



Preparation of carboxylate-functionalized cellulose via solvent-free mechanochemistry and its characterization as a biosorbent for removal of Pb²⁺ from aqueous solution

Wei Zhang^{a,b}, Cuiying Li^a, Mei Liang^a, Yamin Geng^a, Canhui Lu^{a,*}

^a State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China

^b School of Chemical and Biomolecular Engineering and IPST at GT, Georgia Institute of Technology, Atlanta 30332-0620, Georgia

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ABSTRACT

Carboxylate-functionalized cellulose can be used as a low cost but effective biosorbent for heavy metals remediation. In this study, it was simply fabricated from wood cellulose and succinic anhydride via solvent-free mechanochemistry in the absence of catalyst at ambient temperature through pan-milling. Fourier transform infrared spectra (FT-IR) confirmed the realization of mechanochemical esterification of cellulose. Reaction kinetics study showed that this solid-state mechanochemical reaction was governed by “slow followed by fast” kinetics model. The reaction sites were mainly at the new surface of cellulose powder where hydrogen bondings in cellulose were broken up and hydroxyl groups were activated due to the fairly strong forces imposed by the pan-mill. X-ray photoelectron spectroscopy (XPS) indicated that the mechanochemical succinylation of cellulose occurred even in a short milling time. The exponential increment of surface area of cellulose during pan-milling was correlated to the increasing substitution degree. Preliminary adsorption studies showed that the modified cellulose possessed excellent adsorption capacity towards Pb²⁺, with lead ion uptake value of 422 mg/g and 84.4% metal removal from a 500 mg/g Pb²⁺ solution, significantly higher than those values for unmodified cellulose.

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1. Introduction

Water contamination caused by heavy metals has become a worldwide environmental problem owing to their toxic effects and accumulation through the food chain. Lignocellulosic materials such as coir pith, bagasse, cocoa shells, can retain metals from water solutions due to the presence of aliphatic hydroxyl and carboxylic groups, which have an affinity of metal ions. However, the adsorption capacity for direct application of these materials was rather low. Recent research on carboxylate-functionalized cellulose has revealed that these materials exhibit a specific binding ability towards highly toxic heavy metals as a consequence of a soft Lewis acid–soft Lewis base interaction (Pearsons' theory). Their chemical stability in acidic media as well as the possibility of regeneration by washing with concentrated HCl allows the reuse of these adsorbent materials for several cycles [1–7]. However, the current synthetic routes for such biosorbents always involve organic solvents like pyridine, N,N-dimethyl formamide (DMF), which are also harmful to the human body. Several ecologically benign methods have recently been developed

to modify biomass, including solvent-free microwave radiation, oven-dried treatments, etc. [8]. Herein, we report another simple and alternative method, solvent-free mechanochemistry, to prepare carboxylate-functionalized cellulose at ambient conditions. This approach appears to be an energy intensive technique when compared with the conventional solvent-based chemical synthesis. As a heterogeneous solid-phase reaction, several processes may occur during the mechanochemical synthesis: dispersion of the components, generation of the contacts between them and the mass transfer at the contact zones. All these processes are caused only by the mechanical impact on the mixture of solid reagents. Previously, several stress-induced mechanochemical reactions of solid materials and organic reagents without solvent and heating have been reported [9–14]. However, as far as we know, this technique has rarely been applied on cellulose modification. In this investigation, succinic anhydride, a non-toxic solid reactant that is quite stable at room temperature, was utilized for introducing carboxylic groups onto cellulose through ring-opening esterification reaction with cellulose hydroxyls. The apparatus of choice for the mechanochemical reaction was our self-designed pan-mill. Our previous investigations showed that this equipment is much more efficient in mechano-activation of cellulose as compared to conventional ball-mill, opening a potential way for synthesizing cellulose derivatives mechanochemically on an industrial scale [15,16]. The

* Corresponding author. Tel.: +86 28 85460607; fax: +86 28 85402465.

E-mail address: canhuilu@263.net (C. Lu).

morphological and structural development of materials during the milling process would be analyzed by means of scanning electron microscopy (SEM), Fourier transform infrared spectra (FT-IR), X-ray photoelectron spectroscopy (XPS), etc. The mechanochemical reaction kinetics was discussed and compared with solvent-based one. The adsorption capacity of modified cellulose was preliminarily explored using Pb^{2+} solution.

