

Preparation of cellulose derived from corn stalk and its application for cadmium ion adsorption from aqueous solution

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ABSTRACT

Cellulose was isolated from corn stalk and modified by graft copolymerization to produce an absorbent material (AGCS-cell), which was characterized by scanning electron microscope and energy disperse spectroscopy (SEM-EDS), X-ray diffraction (XRD) and solid-state CP/MAS ¹³C NMR. The results showed that AGCS-cell had better adsorption potential for cadmium ion than unmodified cellulose because of the addition of functional groups (—CN and —OH groups) and the lower crystallinity. The Langmuir isotherms gave the best fit to the data and gave an adsorption capacity was 21.37 mg g⁻¹, which was close to unpurified cellulose (AGCS) and reflected the feasibility of using AGCS-cell as an adsorbent to remove cadmium ions.

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1. Introduction

Cadmium is well known as one of the most hazardous heavy metals and has resulted in serious water contamination. In 2008, worldwide primary production of cadmium was 19,600 tons (Tolcin, 2008) and some cadmium ions are released into the environment affecting ecological life (Hall, Scott, & Killen, 1998). Cadmium toxicity has been disclosed as early as 1955 in Fuchu, Toyama prefecture, Japan as Itai-itai disease, which is a bone disease with fractures and badly pain (Nordberg, 2009). Shangba village, locates on downstream of the Guangdong Dabaoshan mine in China, is nationally known for a high mortality rate because of esophageal cancers and liver cancer (Zhuang, McBride, Xia, Li, & Li, 2009), which has been caused mostly by cadmium contamination of acid mine drainage (AMD). Cadmium has been considered one of the most important pollutants by the EEC countries (Barbur, 1983) and by the USEPA (Vimala & Das, 2011). The permissible limits of cadmium concentration in drinking water by WHO and China are 0.003 and 0.005 mg l⁻¹, respectively.

Hence, it is important to remove cadmium ions from aqueous solution.

Recently, adsorption has been shown to be an effective process for the removal of heavy metals from aqueous solution. The main advantage of this technique is its good selectivity of various adsorbents (Crini, 2005). Consequently, many studies aimed at developing useful adsorbents, and agricultural wastes are receiving more and more attention because of their biodegradable, renewable, biocompatible and nontoxic nature. Corn stalk is an agricultural waste principally composed of cellulose, hemicellulose and lignin (Park, Yun, & Park, 2006). These biopolymers have abundant and specific functional group such as hydroxyl (—OH) groups (Liu, Sun, & Ye, 2006), which have affinities for heavy metal ions. In cellulose hydroxyl groups are involved in intermolecular hydrogen bonds (O'Connell, Birkinshaw, & O'Dwyer, 2008), thus leading to low adsorption capacities. Chemical modification is carried out to achieve efficient adsorption capacity for heavy metal ions (Kamel, Hassan, & El-Sakahawy, 2006). Because more active binding sites are provided, better ion-exchange properties are obtained, and new functional groups are formed through chemical modification (Wan Ngah & Hananfiah, 2008). So far, two main chemical approaches can be used to produce heavy metal adsorbents. One is a direct modification of cellulose (surface modification), where useful functional groups can be attached to hydroxyl groups of cellulose through a variety of chemistries (O'Connell et al., 2008). Many studies have focused on direct modification of agricultural wastes such as

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corn cob (Leyva-Ramos, Bernal-Jacome, & Acosta-Rodriguez, 2005), coconut copra meal (Ho & Ofomaja, 2006) and corn stalk (Zheng, Dang, Yi, & Zhang, 2010). The other is graft copolymerization, where side chains with functional groups are covalently attached to the main chain of the polymer backbone to form a branched copolymer (O'Connell et al., 2008). Graft copolymerization is successfully used in some agricultural wastes modification, e.g. banana stalk (Shibi & Anirudhan, 2002) and sunflower stalk (Hashem, 2006). In our previous work, we suggested that the cellulose of corn stalk modified by graft polymerization played an important role in cadmium adsorption (Zheng, Dang, Zhu, et al., 2010). But cellulose only accounts for 45.2% to the dry material in corn stalks, and other components were also modified by the grafting procedure, which implied that the adsorption capacity of corn stalk copolymers was total adsorption capacities for all constituents. It is necessary to provide more evidences about cellulose effects and test its adsorption ability in further. Meanwhile, cellulose is produced about 10^{11} tons for annual world biosynthesis (Sun, Sun, Zhao, & Sun, 2004), and had adsorption potential for heavy metals if it can be efficiently isolated. Recently cellulose has been successfully isolated from ryegrass leaves (Liu, Xu, et al., 2006), sugarcane bagasse (Liu et al., 2007), and barley straw (Sun, Xu, Sun, Xiao, & Sun, 2005), which provide the better methods for cellulose isolation. Lignin extraction from corn stalk has already been reported (Sun, Wang, Zhang, Fowler, & Rajaratnam, 2011), but little research had been done for cellulose of corn stalk. The purpose of this work is to investigate the properties of the modified cellulose obtained from corn stalk comparing with corn stalk copolymer without purification. Accordingly, their structures were characterized by SEM-EDS, XRD and solid-state CP/MAS ^{13}C NMR spectra, and the adsorption capacities of samples were tested in a batch adsorption experiment.

