Carbohydrate Polymers 79 (2010) 1140–1149

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode

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ARTICLE INFO

Article history:
Received 15 September 2009
Received in revised form 19 October 2009
Accepted 22 October 2009
Available online 25 October 2009

Keywords:
TG analysis
FTIR analysis
Modified wheat straw
Copper ion
Methylene blue
Adsorption

ABSTRACT

The citric acid modified wheat straw (MWS) was characterized and the adsorption properties of copper ion and methylene blue (MB) onto MWS were investigated in single adsorbate system by batch techniques. The mass loss during thermo-gravimetric analysis can be divided into steps related to moisture, cellulose and lignin. There were carbonyl group, hydroxyl group, etc. on surface of adsorbent from FTIR. Kinetic studies indicated that Cu^{2+} and MB adsorption followed the pseudo-second-order model. The adsorption may be controlled by external mass transfer followed by intra-particle diffusion mass transfer. The adsorption equilibrium data were fitted well by both the Freundlich and Langmuir models. The maximal equilibrium quantity of Cu^{2+} and MB from Langmuir model on MWS was 39.17 and 396.9 mg g^{-1} at 293 K, respectively. The thermodynamics parameters of adsorption systems indicated spontaneous and endothermic process.

1. Introduction

There are many billion kilograms of agricultural waste products in China. These materials are considered a significant waste disposal problem. They are often used as foodstuff, energy fuel, or compost, etc. But many are treated as waste. So it is promising to develop the other ways in order to utilize these by-products. Agricultural waste materials are economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable, low in cost and more efficient, and are seem to be viable option for heavy metal and dye remediation (Crini, 2006; Gupta & Ali, 2008; Gupta & Suhas, 2009; Khan, Li, & Huang, 2008; Sud, Mahajan, & Kaur, 2008; Wan Ngah & Hanafiah, 2008). Some of these by-products such as rice husk, wheat straw, cereal chaff, wheat husk, peanut hull, soybean hulls, hazelnut shells, sugar beet pulp, e-oiled soya, carbon from wood and fallen leaf, etc. have been used to remove metal ions or dyes from solution (Ahluwalia & Goyal, 2007; Cimino, Passerini, & Toscano, 2000; Dang, Doan, Dang-Vuc, & Lohi, 2009; Gupta, Jain, & Varshney, 2007; Gupta, Mittal, Krishnan, & Mittal, 2006; Han, Ding, et al., 2008; Han, Han, et al., 2008; Han, Wang, et al., 2006, 2009; Han, Zhang, Zou, Shi, & Liu, 2005; Han, Zhang, et al., 2006; Han et al., 2007; Krishnani, Meng, Christodoulatos, & Boddu, 2008; Sud et al., 2008; Teixeira Tarley & Zezzi Arruda, 2004; Tsang et al., 2007; Wu et al., 2009). There are several advantages over commercial resins and activated carbon in that they are less expensive, biodegradable and come from renewable resource.

However, the application of untreated plant wastes as adsorbents can also bring several problems such as lower adsorption capacity, higher chemical oxygen demand (COD) and biological chemical demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compounds contained in the plant materials (Wan Ngah & Hanafiah, 2008). Therefore, plant wastes need to be modified or treated before being applied for the decontamination of heavy metals and dyes. Furthermore, modification of agricultural by-products can be carried out to achieve adequate structural durability, enhance their natural ion exchange capability and add value to the by-product (O'Connell, Birkinshaw, & O'Dwyer, 2008; Vaughan, Seo, & Marshall, 2001).

Pretreatment methods using different kinds of modifying agents such as base solutions (sodium hydroxide) mineral and organic acid solutions (hydrochloric acid, phosphoric acid, tartaric acid, citric acid, thioglycollic acid), organic compounds (ethylenediamine, formaldehyde), etc. for the purpose of removing soluble organic compounds, eliminating color of the aqueous solutions and increasing efficiency of metal and dye adsorption have been performed by many researchers (Gong, Sun, et al., 2008; Gong, Zhong, et al., 2008; Gong, Zhu, et al., 2008; Gurgel, Freitas, & Gil, 2008; Marshall, Wartelle, Boler, Johns, & Toles, 1999; Ong, Lee, & Zainal, 2007; Šæiban, Klašnja, & Škrbiæ, 2008; Vaughan et al., 2001; Wong, Lee, Low, & Haron, 2003). But these studies only discuss the adsorptive behavior of metal ions or dyes.

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0144-8617/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2009.10.054

Wheat straw is abundant and inexpensive in north region of China. It is often used as a waste or feedstuff. Wheat straw has been used as adsorbent to remove heavy metal ions (Dang et al., 2009; Doan, Lohi, Dang, & Dang-Vu, 2008) and dyes from solution (Robinson, Chandran, & Nigam, 2002). Thermo-chemical esterifying citric acid on wheat straw can enhance wheat straw ability of cationic dye adsorption. But there is few study on the research which simultaneously discuss the behavior of metal and dye adsorption onto agricultural by-product, except other materials used as adsorbents (Aksu & Isoglu, 2007; Wang & Ariyanto, 2007; Wu et al., 2009).

