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Preparation of xylan citrate—A potential adsorbent for industrial wastewater treatment

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ABSTRACT

The novel and degradable xylan citrate was prepared by the environmental-friendly semi-dry oven method. Xylan reacted with citric acid (CA) to yield xylan citrate at high temperature. The influence of the different weight ratios of CA and xylan on the product yield, the carboxyl group content and degree of esterification were comparatively discussed. The results showed that there were higher carboxyl group content and degree of esterification in modified xylan than native xylan. The product yield of 128.2%, the carboxyl group content of 1174.3 meq/100 g and degree of esterification of 33.1% were achieved at the CA/xylan weight ratio of 2.4 in the absence of catalyst. Furthermore, the adsorption capacity of xylan after modification was improved greatly. These materials with better properties can enhance their water affinity, and improve their adsorption of copper ions and methyl orange in aqueous solution due to carboxyl groups.

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1. Introduction

Hemicelluloses, which are generally defined as the non-cellulose cell wall polysaccharides of vegetative and storage tissues of annual and perennial plants, represent an immense renewable resource of biopolymers. Hemicelluloses are usually divided into four general groups of structurally different polysaccharide types: xylans, mannans, xyloglucans and mixed-linkage β-glucans (Ebringerova, 2006). Xylan belongs to the most abundant hemicelluloses type in the plant kingdom, and constitutes 25–35% of the dry biomass of woody tissues of dicots and lignified tissues of monocots and occurs up to 50% in some tissues of cereal grains (Petzold, Schwikal, Gunther, & Heinze, 2006). Xylan of all higher plants possesses β-(1→4) linked xylose units as the backbone, usually substituted with sugar- and *O*-acetyl groups. Due to the functional properties of xylan, the application potential of xylan is immense and widespread as gels, films, coatings, adhesives, and additives in food, pharmacy, papermaking industry as well as in other industrial branches (Ebringerova, Hromadkova, & Heinze, 2005; Hansen & Plackett, 2008; Lindblad, Ranucci, & Albertsson, 2001; Ren, Peng, Sun, & Kennedy, 2009; Ren, Sun, Liu, Chao, & Luo, 2006; Ren, Sun, & Peng, 2008). They are shown to serve as biodegradable components in composites with nature polymers or synthetics or as pre-polymers for production of new functionalized polymeric materials, which represent the promising potential to substitute environmentally friendly products for synthetics polymers.

Recently, bio-adsorbent from biomass as a potential alternative to conventional adsorbent has been widely attracted attention. The bio-adsorbent has many good features over conventional adsorbent such as hydrophilic, low cost, biodegradability, high efficiency, minimization of chemical or biological sludge, and good reusability (Li & Bai, 2006). More attentions have been paid on the exploration of bio-adsorbents from starch (Dong et al., 2010), cellulose (Mahmoud, Salleh, Karim, Idris, & Abidin, 2012; Yang, Fu, Liu, Zhou, & Li, 2011), lignin (Wu, Zhang, Guo, & Huang, 2008), agricultural wastes (Dos Santos, De Souza, Tarley, Caetano, & Dragunski, 2011; Saad, Isa, & Md Bahari, 2010). Up to now, few studies have been focused on the xylan-based bio-adsorbent (Peng, Zhong, Ren, & Sun, 2012). There are large amounts of hydroxyl groups on the backbone of xylan, and it exhibits the promising potential as bio-adsorbent after modification.