2. Materials and methods

2.1. Materials and chemicals

Raw corn stalk (RCS) was supplied from a farm in Guangzhou city, China. After removing the leaves and completely washing with fresh water, RCS was cut into granules and sieved for a particle size of 0.45 mm, then washed three times with deionized 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 purchased from Chemical Reagent Co. Ltd. (Guangzhou, China). Acrylonitrile (AN) was directly used without further purification. Cadmium stock solution was prepared from cadmium chloride in deionized water. Diluted HCl and NaOH solution was used for pH adjustment. An orbital shake was used for adsorption experiments. The concentration of cadmium was determined by ICP-OES (OPTIMA 5000).

2.2. Isolation

Cellulose was isolated mainly from RCS following the methods (Liu et al., 2007). First, RCS was treated with sodium chlorite at pH value 3.8–4.0 (adjusting with acetic acid) at 75°C for 2 h, then filtrated to collect the residue, washed them with deionized water and ethanol (95%), and dried in an oven at 50°C . Second, these dried residues were holo-cellulose and needed to be extracted with 10% KOH at room temperature for 10 h. After filtration, washed new residues until them neutral, and continued to wash them with ethanol (95%) several times. Finally, the samples were dried in an oven at 50°C for 16–20 h. The cellulose was successfully obtained from corn stalk.

2.3. Modification

Graft copolymerization was conducted in a 500 ml four-neck flask with stirrer in temperature controlled water-bath (40°C). Dried cellulose (3 g) was immersed in deionized water (300 ml), purified N_2 (99.999%) was passed through the vessel for 15 min and then KMnO_4 (1.0 g) as initiator was added to the flask to stirred for 60 min. Acrylonitrile (AN, 10.0 ml, 98%) as monomer, N,N'-methylenebisacrylamide (MBA, 0.03 g) as cross linker and H_2SO_4 (0.10 ml, 98%) as catalyst were added, and stirred continuously for 60 min reaction. After reaction, the modified sample was filtered, washed with ethanol (95%) and deionized water, and dried to a constant mass. Furthermore, they were extracted using N,N-dimethylformamide (DMF, 99.5%) in a soxhlet for 48 h in order to remove the AN homopolymer. The product was successively washed with ethanol (95%) and deionized water, then air dried. The modified cellulose was named as AGCS-cell. AGCS was directly obtained from RCS following the same method.

The graft yield (G) and grafting efficiency (GE) can be calculated following the equation (Ali, Saikia, & Sen, 1997)

$$GE\% = \frac{W_2 - W_0}{W_1 - W_0} \times 100 \quad (1)$$

where W_0 is the weight of original cellulose in gram, W_1 is the weight of sample after copolymerization and W_2 is the weight of sample after copolymerization and extraction.

2.4. Characterization

Micrographs of adsorbents were examined using a thermal field emission environmental scanning electron microscope (SEM S-3700N) and energy disperse spectroscopy (EDS Quantax). The acceleration voltage (Acc. V) was 10.0 kV, and the vacuum-mode was high vacuum. The samples were coated with gold. The crystallinity of samples was characterized using X-ray diffraction (XRD, D/max-III A, Rigaku) with the 2θ angle varying between 4 and 60°C . CP/MAS ^{13}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 μs . Each spectrum was obtained with an accumulation of 4070 scans.

2.5. Batch adsorption experiments

Batch adsorption experiments were performed using 0.5 g of adsorbents in conical flasks containing 50 ml of cadmium solution at known pH and temperature. The contents were shaken at 120 rpm. In the adsorption isotherm experiments, 0.5 g of adsorbent was added in 50 ml of cadmium solution at various concentrations at 293 K. Each cadmium ion concentration was measured three times and the average value, was used to calculate the equilibrium metal uptake q_e (mg g^{-1}) of the adsorbent using the following mass balance equation:

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

where C_0 and C_e are the initial and equilibrium concentrations.

3. Results and discussion

3.1. Modification and adsorption mechanism

As can be seen in Fig. 1, cellulose, hemicellulose and lignin are main constituents of corn stalk and three types of