2. Experimental

2.1. Materials

The starting materials were hardwood fibers with 98% cellulose content as reported by the Canadian supplier and analytical grade succinic anhydride commercially obtained from Chengdu Kelong Chemical Plant, China. Analytical grade lead nitrate (Longxi Chemical Plant, China) was the heavy metal salt used. Deionized water was used throughout the experiment.

2.2. Preparation of carboxylate-functionalized cellulose

Mechanochemical synthesis of carboxylate-functionalized cellulose was performed within the pan-mill mechanochemical reactor. Fig. 1 shows a digital camera photograph of the equipment, and Fig. 2 is a schematic diagram of the inlaid mill-pan. The main structural parameters of the pan-mill are: radius R , division number n , slot number m , bevel angle α and slot top width δ . A series of cellulose fibers/succinic anhydride mixture with different mass ratios were subjected to a high-speed blending machine prior to being fed in the hopper set at the middle of the moving pan and subsequently driven by the screw system to the mill-pan. Milled powder was discharged from the brim of the pans. The discharged powder was then collected for the next milling cycle. The milling procedure was regulated at a rotating speed of



Fig. 1. Digital camera photograph of the pan-mill mechanochemical reactor.

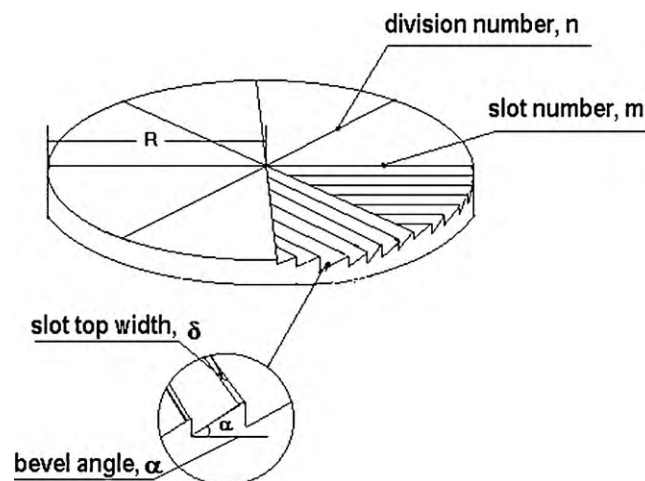


Fig. 2. Schematic diagram of the main part of pan-mill, the inlaid pan.

60 rpm and a specific pressure. The heat generated during milling was taken away by running water, thus the mechanochemical reaction could proceed at room temperature. The obtained powder was Soxhlet extracted with ethanol for 48 h to ensure thorough removal of residual succinic anhydride.

2.3. Adsorption experiments

Prior to the adsorption experiments, the esterified cellulose was treated with 1 N NaHCO_3 (1 h, 25 °C), washed with distilled water and ethanol and finally dried for 8 h at 105 °C. The solution of 500 mg/g lead concentration was prepared using analytical grade $\text{Pb}(\text{NO}_3)_2$. Then 0.1 g adsorbent with 100 mL Pb^{2+} solution was placed in 250 mL stoppered conical flasks in a shaking thermostat machine at a speed of 120 rpm. The adsorption temperature was set at 25 °C. At predetermined times, the samples were withdrawn and centrifuged at 12,000 rpm for 10 min to remove any suspended particles and the supernatant solutions were analyzed for lead using a graphite furnace atomic absorption spectrophotometer (AAS) (SpectrAA 220Z, Varian, USA). The amount of bound lead per gram of the biosorbent q_e was calculated as follows:

$$q_e = \frac{(C_0 - C_e) \times V}{1000 \times w} \quad (1)$$

where C_0 and C_e are the initial and final lead ion concentration (mg/L) in solution, respectively, V is the volume of solution in mL and w is the weight of biosorbent in g.