The chemical modification of xylan provides encouraging opportunities to prepare the materials with special properties which can improve or extend their applications in industries. Citric acid (CA) is inexpensive and non-toxic chemicals which can react with the polysaccharides such as starch (Kahar, Isamil, & Othman, 2012; Reddy & Yang, 2010; Yoon, Chough, & Park, 2006, 2007; Yu, Wang, & Ma, 2005), xylan (Salam, Pawlak, Venditti, & Ei-tahlawy, 2011; Salam, Venditti, Pawlak, & Ei-Tahlawy, 2011), and cellulose (Yang & Wang, 1996; Yang, Wang, & Kang, 1997) for improving the superior hydrophilic properties

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of polysaccharides. The incorporation of carboxylic acid groups into xylan by the cross-linked reaction of xylan with CA is of interest to develop special chemical and physical functionality in xylan. In our present investigation, the modification of xylan with CA by a semi-dry oven method in the presence or in the absence of catalyst was firstly comparatively discussed as well as the adsorption properties. The product yields, the carboxyl content and degree of esterification were determined by acid-based titration. The xylan citrate was characterized by Fourier transform infrared (FTIR) and thermogravimetric analysis (TGA). The water affinity of xylan citrate was also investigated, compared to xylan. Additionally, the potential applications of xylan citrate to remove metal ions and methyl orange from the aqueous solution were studied with the aim for industrial application.

2. Experimental

2.1. Materials

Xylan from beech wood with xylose residues of greater than 90% was purchased from Tokyo Kasei Kogyo Co., Ltd. (TCI, Japan). CA, sodium hypophosphite (SHP), copper nitrate and methyl orange were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China) and they were all analytical-reagent grade. Deionized water was used in all experiments.

2.2. Modification of xylan with CA in semi-dry condition

The typical procedure to prepare xylan citrate by the semi-dry oven method is as follows. 0.33 g of xylan was dispersed in a minimal amount of water (4 mL) at 60 °C for 60 min. The required amount of CA was added into 2 mL of distilled water in a glass beaker. Xylan solution and CA solution were blended under highly stirring condition for 30 min. The mixture was placed in air oven to dehydrate at 100 °C for 30 min. Subsequently, the mixtures were allowed to react in the oven at 120 °C for 5 h. The time and temperature for reaction were determined according to the reaction procedure of starch with CA (Salam, Pawlak, & Venditti, 2010). Finally, the cross-linked reaction products were slurried in 70% ethanol under stirring for more than 2 h and then washed with 95% ethanol for three times to remove unreacted CA. Then the products were transferred to glass container and were dried at 50 °C in a vacuum drying oven for 24 h. Note that 0.3 g of SHP was dissolved with xylan in distilled water simultaneously if the catalyst was present in this reaction.

2.3. Determination of yield, carboxyl group content and degree of esterification

The yield of resulting products was determined based on xylan weight added in the reaction, which was calculated as the following:

$$\text{Yield of the product } (Y, \%) = \frac{W_1}{W_0} \times 100 \tag{1}$$

where W_1 is the weight of the resulting product, and W_0 is the weight of the dried xylan added in the reaction.

The procedure to determine the carboxyl content of xylan citrate was depicted as follows: using an acid–base titration, a known amount of resulting product dissolved in excess 0.1 N NaOH (pH 12.5) was allowed to react with the sample as an ester for 1 h. The remaining excess amount of NaOH was determined by titration with 0.1 N HCl using phenolphthalein as an indicator (Wing, 1996) and the carboxyl group content in milliequivalents of acidity per 100 g was determined as Eq. (2):

$$\text{Carboxyl content} = \frac{(V_a - V_b) \times N \times 100}{W} \tag{2}$$

where N is the normality of HCl (eq/L), V_b is the volume of HCl without sample (mL), V_a is the volume of HCl in presence of sample (mL), and W is the weight of sample (g).

The determination of degree of esterification (DE) for xylan citrate was followed as below. The synthesized product was dissolved in DMSO in a conical flask for 12 h, and then excess NaOH was added to the solution to saponify the ester for 2 h. The excess NaOH was determined by titration with calibrated HCl (Kiyose, Shimamoto, Shuto, & Taniguchi, 1999; Pushpamalar, Langford, Ahmad, & Lim, 2004) to determine the percent esterification:

$$\text{Degree of esterification (DE, \%)} = \frac{6.005 \times (V_a - V_b) \times F \times 100}{W} \tag{3}$$

where F is the normality of HCl (eq/L), V_b is the volume of HCl without sample (mL), V_a is the volume of HCl in presence of sample (mL), and W is the weight of sample (g).