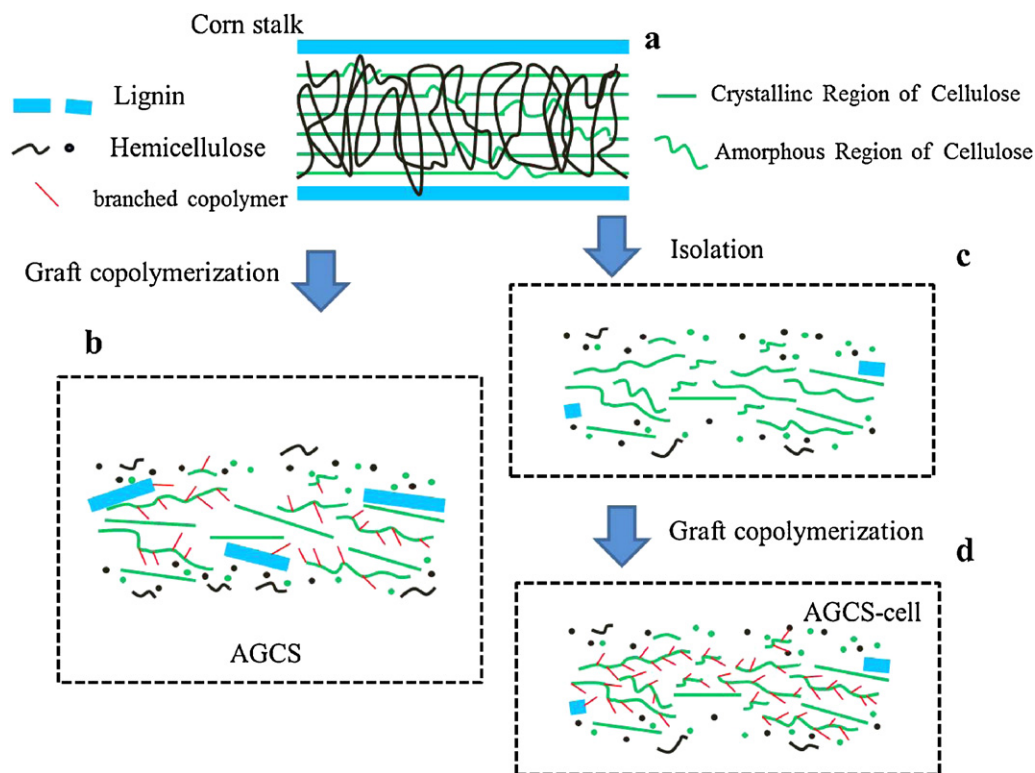


Fig. 1. Structure of (a) corn stalk, (b) AGCS, (c) isolated corn stalk and (d) AGCS-cell.

polymers, which are strongly intermeshed and chemically bonded by non-covalent forces and by covalent cross-linkages (Pérez, Muñoz-Dorado, de la Rubia, & Martínez, 2002). Cellulose has mainly crystal and amorphous region, and the crystal region are interrupted every 60 nm with the amorphous region (Fig. 1a). In the previous research, corn stalk was modified using graft copolymerization to produce AGCS (Zheng, Dang, Zhu, et al., 2010), which implied that other constituents were still in present in corn stalk and modified together with cellulose (Fig. 1b). Based on previous work (Zheng, Dang, Zhu, et al., 2010), cellulose was firstly isolated from corn stalk before modification, and other components in AGCS-cell were lost compared with AGCS (Fig. 1c). In contrast, more cellulose fibers were exposed and amorphous region became larger obviously, thus leading to more branch copolymer grafting on the main chain of a polymer backbone of cellulose (Fig. 1d).

Fig. 2 showed the modification and adsorption mechanism for AGCS-cell. First, cellulose reacted with the initiator (KMnO_4) to form the free radical sites at C-2 or C-3 in cellulose structure (Fig. 2a), 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 leading to cyano group ($-\text{CN}$) introducing to cellulose backbones. Since MBA as cross linker was presented in modification, the cellulose comprised a dimensional cross linked structure between cellulose backbones (Fig. 2b). $-\text{CN}$ and $-\text{OH}$ group played an important part in cadmium adsorption, because the nitrogen of the $-\text{CN}$ group and the oxygen of the $-\text{OH}$ group are considered a strong Lewis base due to the presence of vacant double electrons. These doublets can make a complex for coordination with chemical entities low in electrons, such as metal ions (Aydın, Bulut, & Yerlikaya, 2008). Thus both $-\text{CN}$ group in the grafted polymer chains and $-\text{OH}$ group in cellulose had binding capabilities for cadmium ions (shown in Section I of Fig. 2c). The dimensional cross

linked structure in cellulose could make cadmium ions stick in the network structures (shown in Section II of Fig. 2c).

3.2. Adsorbent characterization

3.2.1. SEM-EDS

SEM micrographs and energy disperse spectroscopies of RCS, AGCS and AGCS-cell were shown in Fig. 3. In SEM micrographs, RCS's surface was rough and inhomogeneous, and single cellulose was hardly observed (Fig. 3a), but was easily seen in AGCS and AGCS-cell. In particular in AGCS-cell, single cellulose was more obviously due to isolation. Further in AGCS and AGCS-cell micrographs, the modified cellulose had deposits of polymer leading to uneven surfaces on the cellulose surface (Fig. 3b and c) (Saikia & Ali, 1999). The deposits of polymer could be calculated using Eq. (1), and their *GE* values were about 42.3 and 82.0% for AGCS and AGCS-cell, respectively. Isolated cellulose had a higher *GE* value because of better grafted effects. Moreover, the width of cellulose in AGCS-cell ($4.6 \mu\text{m}$) was less than AGCS's ($8 \mu\text{m}$), and much less than the value of the literature which reported the width range of cellulose in corn stalk is $10\text{--}20 \mu\text{m}$ (McGovern, Coffelt, Hurter, Ahuja, Wiedermann, 1987). The results were mainly caused by MBA and attributed to the good crosslinked structure of the purified form (Fig. 2b). In energy disperse spectroscopies, compared with RCS, there was Mn element in AGCS and AGCS-cell as KMnO_4 (initiator) adding. Counts of N element were weak though $-\text{CN}$ groups were introduced, which indicated that N concentration is much less than C and O elements. The prepared samples were coated with gold.