2.4. Measurements

Examinations of cellulose morphologies before and after mechanochemical modification were performed using a scanning electron microscopy (SEM) (JEOL JSM-5600, Japan). A thin layer of Pd–Au alloy was coated on the specimen prior to measurement to prevent charging on the surface. SEM was operated at an accelerating voltage of 20 kV. The extent of modifications was determined by FT-IR using a Nicolet 560 FT-IR spectrometer, taking 32 scans for each sample with a resolution of 2 cm^{-1} , ranging from 400 to 4000 cm^{-1} . The chemical character of the sample surfaces was studied with XPS (XSAM800, Kratos, Britain) equipped with a monochromatic Al $K\alpha$ X-ray source and operated at 12 kV and 15 mA. The pressure in the analyzing chamber was maintained at 6.7×10^{-7} Torr or lower during the measurement. All specimens were analyzed at a photoelectron take-off angle of 45°. Dynamic contact angle with water for both pristine cellulose and modified cellulose was measured by a drop shape analysis sys-

tem (model DSA 100, Kruss Co., Germany) on uncompact powder stuck on a fixed glass support. At least 5 specimens of each sample were measured, with degree of reproducibility within $\pm 5^\circ$. The concentration of carboxylate groups on the processed cellulose was determined by back-titration method. An amount of 0.1 g carboxylate-functionalized cellulose was suspended in 100 mL of an aqueous 0.01 mol/L NaOH solution for 1 h under constant stirring. After filtration, the excess of NaOH was back-titrated with 0.01 mol/L HCl solution. The concentration of carboxylic functions was calculated by:

$$C_{\text{COOH}} = \left[\frac{(C_{\text{NaOH}} \times V_{\text{NaOH}}) - (C_{\text{HCl}} \times V_{\text{HCl}})}{m_{\text{cell}}} \right] \quad (2)$$

where C_{NaOH} is the concentration of the NaOH solution (mmol/L), C_{HCl} is the concentration of the HCl solution (mmol/L), V_{NaOH} is the volume of the NaOH solution (L), V_{HCl} is the volume of HCl spent in the titration of the excess base (L) and m_{cell} is the cellulose mass (g).

3. Results and discussion

3.1. Morphological observation

One of the most significant changes of solid materials during a mechanochemical procedure is their morphological alteration. As can be seen from Fig. 3, the starting wood pulp consisted of tangled fibers with relatively smooth surface; however, the mechanochemically treated cellulose completely lost its fibrillar structure and was pulverized into powder form with diameters in the range of 0.2–30 μm . The pan-mill type mechanochemical reactor used in this experiment has excellent pulverizing and dispersing effects on polymeric materials owing to the ingenious design derived from traditional Chinese stone mill. It can exert a strong squeezing force in both radial and tangential directions, like a pair of three-dimensional scissors. The obtained powdery product had a much larger specific surface area as compared with their original form. This may largely improve its adsorption capacity towards heavy metal ions, since the contact surface between adsorbent and the liquid phase plays an important role in the adsorption phenomenon. Tarley and Arruda pointed out that the main processes of metal adsorption onto solid adsorbents were those based on adsorption on the particle surface, and they observed a higher adsorption capacity of Cd^{2+} and Pb^{2+} for rice husks with smaller size [17]. Similar results for cadmium adsorption on chitin were also reported [18]. Therefore, it can be concluded that the mechanochemically modified cellulose presents an adequate morphological profile to retain metal ions.

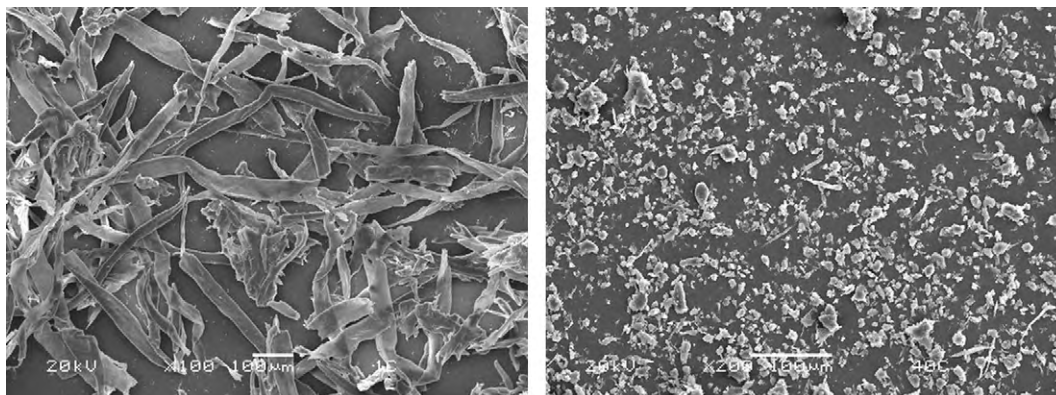


Fig. 3. SEM images of cellulose fibers before and after mechanochemical reaction (left) original cellulose fibers (right) modified cellulose powder after mechanochemical reaction.