2.4. Swelling experiment in distilled water

The swelling measurements for all the samples were carried out in distilled water. The swelling ratio (SR) was measured by weighting samples before and after their immersion in distilled water for about 24 h at room temperature (Salam, Pawlak, et al., 2011). The SR is defined as following:

$$\text{SR} = \frac{W_s - W_d}{W_d} \tag{4}$$

where W_s is the weight of the immersed samples, and W_d is the weight of the dried samples.

2.5. Copper ions removal experiment

To explore the effect of carboxyl group content of xylan citrate on the copper ions absorption, batch experiments of the adsorption were conducted at room temperature in a 250-mL stoppered conical flask and were equilibrated at 400 rpm in a constant temperature oscillator. Xylan citrate with different carboxyl group contents and xylan were slurried in 500 mg/L $Cu(NO_3)_2$ solution for 24 h, respectively. The pH was adjusted to 4.5 with 0.1 N NaOH and 0.1 N HNO_3. After filtration, the concentration of copper ions was determined by atomic absorption spectrophotometer (Hitachi Z-2000, Japan). The amount adsorbed per unit mass of samples at equilibrium (Q) was calculated as the following:

$$Q = \frac{(C_0 - C_e) \times V}{W} \tag{5}$$

where C_0 and C_e indicate the initial and equilibrium copper concentrations, respectively (mg/L), V is the volume of the solution (L), and W is the weight of the sample (g).

2.6. Methyl orange removal experiment

To investigate the effect of carboxyl group content on the methyl orange absorption, batch experiments of the adsorption were conducted at room temperature in a 250-mL stoppered conical flask and were equilibrated at 400 rpm in a constant temperature oscillator. Xylan citrate with different carboxyl contents and xylan were slurried in methyl orange solution (20 mg/L) for 24 h, respectively. The pH was adjusted to 2.5 with 0.1 N NaOH and 0.1 N HNO_3. After filtration, the concentration of methyl orange was determined by

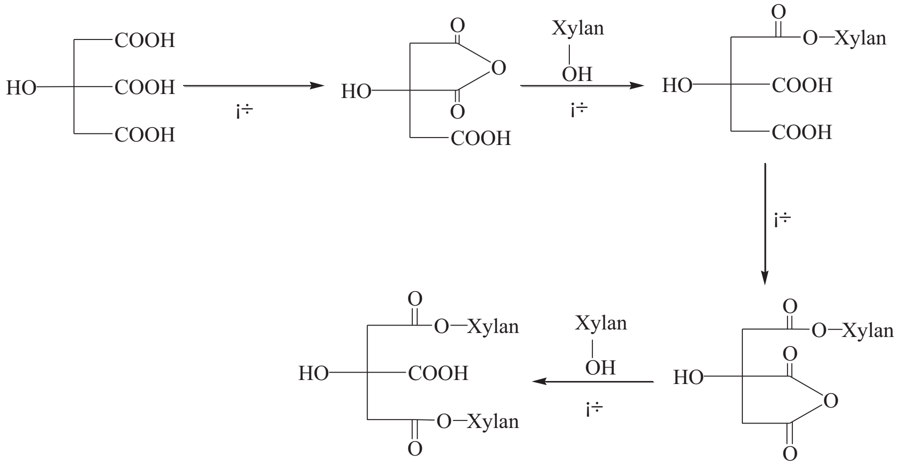

Fig. 1. Mechanism of xylan reacted with citric acid.