3.2.2. XRD

Fig. 4 shows the XRD patterns for RCS, AGCS and AGCS-cell. Generally in XRD patterns, they have 2θ diffraction peaks at 15.5 and 22.5° , which are assigned to the crystalline domain of cellulose structure (Zheng, Dang, Zhu, et al., 2010). The intensity of the peaks in cellulose of RCS was highest, which indicated it

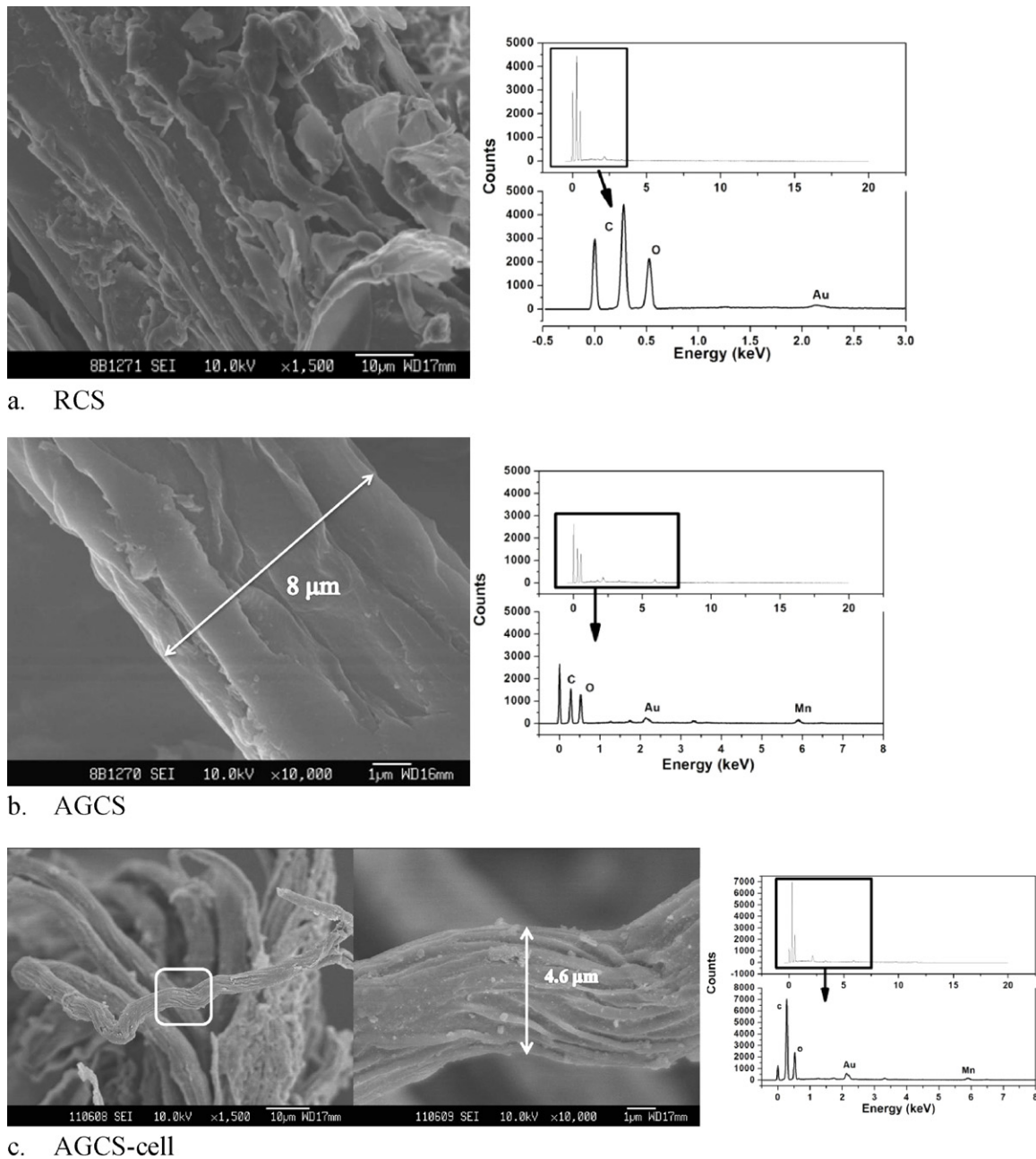


Fig. 3. Scanning electron micrographs and energy dispersive spectroscopies of (a) RCS, (b) AGCS and (c) AGCS-cell.