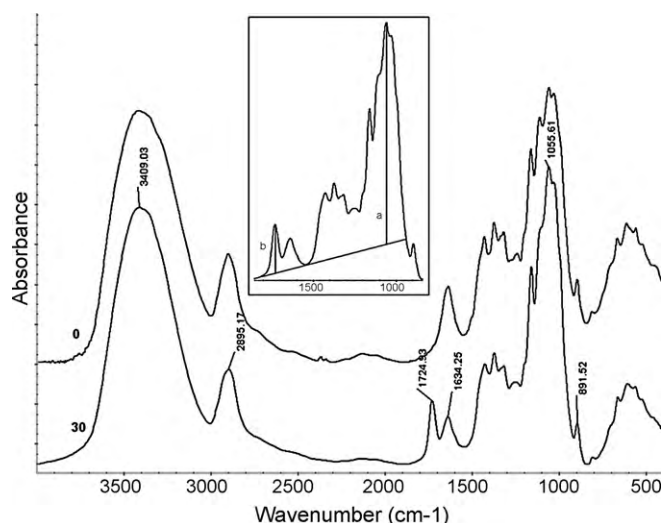
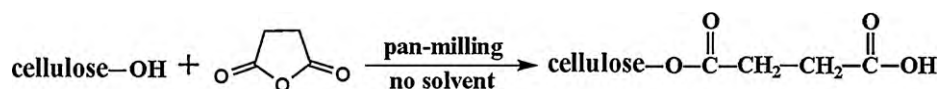


Fig. 4. Absorbance FT-IR spectra of pristine cellulose fiber (0) and succinylated cellulose powder (30) after 30 cycles of pan-milling (with initial cellulose/succinic anhydride mass ratio of 10/3).

3.2. FT-IR spectra and contact angle measurements

Esterification has been the most widely used and successful chemical modification of cellulose. Unlike acetic anhydride, succinic anhydride is unable to swell cellulose, as it is a solid substance at ambient conditions. Therefore, a suitable solvent or catalyst should be added to the reaction system to increase the accessibility of the hydroxyl groups on cellulose to the reactants. However, the use of solvent would require complicated separation procedures to recover the chemicals after reaction and the organic solvents are often harmful to human health. In this study, succinylation of cellulose was performed using a solid-state mechanochemical procedure in the absence of catalysts to eliminate organic solvents in the reaction system. The progress of the mechanochemical esterification reaction was verified by FT-IR analysis. Fig. 4 compares the absorbance FT-IR spectrum of pristine cellulose fiber with that of modified cellulose after 30 cycles pan-milling. The pristine cellulose fiber exhibited standard FT-IR spectrum of cellulose associated with its high purity [19]. It has been reported that a monoester derivative with the succinyl group was formed when cellulose reacted with the succinic anhydride, according to the chemical reaction equation showed in Scheme 1 [20].

Indeed, from the spectrum of modified cellulose, the broad $-\text{OH}$ absorption band occurring in the region of $3200\text{--}3600\text{ cm}^{-1}$ and the new peak at 1724 cm^{-1} assigned to $\text{C}=\text{O}$ stretching vibration of car-



Scheme 1. Mechanochemical esterification of cellulose with succinic anhydride.

bonyl group, consisting with the increased intensity of C–O ester group stretching at 1165 cm^{-1} , indicated that mechanochemical esterification reaction between cellulose and succinic anhydride arose during pan-milling. As expected, the absence of peaks at 1850 and 1780 cm^{-1} of succinylated polymers confirmed that the products were free of unreacted succinic anhydride after purification. Noticeably, the –OH stretching adsorption band at 3400 cm^{-1} did not appreciably change upon cellulose succinylation. This is because only the surface hydroxyls that are accessible to succinic anhydride can be succinylated during the mechanochemical reaction. Moreover, the esterification reaction with succinic anhydride also gives an equal amount of hydroxyl groups at the end of grafted succinyls.