UV-Vis spectrophotometer (TU-1810, China). The amount adsorbed per unit mass of samples at equilibrium (Q) was calculated as the following:

$$Q = \frac{(C_0 - C_e) \times V}{W} \tag{6}$$

where C_0 and C_e indicate the initial and equilibrium methyl orange concentrations, respectively (mg/L), V is the volume of the solution (L), and W is the weight of the sample (g).

2.7. *Characterization of xylan and xylan citrate*

FTIR transmission spectra of xylan and xylan citrate were measured by using a Nicolet 750 spectrophotometer (Thermo Fisher Nicolet, FL, USA) within the wave number range 400–4000 cm^{-1}, and the 1% finely ground samples were mixed with KBr to press a plate for measurement.

Thermal analysis was performed using thermogravimetric analysis (TGA) on a simultaneous thermal analyzer (TGA Q500, TA Instruments, New Castle, USA). The apparatus was continually flushed with nitrogen. The sample was weighed between 9 and 11 mg and was heated from room temperature to 700 °C at a heating rate of 20 °C/min.

3. Results and discussion

3.1. *Mechanism of modification of xylan with CA*

The reaction of xylan with CA belongs to the esterification and cross-linked reaction. When citric acid is heated, the carboxyl groups in the citric acid dehydrate to form citric anhydrides. And later they react with hydroxyl groups in xylan to form xylan citrate at high temperature, as seen in Fig. 1. On further reaction other two carboxyl groups in the end of CA dehydrate again, and then react with hydroxyl groups in xylan to form xylan citrate, which yields cross-linked xylan citrate (Tharanathan, 2005). This reaction can be controlled to maximize reaction efficiency, minimize crosslinking, and maximize carboxyl group content by varying the reaction conditions.

3.2. *The reaction of xylan with CA in the presence of catalyst*

Xylan is allowed to being reacted thermochemically with CA to potentially yield biodegradable products possessing high carboxyl groups. Compared to the method of using the large amount of solvent, by the semi-dry oven method the removal of a small quantity of distilled water from the system in oven contributes to the reaction forward, and CA availably produces citric anhydride and is in close proximity to xylan (Wing, 1996). Therefore, the semi-dry oven method was applied in our investigation. In addition, SHP as a catalyst was used in this study because phosphorous contain salts increase crosslinking efficiency of cellulose with CA, which were reported in a few literatures (Andrews, Blanchard, & Reinhardt, 1993; Andrews & Trask-Morrell, 1991). After modification, xylan citrate powders are dark brown, and their color is deeper and darker than native xylan, which is expected since crystals of CA change from white to orange upon heating to 120 °C (Salam, Pawlak, et al., 2011). The data in Table 1 shows the reaction to yield a water insoluble product by varying the weight ratios of CA and xylan in the presence of catalyst under known reaction condition. Increasing CA/xylan weight ratios from 1.8 to 4.8 first resulted in an increase in yield from 118.9% to 141.2%, and then a decrease from 141.2% to 101.5%, indicating that the large amounts of CA added easily caused the degradation of xylan at high temperature. Carboxyl group contents increased from 585.7 meq/100 g to 702.9 meq/100 g with increase in the weight ratios of CA and xylan from 1.8 to 3.6 and then no increase at the CA/xylan weight ratio up to 4.8.

Table 1
Influence of the CA/xylan weight ratio on the extent of reaction.

The weight ratio[a]	Yield (%)	Carboxyl content (meq/100 g)	DE (%)
1.8	118.9	585.7	29.5
2.4	130.0	673.5	35.2
3.0	141.2	643.0	39.9
3.6	123.9	702.9	43.2
4.8	101.5	700.8	43.2
Xylan	–	180.1	–

[a] The weight ratio of CA and xylan.

