



## Removal of cadmium(II) from aqueous solution by corn stalk graft copolymers

Liuchun Zheng<sup>a,b</sup>, Zhi Dang<sup>a,b,c,\*</sup>, Chaofei Zhu<sup>a,b</sup>, Xiaoyun Yi<sup>a,b</sup>, Hui Zhang<sup>a,d</sup>, Congqiang Liu<sup>e</sup>

<sup>a</sup> College of Environmental Science and Engineering, South China University of Technology, Guangzhou 510006, PR China

<sup>b</sup> The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, Guangzhou 510006, PR China

<sup>c</sup> State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, PR China

<sup>d</sup> School of Environmental Science and Engineering, Guilin University of Technology, Guilin 541004, PR China

<sup>e</sup> State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Science, Guiyang 550002, PR China

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### ABSTRACT

Corn stalk was modified using graft copolymerization to produce adsorbent (AGCS), which was characterized by elemental analysis, fourier transform infrared, X-ray diffraction, solid-state CP/MAS <sup>13</sup>C NMR spectra, thermogravimetric analysis and differential scanning calorimeter. AGCS, having cyano group (–CN) after grafted successfully, exhibits more high adsorption potential for Cd(II) than unmodified forms. The efficiency of AGCS for removal of cadmium ions was evaluated. Factors affecting Cd(II) adsorption such as pH value and adsorbent dosage were investigated. More than 90% removal was achieved at pH 3.0–7.0 and the adsorption increased from 16.0% to 99.2% with increase of adsorbent dose. In addition, two isotherm models, namely, Langmuir and Freundlich were also analyzed to determine the best fit equation for adsorption of Cd(II) on AGCS.

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### 1. Introduction

Cadmium pollution in aqueous solution is a result of human activities, such as metalliferous mining, metallurgical industries, waste disposal, electronics and metal finishing industry (ÓConnell et al., 2008). Cadmium ions are not biodegradable and can be accumulated easily in living tissue, thus can be readily adsorbed into the human body throughout the food chain (Mohan and Sreelakshmi, 2008). Exceeding the micronutrient level of human body, cadmium ions affect the enzyme activity because of replacing zinc(II) ions in metallo-enzymes (Gary et al., 2008), and cause lung fibrosis, dyspnea, weight loss (Sud et al., 2008), even disfunction of the kidney (Volesky and Holan, 1995). Therefore, cadmium must be removed before discharge.

Adsorption is found to be effective for the removal of heavy metals from aqueous solution (Escudero et al., 2008) and has been widely studied over the last few decades (Chen and Wu, 2000). Activated carbon is the most widely used adsorbent. But the high cost and its loss during the regeneration restrict its application (Sud et al., 2008). Consequently, more and more attentions have been focused on agricultural waste as low-cost adsorbents which have metal-binding capacities. These agricultural wastes are avail-

able from many materials such as sugarcane bagasse (Gary et al., 2008), grape stalk (Escudero et al., 2008), sunflower stalk (Hashem, 2006), corncob (Leyva-Ramos et al., 2005), banana stalk (Shibi and Anirudhan, 2002) and saw dust (Gaey et al., 2000).

Corn stalk is also an abundant agricultural waste and usually has a high volume, underutilized and high levels of cellulose (Park et al., 2006). Cellulose is a large, linear-chain polymer with huge numbers of hydroxyl groups, which have an affinity for cadmium. But the hydroxyl groups stick out from the chain and form intermolecular hydrogen bonds (ÓConnell et al., 2008), these lead to the low adsorption capacities of raw corn stalk. Modification can be carried out to destroyed the hydrogen bonds and achieve efficient adsorption capacity. ÓConnell et al. (2008) have recently noted that two main approaches can be used to produce heavy metal adsorbents. One is a direct modification of cellulose. Some chelating or binding functional groups can be attached to hydrogen groups of cellulose through a variety of chemistries. Many researches focus on direct modification for many agricultural wastes (Bulut and Tez, 2007; Ho and Ofomaja, 2006; Low et al., 2000; Leyva-Ramos et al., 2005; Kumar and Bandyopadhyay, 2006) and our research for corn stalk has been done (Zheng et al., 2010). Another powerful modification is graft copolymerization, side chain grafts with functional groups are covalently attached to a main chain of a polymer backbone to form branched copolymer. Graft copolymerization is successfully used in some agricultural wastes modification recently (Shibi and Anirudhan, 2002; Hashem, 2006; Abdel-Aal et al., 2006). There has little research work in corn stalk, though is a huge biomass of agricultural wastes in the world.

\* Corresponding author. Address: College of Environmental Science and Engineering, South China University of Technology, Guangzhou Higher Education Mega Center, Guangzhou 510006, PR China. Tel.: +86 20 39380522; fax: +86 20 39380569.

E-mail address: [chzdang@scut.edu.cn](mailto:chzdang@scut.edu.cn) (Z. Dang).

In the present research, graft copolymerization was used to modify corn stalk. Chemical initiation is a relatively cheap, little homopolymer and easy application technique (ÓConnell et al., 2008), and potassium permanganate (KMnO<sub>4</sub>)/sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) system was adopted as a redox initiator in copolymerization. Acrylonitrile (AN) as monomer and *N,N'*-methylenebisacrylamide (MBA) as cross linker were added in the reaction process. The radical formation on the monomer results in homopolymer of monomer when the radical formation for initiation reaction may occur on the monomer (ÓConnell et al., 2008), thus *N,N*-dimethylformamide (DMF) was used to abstract grafted corn stalk in order to remove the AN homopolymer. The final product was determined by elemental analysis, Fourier transform infrared (FTIR), X-ray diffraction (XRD), solid-state CP/MAS <sup>13</sup>C NMR spectra, thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC). The adsorbent for removal of cadmium ions was tested in a batch adsorption experiment.