It was noticed that the intensity of the carbonyl groups, the sum of esters and carboxylic acids, increased with milling cycles. In order to quantify the overall extent of substitution of cellulose, ratio r was therefore calculated from comparison between the intensity of carbonyl vibration band (marked as b) and C–O stretching vibration of the cellulose backbone (marked as a) which was not affected by chemical modification applied. The values of r were plotted as a function of numbers of milling cycles in Fig. 5. It can be identified that r increased gradually when the milling occurred. An exponential growth model was used to fit the experimental results of Fig. 5. The chemical kinetics equation drawn from the fitting curve was shown in the figure. The high correlation coefficient of the equation indicated that this model can explain the reaction kinetics satisfactorily. This reaction kinetics was quite different from that of solvent-based surface esterification reaction of cellulose that obeyed a “fast followed by slow” kinetics model [21]. It can be explained by the fact that the reagent-accessible hydroxyls are limited due to the constant surface area of cellulose in a solvent-based system. However, for mechanochemical reactions, the surface area of cellulose increases exponentially when milling proceeded, and a large amount of activated hydroxyls are generated on the new surface that can react with succinic anhydride during pan-milling.

To further confirm the realization of mechanochemical reaction of cellulose, water contact angle measurements were used

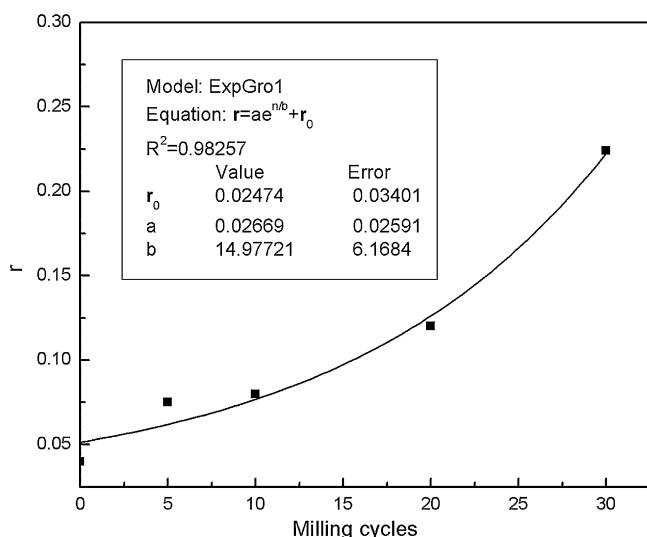


Fig. 5. Dependence of r on cycles of pan-milling (from FT-IR, see text for definition).

to detect water affinity of as-prepared samples. Fig. 6 shows the comparison of dynamic water contact angle measurements carried out with water placed on the surface of cellulose before and after mechanochemical treatment. Both samples exhibited hydrophilic characteristics. As expected, the succinylated cellulose powder showed a higher water affinity associated with a much faster decrease at the initially lower contact angle, which strongly suggested the replacement of surface hydroxyl groups by more hydrophilic carboxylic groups during mechanochemical reaction.

In order to provide quantitative information on the formed carboxylate sites, chemical titration was performed to measure the concentration of the carboxylate groups (C_{COOH}) on the processed cellulose. The results showed that 30 cycles of pan-milling of cellulose/succinic anhydride with mass ratio of 3:2 gave a C_{COOH} of 2.70 mmol/g for the product. Osvaldo et al. reported a C_{COOH} of 3.83 mmol/g for carboxylate-functionalized sugarcane bagasse based on chemical modifications in solvent [22]. However, the dosage of succinic anhydride for their system is much higher than that for ours. If a larger amount of succinic anhydride was used in the mechanochemical process, a higher C_{COOH} could be expected.

3.3. XPS analysis

X-ray photoelectron spectroscopy (XPS) has been widely applied to investigate surface chemistry of polymers. In this study, XPS method was employed to detect chemical changes of cellulose surface after different cycles of pan-milling with succinic anhydride. Fig. 7 shows the XPS spectra for cellulose before and after mechanochemical treatment. The C_{1s} binding energy depends on the number of bonds between the carbon and oxygen. Generally, the high-resolution C_{1s} peak can be deconvoluted into four different peaks: C1 (C–C or C–H), C2 (C–OH), C3 (O–C–O or C=O), C4 (O=C–O) with binding energies of 284.7 , 286.3 , 287.5 and 289.0 eV , respectively. The pristine cellulose fiber only showed C2 and C3 peaks, in agreement with the results reported for pure cellulose, which did not contain any hydrocarbons or carboxyl groups [20].