(Amuda, Giwa, & Bello, 2007). The Langmuir equation can be represented in a linear form (Sangi, Shahmoradi, Zolgharnein, Azimi, & Ghorbandoost, 2008),

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{bq_{max}} + \frac{C_{eq}}{q_{max}} \quad (3)$$

where C_{eq} is the equilibrium concentration of the remaining heavy metal in the solution (mg l^{-1}), q_{eq} is the amount of a metal adsorbed per mass unit of adsorbent at equilibrium (mg g^{-1}), q_{max} is the amount of adsorbent at complete monolayer coverage (mg g^{-1}), and b (l mg^{-1}) is a Langmuir constant that relates to the heat of adsorption. The q_{max} and b values were calculated from the slopes ($1/q_{max}$) and intercepts ($1/bq_{max}$) of linear plots of C_{eq}/q_{eq} versus C_{eq} .

In the Langmuir equation, a useful parameter R_L , named a dimensionless equilibrium parameter, also can be considered and calculated as follow (Gupta & Babu, 2009),

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

where b is Langmuir constant (l mg^{-1}) and C_0 is initial concentration (mg l^{-1}). R_L value is between 0 and 1 for the favorable adsorption, while $R_L > 1$ indicates the unfavorable adsorption, and $R_L = 1$ represents the linear adsorption, but the adsorption process is irreversible if $R_L = 0$.

The Freundlich isotherm model is the empirical relationship and an assumption based on metals adsorption on a heterogeneous surface (Amuda et al., 2007). It has a linear form (Sangi et al., 2008),

$$\ln q_{ep} = \frac{1}{n} \ln C_{eq} + \ln K_F \quad (5)$$

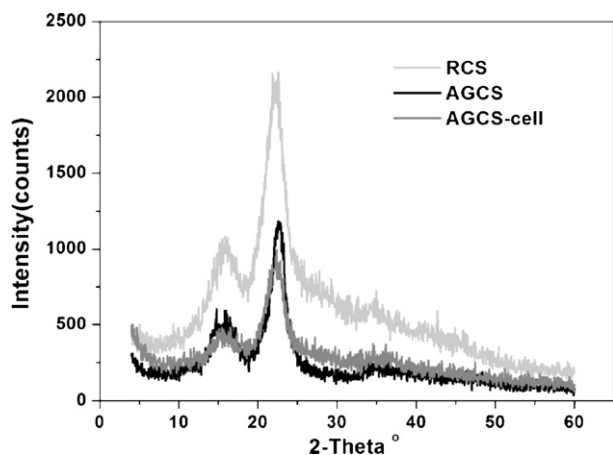


Fig. 4. XRD pattern of RCS, AGCS and AGCS-cell.

where K_F and n are the Freundlich constant and calculated from the slopes (n) and intercepts ($\ln K_F$) of linear plots of $\log q_{eq}$ versus $\ln C_{eq}$.

Tempkin isotherm can be taken into account of the adsorbent–adsorbate interaction because of it contains a factor (B_T) in the equation. The linear form of Tempkin equation is given (Gupta & Babu, 2009),

$$q_{ep} = B_T \ln A_T + B_T \ln C_{ep} \quad (6)$$

where $B_T = (RT)/b_T$, T is the absolute temperature in K and R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). The constant b_T is the heat of adsorption and A_T is the equilibrium binding constant (l min^{-1}) corresponding to the maximum binding energy.

Generalized isotherm is a combination of Langmuir and Freundlich isotherms, and its linear form is (Gupta & Babu, 2009),

$$\log \left(\frac{Q_m}{q_{ep}} - 1 \right) = \log K_C - N_b \log C_{ep} \quad (7)$$

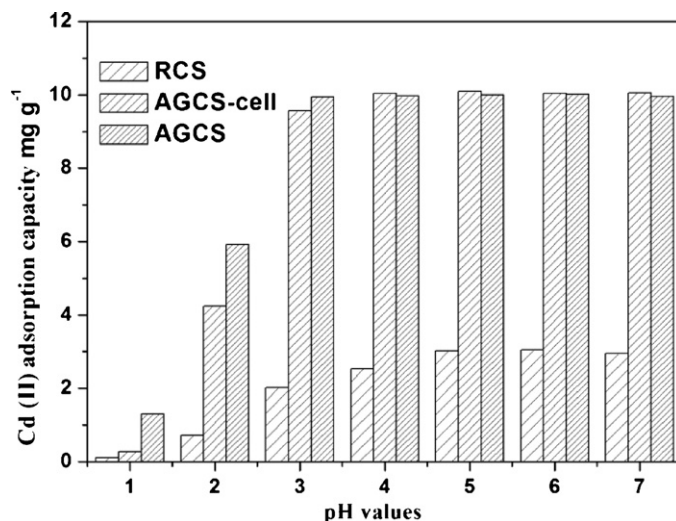


Fig. 6. Adsorption capacity of Cd(II) by RCS, AGCS-cell and AGCS in different pH values (conditions: initial Cd(II) concentration 100 mg l^{-1} , adsorbent 0.5 g in 50 ml solution, flask shaking at 120 rpm at 293 K during 6 h contact time).

where Q_m is the maximum adsorption capacity of the adsorbent (mg g^{-1}), K_C is the saturation constant (mg l^{-1}) and N_b is the cooperative binding constant. The values of K_C and N_b are obtained from the slope and intercept of the plot of $\log[(Q_m/q_e) - 1]$ versus $\log C_e$.