The objective of this study was to modify wheat straw with citric acid to enhance the adsorption capacity of the by-product for selected copper ions and methylene blue (MB). The characterization of natural wheat straw (NWS) and modified wheat straw (MWS) was analyzed by FTIR, TGA–DSC (thermo-gravimetric analysis and differential scanning calorimetry) and scanning electron micrograph (SEM) method.

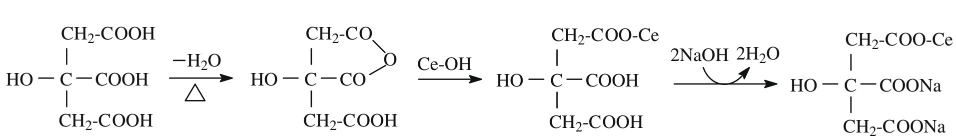
2. Materials and methods

2.1. Preparation of MWS

The wheat straw used in the present investigation was obtained from local countryside. The collected materials were washed with distilled water for several times to remove all the dirt particles. The washed material was dried in an oven at 373 K for a period of 24 h. Then dried straw segment was milled and sieved to retain the 20–40 mesh fractions for chemical modification.

MWS was prepared according to the modified method (Vaughan et al., 2001). Ground wheat straw was mixed with 0.6 mol l^{-1} citric acid (CA) at the ratio of 1:12 (straw/acid, w/v) and stirred for 30 min at 20 °C. The acid straw slurries were placed in a stainless steel tray and dried at 50 °C in a forced air oven for 24 h. Then the thermo-chemical esterification between acid and straw was proceeded by raising the oven temperature to 120 °C for 90 min. After cooling, the esterified wheat straw was washed with distilled water until the liquid did not turn turbidity when 0.1 mol l^{-1} lead (II) nitrate was dropped in. After filtration, MWS was suspended in 0.1 mol l^{-1} NaOH solution at suitable ratio and stirred for 60 min, followed by washing thoroughly with distilled water to remove residual alkali, next dried at 50 °C for 24 h and preserved in a desiccator for use.

The chemical modification of wheat straw can be schematically expressed by equation (Gong, Zhong, et al., 2008):



Note: Ce-OH—Natural wheat straw

2.2. Preparation of MB and copper ion solution

The MB and Cu^{2+} stock solutions were prepared by dissolving accurately weighted dyes and $CuCl_2$ in distilled water to the concentration of 1000 mg l^{-1} and 500 mg l^{-1}, respectively. The experimental solutions were obtained by diluting the dye or Cu^{2+} stock solutions in accurate proportions to different initial concentrations. As experiment result proved that the optional value of solution pH for Cu^{2+} and MB is 5 and 4–10, respectively, the initial pH of the working solution was adjusted by addition of 1 mol l^{-1} HCl or NaOH solution to near 5.

2.3. Experimental methods and measurements

The adsorption tests were performed by batch technique in single system at 293, 303, 313 K, respectively. For kinetic and isothermal studies, a series of 125 ml flask were used and each flask was filled with wheat straw at mass loadings 2 g l^{-1} for Cu^{2+} solution and 1 g l^{-1} for MB solution at different initial concentrations (10 ml), respectively. The conical flasks were then agitated in an orbital shaker at 100 rpm and liquid samples were taken out at a given time interval for Cu^{2+} or MB analyses after centrifugation.

Cu^{2+} concentration was measured using atomic absorption spectrometry at 234.8 nm (AAanalyst300, Perkin-Elmer). MB concentration is determined using a UV spectrophotometer (Shimadzu Brand UV-3000) by monitoring the absorbance changes at a wavelength of maximum absorbance (668 nm).

The data obtained in batch mode studies were used to calculate the equilibrium metal adsorptive quantity. It was calculated for each sample of Cu^{2+} or MB by using the following expression:

$$q_e = \frac{V(c_0 - c_e)}{1000m} \tag{1}$$

where q_e is the equilibrium uptake value (the amount of Cu^{2+} or MB adsorbed onto per unit mass of NWS) in mg g^{-1}, V is the sample volume in ml, c_0 is the initial Cu^{2+} or MB concentration in mg l^{-1}, c_e is the equilibrium adsorbent concentration in mg l^{-1}, and m is the dry weight of MWS in g.

2.4. Wheat straw characterization

The thermal behavior of NWS was obtained by using a thermo-gravimetric analyzer (STA 409 PC, German). About 10 mg of NWS were heated up to 600 °C in oxidant atmosphere at 10 °C min^{-1} temperature rate.

Photomicrography of the exterior surface of NWS and MWS was obtained by SEM (JEOL 6335F-SEM, Japan).

The functional groups present in the wheat straw were characterized by a Fourier transform infrared spectrometer (PE-1710, USA), using potassium bromide discs to prepare the NWS and MWS samples. The spectral range varied from 4000 to 400 cm^{-1}.

3. Results and discussion

3.1. Characterization of NWS and MWS

3.1.1. The curve of TG about NWS

Like all vegetable biomass, NWS are composed of cellulose, hemi-cellulose and lignin. Fig. 1 was shown the curve of TG and DSC about NWS.

The overall mass loss during thermo-gravimetric analyses can be divided into steps related to moisture, hemi-cellulose, cellulose