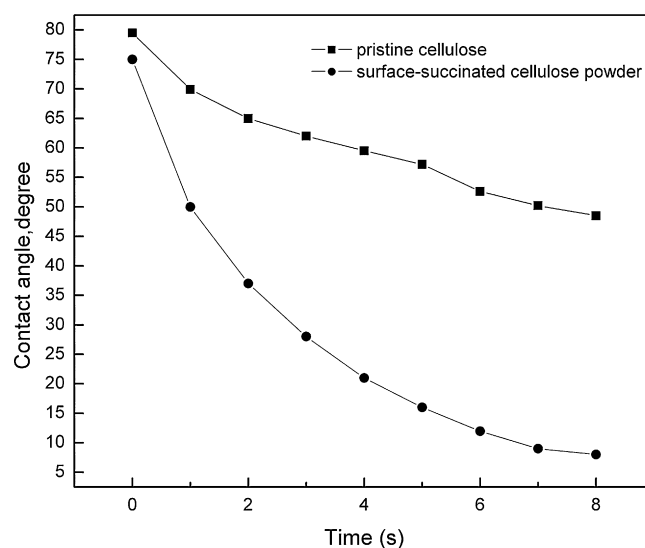


Fig. 6. Dynamic water contact angle of pristine cellulose and surface-succinylated cellulose powder as function of treating time.

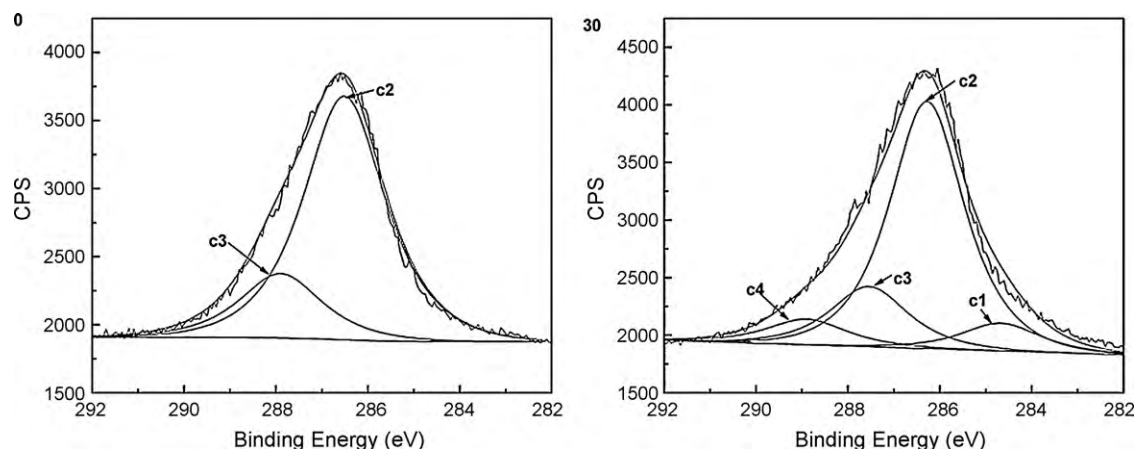


Fig. 7. XPS deconvolution spectra of C_{1s} signal of cellulose before and after mechanochemical treatment: (0) pristine cellulose; (30) after 30 cycles of pan-milling (with initial cellulose/succinic anhydride mass ratio of 10/3).