To further study the esterification, the percent esterification was determined by titration. The percent esterification is the percentage of the reacted hydroxyl groups relative to the total initial hydroxyl groups. An increment in the weight ratios of CA and xylan from 1.8 to 3.6 corresponded to result in an increase in percent esterification from 29.5% to 43.2% (Table 1). Further increasing the CA/xylan weight ratios, no obvious increase occurred. The change trend of percent esterification is similar to that of carboxyl group content, due to the occurrence of the esterification and crosslinking reaction. So the CA/xylan weight ratio of 3.6 was the desirable value.

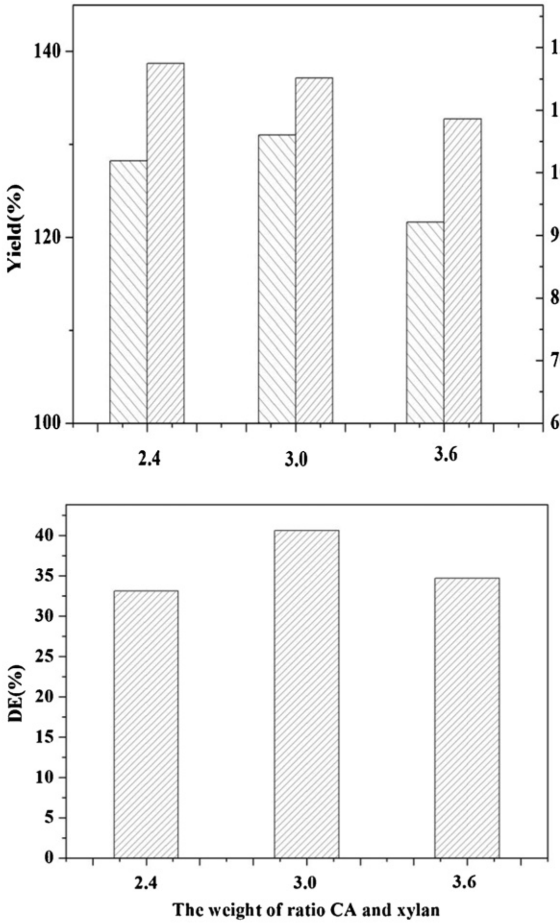

Fig. 2. The effect of weight ratios of CA and xylan on the yield, carboxyl group content and degree of esterification of xylan citrate.

3.3. *The reaction of xylan with CA in the absence of catalyst*

Under the same reaction condition depicted above, the influence of different weight ratios of CA to xylan on the extent of reaction in the absence of SHP is shown in Fig. 2. Obviously the percent yield of xylan citrate first increased and then decreased with increase in the CA/xylan weight ratios from 2.4 to 3.6. However, for the values of carboxyl group content slightly decreased with an increment in CA/xylan weight ratios from 2.4 to 3.6. The maximum value of the carboxyl group content was 1174.3 meq/100 g at the CA/xylan weight ratio of 2.4. For the percent esterification, the reverse trend was present. In the absence of catalyst, the esterification was the main reaction, so the carboxyl group content was enhanced greatly. While in the presence of SHP, the prevailing crosslinking reaction resulted in low carboxyl group content.

3.4. *Adsorption experiment*

As expected, xylan citrate was not dissolved in distilled water at room temperature or high temperature even under stirring condition. Table 2 shows the water adsorption, copper binding and methyl orange adsorption of xylan and xylan citrate. Obviously, a significant increase in water adsorption as well as copper binding and methyl orange capacity was shown for xylan citrate, compared to xylan. This was due to the increment of carboxyl groups in the xylan citrate. Significantly, increasing carboxyl group content, the absorption capacity increased. Furthermore, the absorption capacity of xylan citrates prepared without the addition of SHP was higher than that with the addition of SHP, which can be explained that the addition of SHP caused the relatively low carboxyl group content of xylan citrate mainly due to the dominant crosslinking reaction, and further influenced the absorption capacity. For removal of methyl orange from the aqueous solution, this study only discussed the adsorption of methyl orange of xylan citrate obtained without SHP because of high carboxyl group content on xylan citrate.