The linearized Langmuir, Freundlich, Tempkin and Generalized isotherms equations and constants for RCS, AGCS and AGCS-cell were presented in Tables 1 and 2. The highest R^2 values showed that the Langmuir exhibited a best fit to the adsorption data compared with other adsorption isotherms, which revealed that adsorption system was the monolayer coverage on the surface of these adsorbents, and the surface sites were alike and accommodated only one adsorbed atom. In general, the R^2 values of AGCS-cell in all isotherms were highest because of pure cellulose effects. The R_L values of RCS, AGCS and AGCS-cell were between 0 and 1 and

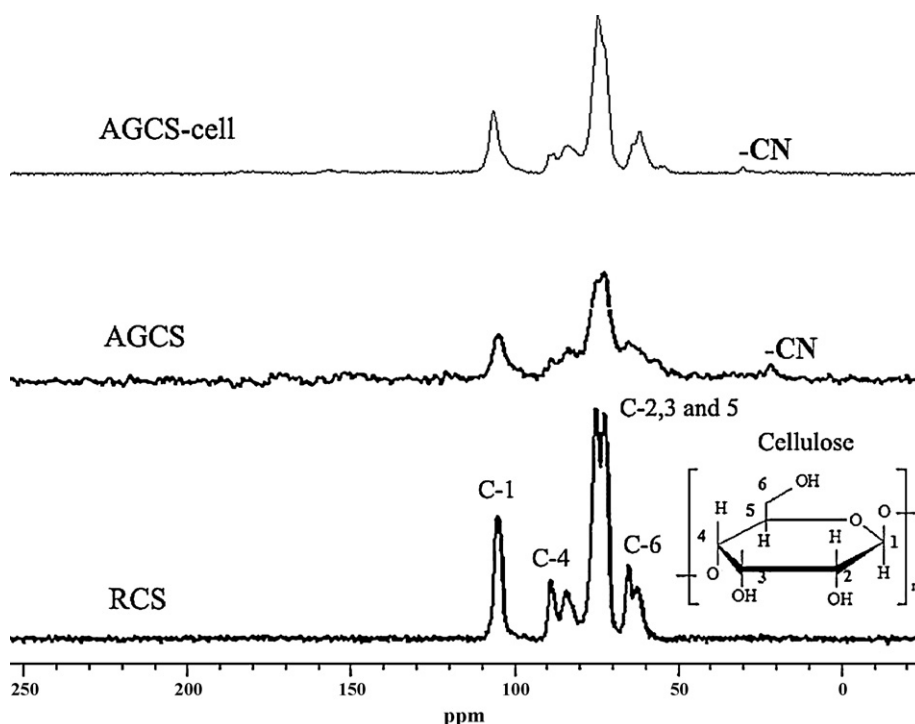


Fig. 5. Solid-state CP/MAS ^{13}C NMR spectra of RCS, AGCS and AGCS-cell.

Table 1
Langmuir isotherm parameters for Cd(II) adsorption onto RCS, AGCS and AGCS-cell (conditions: pH 7.0, adsorbent 0.5 g in 50 ml solution, flask shaking at 120 rpm at 293 K during 6 h contact time).

Isotherm	Parameters	Adsorbents		
		RCS	AGCS	AGCS-cell
Langmuir	Equation	$(c_{eq}/q_{eq}) = 0.2628c_{ep} + 6.6283$	$(c_{eq}/q_{eq}) = 0.0451c_{ep} + 0.2721$	$(c_{eq}/q_{eq}) = 0.0468c_{ep} + 0.0906$
	q_{max} (mg g ⁻¹)	3.81	22.17	21.37
	R^2	0.9221	0.9725	0.9986
	R_L	0.11–0.40	0.01–0.06	0.01–0.03

Table 2
Freundlich, Tempkin, and Generalized isotherm for Cd(II) adsorption onto RCS, AGCS and AGCS-cell (conditions: pH 7.0, adsorbent 0.5 g in 50 ml solution, flask shaking at 120 rpm at 293 K during 6 h contact time).