The modified cellulose sample exhibited two new peaks (C1 and C4) in its XPS spectrum, indicating that carboxylic groups were successfully introduced to the surface of cellulose powder during pan-milling. The O/C ratio of treated cellulose (see Table 1) did not change remarkably after being modified due to the similarity in stoichiometry of cellulose and succinic anhydride. Every succinic anhydride molecule reacting with cellulose surface will contribute two C1 carbons and two C4 carbons, which can be verified by XPS spectra, in which the intensity of C1 and C4 peaks appeared almost the same. The area under C1 peak corresponds to the amount of the two introduced carbon atoms without neighboring oxygen atoms, while the area under the C3 peaks corresponds to the amount of one carbon in glucose unit that is bound to two oxygen atoms, therefore the expression:

$$DS = \frac{C1/C3}{2} \quad (3)$$

may give a relative estimation of degree of substitution (DS) of succinic acid. The values are 0.18 and 0.24 for products milled 10 cycles and 30 cycles, respectively. There is not a significant increase in DS from 10 to 30 milling cycles. This is normal because of the high inhomogeneity of solvent-free mechanochemical reaction that mostly happens at the new surface of cellulose where hydroxyls are activated by mechanical energy. Therefore, the DS estimated by XPS analysis, representing degree of substitution of cellulose surface, increased slightly when pan-milling proceeded. Whereas the bulk DS increased remarkably due to the sharply enlarged surface area as the numbers of milling cycles increased.

3.4. Lead absorptivity

To evaluate the metal ions absorptivity of the as-prepared cellulosic biosorbent, lead ion adsorption studies were performed on lead nitrate solution of a concentration of 500 mg/L Pb^{2+} . Since pH plays an important role in the adsorption process, this parameter was controlled at around 6.0, which was suggested as an optimum value to obtain the best adsorption of Pb^{2+} [22]. The testing results showed 5 min were enough to reach the equilibrium adsorp-

Table 1

Atomic composition and carbon deconvolution of cellulose before and after mechanochemical reaction with succinic anhydride.

Milling cycles	O/C	C1 (%)	C2 (%)	C3 (%)	C4 (%)
0	0.53	–	79	21	–
10	0.43	7	68	19	6
30	0.48	8	68	17	7

Table 2

Removal of lead ion from solutions by cellulose biosorbent.

Cellulose	C_e (mg/L)	q_e (mg/g)	% Removal
Control	368	132	26.4
Modified	78.2	421.8	84.4

tion level. Pb^{2+} adsorption data for both modified cellulose and control sample are listed and compared in Table 2. The Pb^{2+} concentration of the solution decreased to 78.2 mg/L at equilibrium by using modified cellulose as biosorbent, resulting in the metal uptake and metal removal of 421.8 mg/g and 84.4%, respectively. The control sample prepared by milling for the same cycles without succinic anhydride exhibited metal uptake of 132 mg/g and metal removal of 26.4%. It is obvious that the mechanochemically modified cellulose possesses superior performance of heavy metal adsorption over unmodified cellulose, in accordance with previous reports on carboxylate-functionalized sugarcane bagasse and cellulose [22,23].

For a typical solvent-based synthetic route for the preparation of succinylated cellulose, a large quantity of hazardous organic solvent and excessive succinic anhydride (3.8–4.5 times of that used in our experiment) are required to achieve sufficient cellulose modifications. Moreover, the solvent-based synthesis has to last 18–24 h to complete the reaction [22,23]. On the other hand, 1 h mechanochemical modification of cellulose can endow the product excellent adsorption capacity of metals. The large surface area produced during mechanochemical process and the abundantly covered carboxylic groups on the cellulose surface as well as the mechanochemically activated hydroxyl groups are the main reasons for its excellent adsorption property.

This is just a preliminary adsorption study; more sophisticated investigations on the adsorption behaviors of various metal ions are now underway and will be reported later.

4. Conclusions

This work presents a feasible and green approach to synthesize carboxylate-functionalized cellulose for heavy metal cleanup applications. The novelties and merits of mechanochemistry in fabricating such biosorbent include: (1) being an environmentally benign procedure without any solvents and catalysts; (2) the abundant, renewable raw material of cellulose and cheaply available succinic anhydride make cost of production very low; (3) the short reaction time of 1 h further makes costs of production economized, and the pan-mill mechanochemical reactor used in our experiment

is capable for mechanochemical reaction applied in an industrial scale; (4) the simultaneous surface increasing together with sufficient surface chemical modification during mechanochemical processes provide the products with excellent adsorption capacity.

In summary, the results described above indicate that solvent-free mechanochemistry has a potential to become an alternative to conventional solvent-based cellulose chemistry. Continuing research to establish the suitability of the mechanochemical synthesis to different reaction types may lead to the development of novel green technologies for fully utilizing cellulose.

Acknowledgements

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