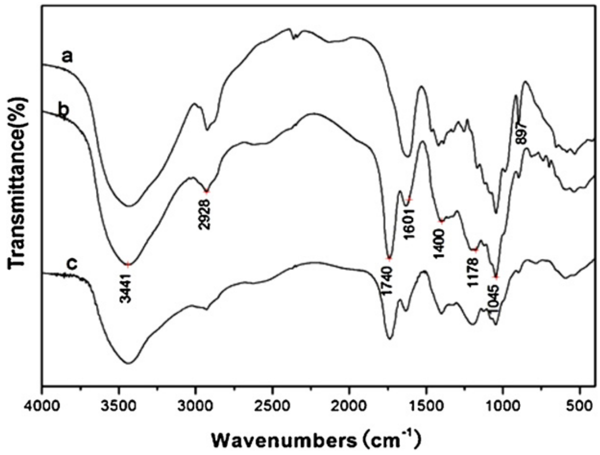

Fig. 3. FTIR spectra of xylan (a), xylan citrate samples prepared at the CA/xylan weight ratio of 2.4 (b) in the presence of SHP and 2.4 (c) in the absence of SHP.

3.5. *FTIR spectra*

The FTIR spectra were used to confirm the changes in the structure of xylan before and after modification and to determine the esterification process between xylan and citric acid, which is shown in Fig. 3. For the unmodified xylan, the absorptions at 3450, 2933, 1466, 1414, 1248, 1163, 1043, 987 and 897 cm^{-1} seen in spectrum a are indicative of xylan (Fang, Sun, Tomkinson, & Fowler, 2000). A sharp band at 897 cm^{-1} is assigned to β-glucosidic linkages between the sugar units, indicating that the xylose residues forming the backbone of the macromolecule are linked by β-form bonds. The low intensity of the band at 987 cm^{-1} suggests the presence of arabinosyl units, which are attached at position 3 of the xylopyranosyl constituents (Ebringerova, Hromadkova, Alfoldi, & Berth, 1992). The region between 1466 and 1044 cm^{-1} relates to the C—H and C—O bond stretching frequencies. The band range from 3200 to 3400 cm^{-1} corresponds to the vibration stretching of inter- and intramolecular hydrogen bonds of xylan. A symmetric C—H vibration band is at 2933 cm^{-1}.

Comparatively, a signal at 1601 cm^{-1} is ascribed to the COO^{-} group in carboxymethyl hemicelluloses (Bajpai & Shrivastava, 2005). The band around 1400 and 1328 cm^{-1} are assigned to CO stretching and OH bending vibration on —COOH groups, respectively. Moreover, the peak was observed at around 1740 cm^{-1} which is indicative of ester group (carbonyl groups) in spectra b and c, indicating that citric acid was grafted on the chain of xylan. That identification had been reported by Shi et al. (2007). In addition, the absorption bands at 3449 cm^{-1} decreased, which was due to the conversion of hydroxyl to esters.

3.6. *Thermal analysis*

In thermogravimetric analysis, the loss in mass due to volatilization of the degradation products was monitored as a function of temperature. The thermogravimetric behavior of xylan reacted with citric acid was evaluated with a 10 °C/min heating rate under nitrogen, which is illustrated in Fig. 4. A slight weight loss was attributed to water evaporation below 100 °C. However, the weight

Table 2
Effect of the weight ratio of CA/xylan in the presence or absence of SHP on the water absorption, copper binding and methyl orange removal.

The weight ratio[a]	Catalyst	Water adsorption (%)	Copper (mg/g)	Methyl orange (mg/g)
2.4	SHP	491.8	41.4	–
3.0	SHP	367.5	38.7	–
3.6	SHP	321.9	36.9	–
2.4	–	778.9	74.8	1.02
3.0	–	826.0	80.4	0.93
3.6	–	691.7	83.8	1.69
Xylan	–	224.1	11.4	$\ll$0.1

[a] The weight ratio of CA and xylan.