Adsorbent	Freundlich		Tempkin		Generalized	
	Equation	R^2	Equation	R^2	Equation	R^2
RCS	$\ln q_{eq} = 0.599 \ln c_{eq} - 1.8241$	0.82	$q_{ep} = 0.2432 \ln C_{ep} + 1.9686$	0.05	$\log((22.17/q_{ep}) - 1) = 0.9945 \log c_{eq} - 2.8709$	0.10
AGCS	$\ln q_{eq} = 0.0993 \ln c_{eq} + 2.5517$	0.41	$q_{ep} = 2.0461 \ln C_{ep} + 11.123$	0.38	$\log((22.17/q_{ep}) - 1) = -0.4729 \log c_{eq} + 0.1115$	0.64
AGCS-cell	$\ln q_{eq} = 0.0459 \ln c_{eq} + 1.2252$	0.75	$q_{ep} = 0.9507 \ln C_{ep} + 16.38$	0.73	$\log((21.37/q_{ep}) - 1) = -0.3914 \log c_{eq} - 0.6771$	0.94

considered to be the favorable adsorption. According to the Langmuir, the maximum adsorption capacities for cadmium ions on RCS, AGCS and AGCS-cell were 3.81, 22.17 and 21.37 mg g⁻¹, respectively. The adsorption capacities for cadmium ions on AGCS and AGCS-cell were higher than on RCS due to functional groups and structures. Particularly, the adsorption ability of AGCS-cell was close to AGCS, which may be imply that the total adsorption capacities of all constituents in AGCS was almost equal to the isolated cellulose in AGCS-cell. Similarly, some constituents such as lignin and hemicellulose were removed from AGCS-cell, which led to the adsorption capacities loss. But better exposed cellulose could be improved their heavy metal uptake, just to make up the loss part. Therefore, cellulose was considered as a main constituent and confirmed to be a most important role in cadmium ions removal in AGCS and AGCS-cell.

4. Conclusions

This work demonstrated that the cellulose was isolated from corn stalk and modified using graft copolymerization further to produce AGCS-cell, which could effectively remove cadmium ions from aqueous solution. The GE value and adsorption capacity of AGCS-cell were 82.0% and 21.37 mg g⁻¹, respectively. Furthermore, the adsorption ability of AGCS-cell was close to the AGCS, which indicated the better isolated and modified cellulose was found to be a potential adsorbent. Finally, the linearization of Langmuir isotherm described adequately the equilibrium data.

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References

Ali, F., Saikia, C. N., & Sen, S. R. (1997). Grafting of acrylonitrile onto high-cellulose extracted from *Hibiscus sabdariffa*. *Industrial Crops and Products*, 6, 121–129.

- Amuda, O. S., Giwa, A. A., & Bello, I. A. (2007). Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. *Biochemical Engineering Journal*, 36, 174–181.
- Anirudhan, T. S., Divya, L., & Suchithra, P. S. (2009). Kinetic and equilibrium characterization of uranium (VI) adsorption onto carboxylate-functionalized poly (hydroxyethylmethacrylate) – grafted lignocellulosics. *Journal of Environmental Management*, 90, 549–560.
- Aydın, H., Bulut, Y., & Yerlikaya, Ç. (2008). Removal of copper(II) from aqueous solution by adsorption onto low-cost adsorbents. *Journal of Environmental Management*, 87, 37–45.
- Barbur, A. K. (1983). Environmental aspects of zinc, lead, and cadmium production and use. Sir Horne memorial lecture. *Chemistry and Industry*, 6, 409–415.
- Crini, G. (2005). Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in Polymer Science*, 30(1), 38–70.
- Gupta, S., & Babu, B. V. (2009). Utilization of waste product (tamarind seeds) for the removal of Cr(VI) from aqueous solutions: Equilibrium, kinetics, and regeneration studies. *Journal of Environmental Management*, 90, 3013–3022.
- Hall, L. W., Jr., Scott, M. C., & Killen, W. D. (1998). Ecological risk assessment of copper and cadmium in surface waters of Chesapeake bay watershed. *Environmental Toxicology and Chemistry*, 17, 1172–1189.
- Haluk, A., Yasemin, B., & Çiğdem, Y. (2008). Removal of copper(II) from aqueous solution by adsorption onto low-cost adsorbents. *Journal of Environmental Management*, 87, 37–45.
- Hashem, A. (2006). Amidoximated sunflower stalks (ASFS) as a new adsorbent for removal of Cu(II) from aqueous solution. *Polymer-Plastics Technology and Engineering*, 45, 35–42.
- Ho, Y. S., & Ofomaja, A. E. (2006). Biosorption thermodynamics of cadmium on coconut copra meal as biosorbent. *Biochemical Engineering Journal*, 30, 117–123.
- Kamel, S., Hassan, E. M., & El-Sakahawy, M. (2006). Preparation and application of acrylonitrile-grafted cyanoethyl cellulose for the removal of copper(II) ions. *Journal of Applied Polymer Science*, 100, 329–334.
- Leyva-Ramos, R., Bernal-Jacome, L. A., & Acosta-Rodriguez, I. (2005). Adsorption of cadmium(II) from aqueous solution on natural and oxidized corncob. *Separation and Purification Technology*, 45, 41–49.
- Liu, C. F., Sun, R. C., & Ye, J. (2006). Structural and thermal characterization of sugarcane bagasse phthalates prepared with ultrasound irradiation. *Polymer Degradation and Stability*, 91, 280–288.
- Liu, C. F., Sun, R. C., Zhang, A. P., Ren, J. L., Wang, X. A., Qin, M. H., et al. (2007). Homogeneous modification of sugarcane bagasse cellulose with succinic anhydride using a ionic liquid as reaction medium. *Carbohydrate Research*, 342, 919–926.
- Liu, C. F., Xu, F., Sun, J. X., Ren, J. L., Curling, S., Sun, R. C., et al. (2006). Physicochemical characterization of cellulose from perennial ryegrass leaves (*Lolium perenne*). *Carbohydrate Research*, 341, 2677–2687.
- McGovern, J. N., Coffelt, D. E., Hurter, A. M., Ahuja, N. K., & Wiedermann, A. (1987). Other fibers. In *The Joint Textbook Committee of the Paper Industry (Ed.), Pulp and paper manufacture Secondary fibers and non-wood pulping* (pp. 119–121). Atlanta: Tappi Press.
- Nordberg, G. F. (2009). Historical perspectives on cadmium toxicology. *Toxicology and Applied Pharmacology*, 238, 192–200.
- O'Connell, D. W., Birkinshaw, C., & O'Dwyer, T. F. (2008). Heavy metal adsorbents prepared from the modification of cellulose: A review. *Bioresource Technology*, 99, 6709–6724.
- Park, D., Yun, Y., & Park, J. M. (2006). Comment on "Chromate ion adsorption by agricultural by-products modified with dimethyloldihydroxyethylene urea and choline chloride" by Wartelle and Marshall. *Water Research*, 40, 1501–1504.
- Pérez, J., Muñoz-Dorado, J., de la Rubia, T., & Martínez, J. (2002). Biodegradation and biological treatments of cellulose hemicellulose and lignin: An overview. *International Microbiology*, 5, 53–63.

