 150 mL of 5% NaOH solution at 55 °C for 1.5 h, filtrated and washed with purified water thrice and dried at 60 °C for 6 h. Secondly, the dried residues were treated with 35 mL of $NaClO_2$ solution (9.5 g/L) and 100 mL of acetic acid (10%) at 75 °C for 1 h. Third, the filtered product was washed with acetone and purified water successively and the samples were dried at 60 °C for 6 h. Cellulose from RCS was obtained successfully.

2.2.2. Modification of cellulose

Cellulose modification was conducted in a 500 mL three-neck round bottom flask that contained 2 g of cellulose samples, 40 mL of epichlorohydrin and 120 mL of DMF and stirred continuously at 100 °C for 1 h. Then, 16 mL of pyridine was added into the flask and stirred at 100 °C for 1 h; afterwards, 30 mL of diethylamine was mixed into the flask and the contents were stirred at 100 °C for 2 h. After the reaction, the filtrated samples were washed with NaOH solution (0.1 mol/L), HCl (0.1 mol/L), ethanol (50%) and purified water successively and dried at 60 °C for 12 h. The obtained product, MCCS, was used as the adsorbent in the following research.

The synthesis reaction of MCCS can be found in our previous work (Fan et al., 2015). The preparation of MCCS involved the chain reactions between the cellulose/hemicellulose chain and side chains of different grafting chemical reagents. In general, glycosyl was first typically reacted with a crosslinking agent (epichlorohydrin) to produce hydroxy glycosyl ether; then, the organic medium (DMF) was used to enhance the susceptibility of the epoxide ring in epichlorohydrin. Thus, hydroxy glycosyl ether can react effectively with diethylamine in the excessive epichlorohydrin environment.

2.3. Characterization of RCS and MCCS

To investigate the pyrolysis behaviour of RCS and MCCS, the TGA curves were recorded using a thermogravimetric analyser (STA409PC, Netzsch, Germany) at the heating rate of 10 °C/min from 30 °C to 600 °C in a nitrogen atmosphere. An elemental analyser (Vario EL III, Elemeraor, Germany) was used for the determination of N, C and H. The surface morphology and elemental composition of RCS and MCCS were revealed using SEM (S4800, Hitachi, Japan) equipped with an energy dispersive X-ray spectroscope (EX350, Horiba, Japan). The samples were not covered with the golden film to better preserve their surface nature, and a conductive adhesive was used to increase their electroconductivity. The FT-IR spectra were obtained in the range of 4000–400 cm^{-1} on a spectrometer (Vector22, Bruker, Germany) by the KBr pellet method at room temperature.

2.4. Adsorption experiments

Standard nitrate and phosphate stock solution was prepared by dissolving an appropriate amount of sodium nitrate ($NaNO_3$) and potassium dihydrogen phosphate (KH_2PO_4) into water. The nitrate and phosphate solution was obtained by stepwise dilution of the stock solutions with purified water. The batch adsorption procedures were conducted to reveal the adsorption isotherms by adding 0.1 g of MCCS into a series of flasks with the nitrate and phosphate solution (0.5–100 mg/L) for 6 h at initial pH values (6.80 ± 0.10) and different temperature (288, 298 and 308 K). The adsorption kinetics were investigated by mixing 0.1 g of MCCS with 50 mL of nitrate solution (100 mg/L) and 50 mL of phosphate solution (100 mg/L) in each flask at initial pH values (6.80 ± 0.10) and temperature of 288, 298 and 308 K in an orbital shaker at 120 rpm. The investigation was conducted in triplicate. At certain time intervals, MCCS was filtered off and the concentrations of nitrate (210 nm) and phosphate (700 nm) were measured using a UV–visible spectrophotometer (UV2600, Unico, USA).

3. Results and discussion

3.1. Characterization of RCS and MCCS

3.1.1. TGA

TGA is useful in determining the thermal stability and decomposition behaviour of experimental samples (Maria et al., 2011). The TGA curves of RCS and MCCS are shown in Fig. 1. In general, the mass loss of TG curves could be divided into three stages. The first stages for RCS (35 °C to 200 °C) and MCCS (35 °C to 250 °C) may be due to the evaporation of water molecules, corresponding to mass losses of 9.04% and 13.20%, respectively. The second stage, which occurred from 200 °C to 450 °C for RCS and 250 °C to 450 °C for MCCS, was significant for mass loss during the pyrolysis process and 64.82% (RCS) and 55.86% (MCCS) of total mass losses were observed, thereby revealing that the decomposition of cellulose, hemi-cellulose or lignin mainly occurred in these temperature ranges. Mass loss in the third stage (450 °C to 600 °C) was minimal, indicating the presence of stable oxides at high temperature. The significant decomposition temperatures of RCS and MCCS started from 200 °C and 250 °C, respectively, confirming that the modification reaction may increase the stability of the sample composition.

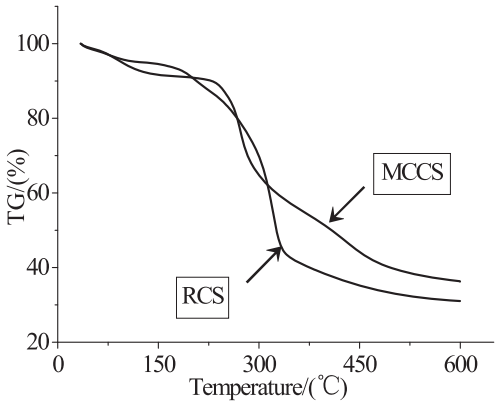

Fig. 1. TGA curves of RCS and MCCS samples.