## 2. Methods

### 2.1. Materials and chemicals

Raw corn stalk (RCS) was obtained from a farm in Guangzhou city, China. After removing the leaves and washing with fresh water, the materials were cut into granules and 0.45 mm sizes were selected using sieves, then washed three times with deionised water and dried in an oven at 50 °C until constant weight for further pretreatment.

All chemicals and reagents used were of analytical grade and obtained from Chemical Reagent Co. Ltd. (Guangzhou, China). Cadmium (II) stock solution was prepared from cadmium chloride in deionised water. All working solutions were prepared by diluting the stock solutions with deionised water. Diluted HCl and NaOH solution was used for pH adjustment. An orbital shake was used for adsorption experiments. The concentration of cadmium (II) was determined by inductively coupled plasma optical emission spectrophotometry (ICP-OPTIMA 5000).

### 2.2. Modification

Modification was conducted in a 500 ml four-neck flask. Dried corn stalk (3 g) was immersed in 300 ml of deionised water at 40 °C, purified N<sub>2</sub> (99.999%) was passed through the vessel for 15 min and then KMnO<sub>4</sub> (1.0 g) as initiator was added to the flask to stirred for 60 min. AN (10.0 ml) as monomer, MBA (0.03 g) as cross linker and H<sub>2</sub>SO<sub>4</sub> (0.10 ml) as catalyst were added, and stirred continuously for 60 min reaction. After the copolymerization, the modified product was filtered, washed with ethanol (95%) and plenty of deionised water, and dried to a constant mass. The corn stalk grafted acrylonitrile copolymer (AGCS) was extracted using DMF in a soxhlet for 48 h in order to remove the AN homopolymer. The product was successively washed with ethanol (95%) and deionised water, then air-dried. Grafting efficiency of AGCS was determined and was found to be about 42.3%.

### 2.3. Characterization

Total N of RCS and AGCS were analyzed using an element analyzer (Element vario EL III, Germany). The total exchange capacity (TEC) was based on the nitrogen content incorporated into the final products (Orlando et al., 2002). TEC is calculated using the following equation (Laszlo, 1996):

$$\text{TEC} = \frac{N\%}{1.4} \quad (1)$$

where TEC is the total exchange capacity (mEq g<sup>-1</sup>) of RCS and AGCS; N% is the total nitrogen of RCS and AGCS, and 1.4 is a correction coefficient.

The chemical structures of RCS and AGCS were characterized by a Fourier transform infrared (FTIR) spectrophotometer and solid-state CP/MAS <sup>13</sup>C NMR spectroscopes. FTIR spectra were obtained on a FTIR spectrophotometer using KBr discs to prepare the samples. The solid-state CP/MAS <sup>13</sup>C NMR spectra were recorded on Bruker AVANCE 400 spectrometer at the frequency of 100 MHz with 4 mm MAS BBO probe. Acquisition time was 0.034 s. The delay time was 3 s and the proton 90° pulse time was 6 us. Each spectrum was obtained with an accumulation of 4070 scans.

The crystallinity of RCS and AGCS was characterized using X-ray diffraction (XRD) (D/max-III A, Rigaku). The sample was exposed to X-rays with the 2θ angle varying between 4 and 60 °C. Thermal stability of RCS and AGCS was performed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a simultaneous thermal analyzer (STA 449C, NETZSCH). The sample weigh was about 3 mg, and the scans were run from 90 to 500 °C at a rate of 10 °C/min under nitrogen flow.

### 2.4. Batch adsorption experiments

All the adsorption experiments were performed at 120 rpm on an orbital shaker with 0.5 g of adsorbents in conical flasks containing 50 ml of Cd (II) solution at 293 K, respectively. In the adsorption isotherm experiments, 0.5 g of adsorbent was added in 50 ml of Cd (II) solution at various concentrations at 293 K.

The measured heavy metal concentration was used to calculate the equilibrium metal uptake  $q_e$  (mg g<sup>-1</sup>) of the adsorbent using the following mass balance equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

The percentage of heavy metal adsorbed was calculated by the following equation:

$$(\% \text{ of adsorbed}) = \frac{100(C_0 - C_e)}{C_0} \quad (3)$$

where C<sub>0</sub> and C<sub>e</sub> are the initial and equilibrium concentrations.

## 3. Results and discussion

### 3.1. Modification mechanism

The AGCS was obtained through the polymerization of AN and RCS (support). In initiator reaction, cellulose of RCS reacted with the initiator (KMnO<sub>4</sub>), the free radical sites formed at C-2 or C-3 in cellulose structure (Fig 1 a). The valences of Mn ions had taken place in a series of changes: Mn<sup>7+</sup>, Mn<sup>4+</sup>, Mn<sup>3+</sup> and Mn<sup>2+</sup>. -OH groups of cellulose could be oxidized to aldehyde groups firstly. But these groups were prone to rearrange and formed enol structure, which further reacted with Mn<sup>4+</sup> or Mn<sup>3+</sup> to form the free radical sites, and then initiated the graft copolymerization reaction when the monomer (AN) was added. The monomer was induced by the free radical sites of cellulose and the covalent bonds between cellulose and monomer were formed to create a chain propagation reaction until termination occurring. Since MBA as cross linker was presented in reaction, the AGCS comprised a dimensional cross linked structure (Fig 1b).

### 3.2. Adsorbent characterization

#### 3.2.1. Elemental analysis

The nitrogen content (N%) of RCS and AGCS were 1.11% and 4.02%. According to Eq. (1), the total exchange capacity (TEC) of RCS and AGCS were 0.79 mEq g<sup>-1</sup> and 2.97 mEq g<sup>-1</sup>, respectively.

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