- Saikia, C. N., & Ali, N. (1999). Graft copolymerization of methylmethacrylate onto high α -cellulose pulp extracted from *Hibiscus sabdariffa* and *Gmelina arborea*. *Bioresource Technology*, 68, 165–171.
- Sangi, M. R., Shahmoradi, A., Zolgharnein, J., Azimi, G. H., & Ghorbandoost, M. (2008). Removal and recovery of heavy metals from aqueous solution using *Ulmus carpinifolia* and *Fraxinus excelsior* tree leaves. *Journal of Hazardous Materials*, 155, 513–522.
- Shibi, I. G., & Anirudhan, T. S. (2002). Synthesis, characterisation and application as a mercury(II) sorbent of banana stalk-polyacrylamide grafted copolymer bearing carboxyl groups. *Industrial and Engineering Chemistry Research*, 41, 5341–5352.
- Sun, X. F., Sun, R. C., & Sun, J. X. (2004). Acetylation of sugarcane bagasse using NBS as a catalyst under mild reaction conditions for the production of oil sorption-active materials. *Bioresource Technology*, 95, 343–350.
- Sun, J. X., Sun, X. F., Zhao, H., & Sun, R. C. (2004). Isolation and characterization of cellulose from sugarcane bagasse. *Polymer Degradation and Stability*, 84, 331–339.
- Sun, X., Wang, H., Zhang, G., Fowler, P., & Rajaratnam, M. (2011). Extraction and characterization of lignins from maize stem and sugarcane bagasse. *Journal of Applied Polymer Science*, 120, 3587–3595.
- Sun, J. X., Xu, F., Sun, X. F., Xiao, B., & Sun, R. C. (2005). Physico-chemical and thermal characterization of cellulose from barley straw. *Polymer Degradation and Stability*, 88, 521–531.
- Tolcin, A. C. (2008). Cadmium. In U.S. Geological Survey (Ed.), *Metals and minerals Minerals yearbook* (pp. 15.1–158). Washington, DC: United States Government Printing Office.
- Vimala, R., & Das, N. (2011). Mechanism of Cd(II) adsorption by macrofungus *Plurotus platypus*. *Journal of Environmental Science*, 23(2), 288–293.
- Wan Ngah, W. S., & Hananfiah, M. A. K. M. (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresource Technology*, 99, 3935–3948.
- Zheng, L., Dang, Z., Yi, X., & Zhang, H. (2010). Equilibrium and kinetic studies of adsorption of Cd(II) from aqueous solution using modified corn stalk. *Journal of Hazardous Materials*, 176, 650–656.
- Zheng, L., Dang, Z., Zhu, C., Yi, X., Zhang, H., & Liu, Q. (2010). Removal of cadmium(II) from aqueous solution by corn stalk graft copolymers. *Bioresource Technology*, 101, 5820–5826.
- Zhuang, P., McBride, M. B., Xia, H., Li, N., & Li, Z. (2009). Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine South China. *Science of the Total Environment*, 407, 1551–1561.