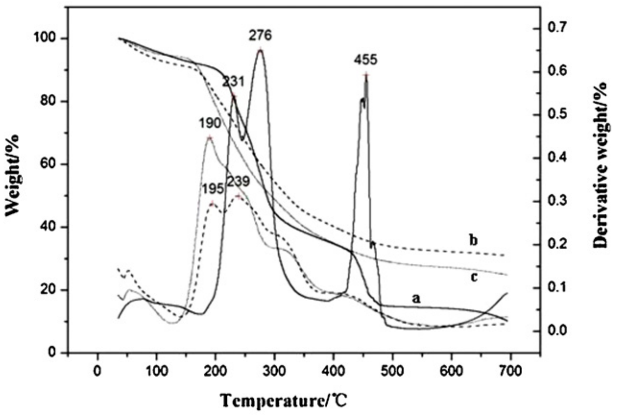

Fig. 4. TG/DTG curves of xylan (a) and xylan citrate samples obtained at the CA/xylan weight ratio of 3.0 in the presence of SHP (b) and in the absence of SHP (c).

loss above 100 °C was caused by the thermal decomposition of samples. The temperatures at 10% weight loss were 212 °C, 178 °C and 167 °C for xylan (a) and xylan citrates obtained with CA/xylan weight ratio of 3.0 in the absence of SHP 3.0 (c) and in the presence of SHP (b), respectively. At 40% weight loss, the decomposition temperatures of xylan and xylan citrates were 273 °C (a), 257 °C (c) and 278 °C (b), respectively. While at 50% weight loss, it corresponded to 282 °C (a), 323 °C (c) and 293 °C (b), respectively, which means that the thermal stability of xylan citrate was higher than xylan at above 270 °C. Importantly, xylan citrate having high degree of cross-linking had higher thermal stability than that with low cross-linked degree. While temperature was below 260 °C, xylan had higher thermal stability than xylan citrate maybe due to unstable carboxyl groups on xylan citrate. The remainder weights at 700 °C were 10% (a), 23% (c) and 33% (b) for xylan and xylan citrates, respectively. The increase residual mass after heating to 600 °C for xylan citrate indicated that the crosslinking is altering the degradation process relative to xylan. The adsorption capacity of xylan citrate containing more carboxyl groups was higher.

In DTG curves, three exothermic peaks corresponding to the maximum weight loss rate were present at 231, 276 and 455 °C for xylan, while at 195 and 239 °C for xylan citrate obtained in the addition of SHP and a maximum exothermic peak at 190 °C for xylan citrate prepared without SHP, which indicated a significantly decrease of thermal stability because of the alteration in chemical structure of xylan. There was no large difference between the samples prepared in the presence and absence of SHP.

4. Conclusion

The novel and degradable xylan citrates with high carboxyl group content, which are potential resource of absorbents for removal of metal ions or methyl orange in the aqueous solution, were successfully prepared by the semi-dry oven method. The factors such as the weight ratio of citric acid to xylan and the addition of SHP showed remarkable influence on the reaction efficiency. The yield, carboxyl group content and degree of esterification of xylan citrate were significant to a large extent increase relative to unmodified xylan. The product yield of 128.2%, the carboxyl group content of 1174.3 meq/100 g and degree of esterification of 33.1 were achieved at the citric acid/xylan weight ratio of 2.4. It was found that an important enhancement in water adsorption as well as copper binding and methyl orange absorption capacity was shown for xylan citrate, compared to xylan which was due to the increment of carboxyl group content in the xylan citrate. Significantly, increasing carboxyl group content, the absorption capacity of xylan citrate increased. The next work will be focused on the blends of xylan citrate with native biomacromolecules such as gelatin and chitosan at high temperature to form bio-adsorbents for further improving absorption, which can be applied in the removal of metal ions and methyl orange from waste water.

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