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Homogeneous acylation of xylan with 3,5-dinitrobenzoyl in ionic liquid and the adsorption property

Weiqing Kong [a], Qingqing Dai [a], Junli Ren [a,*], Nianfang Ma [b]

[a] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China
[b] Biomaterials Research Center, Guangzhou Sugarcane Industry Research Institute, Guangzhou, China

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ABSTRACT

A new xylan ester (xylan 3,5-dinitrobenzoate) as a creatinine adsorbent was prepared by the homogeneous acylation of xylan with 3,5-dinitrobenzoyl chloride in 1-butul-3-methylimidazolium chloride ionic liquid. The influences of reaction conditions on the degree of substitution values of xylan esters were discussed. Results indicated that xylan esters with the degree of substitution range from 1.34 to 1.77 were obtained under the given conditions. The FTIR and ^{13}C NMR spectroscopies provided the evidence of grafting 3,5-dinitrobenzoyl groups onto the backbone of xylan. Moreover, the adsorption properties of the xylan ester for creatinine were also investigated. Isotherm studies showed that the sorption capacities for creatinine were 2.45, 2.08 and 1.86 mg/g for 23, 30 and 37 °C, respectively. Thermodynamic studies performed indicated the sorption process mainly was controlled by the chemical adsorption. Therefore, xylan 3,5-dinitrobenzoate displayed the promising application in the treatment of chronic renal failure by the creatinine adsorption as the new oral adsorbent.

1. Introduction

Biomass, regarded as the abundant, inexpensive, and readily available natural organic resource, has been intensely investigated as a promising candidate for the production of bioenergy, novel biopolymers, and functional biomaterials. Xylan-type hemicelluloses, as the second most abundant biopolymers in the primary and secondary layers of the plant cell wall, are considered to be renewable and inexhaustible resources for the production of biomaterials. Because of their good biodegradability, easy availability, biocompatibility, renewability, and great mechanical properties (Ebringerová & Heinze, 2000; Saha, 2003), increasing emphasis has been placed on converting hemicelluloses to biodegradable and functional materials and polymers (Lindblad, Ranucci, & Albertsson, 2001).

Ionic liquids (ILs), as green solvents or catalysts for the production of bio-based materials and bioenergy from lignocellulosic biomass, have received increasing attentions in the field of green chemistry (Ray, Mittal, & Chung, 2011; Ståhlberg, Sørensen, & Riisager, 2010; Sun, Li, Yuan, Xu, & Sun, 2012) due to their unique properties. Therefore, ILs as green solvents is expected to be the ideal media for the production of high-value added chemicals and bio-based materials based on hemicelluloses. But so far, the study on ionic liquids as the solvents to dissolve xylan-type hemicelluloses and as the homogeneous reaction media is very limited (Ayoub, Venditti, Pawlak, Sadeghifar, & Salam, 2013; Hansen & Plackett, 2011; Peng, Ren, & Sun, 2010; Peng, Ren, Zhong, & Sun, 2011; Ren, Peng, Peng, & Sun, 2013; Wang et al., 2012; Zhang, Yuan, Xu, & Sun, 2013). The ideal degree of substitution (0.21–1.53) of modified hemicelluloses had been achieved in a short period of time (30–120 min) by the acetylation of hemicelluloses with acetic anhydride (Ayoub et al., 2013; Ren, Sun, Liu, Cao, & Luo, 2007), by the esterification of hemicelluloses with maleic anhydride (Peng et al., 2010) and succinic anhydride (Hansen & Plackett, 2011; Peng et al., 2011) in ionic liquids. These encouraging results imply that ionic liquids have great potential as green solvents to prepare functional biomaterials from xylan-type hemicelluloses.

Xylan-type hemicelluloses have free hydroxyl groups which can be used for further functionalization. In recent years, many different kinds of xylan-based function materials have been developed such as films (Luo, Pan, Ling, Wang, & Sun, 2014; Wang et al., 2014), hydrogels (Peng, Zhong, Ren, & Sun, 2012), cationic hemicelluloses (Kong, Ren, Wang, Li, & Sun, 2014; Petzold, Schwikal, Günther, & Heinze, 2005; Schwikal & Heinze, 2007; Schwikal, Heinze, Ebringerová, & Petzold, 2005), carboxymethyl hemicelluloses (Gulati, Park, Maken, & Lee, 2014; Peng, Ren, Zhong, Cao, &

* Corresponding author. Tel.: +86 20 87111861; fax: +86 20 87111861.
E-mail address: renjunli@scut.edu.cn (J. Ren).

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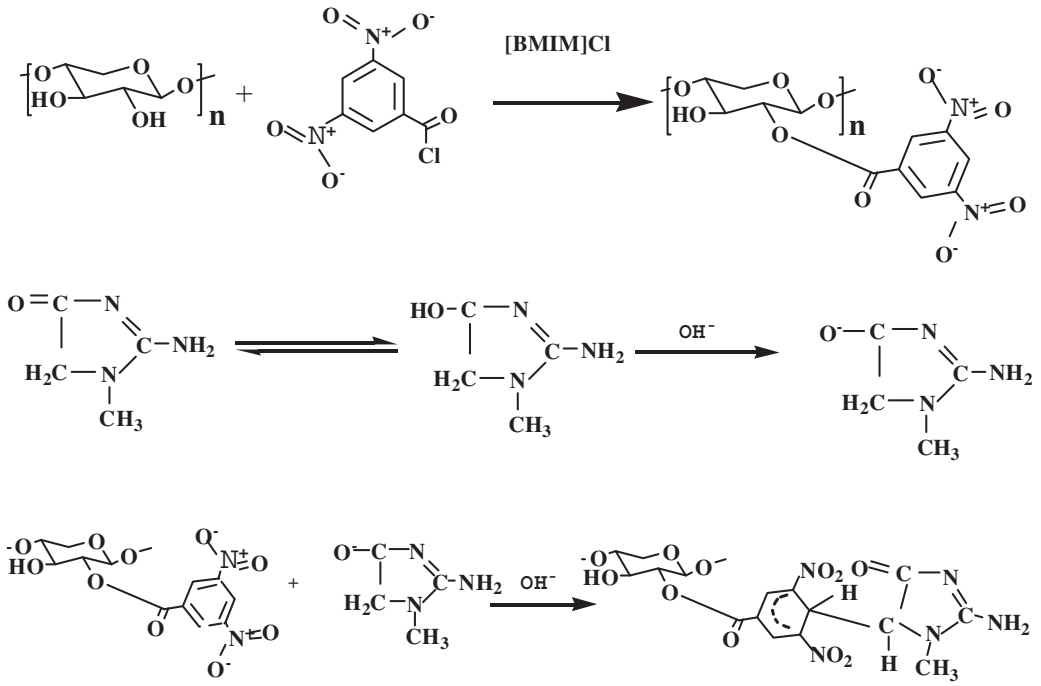

Scheme 1. Reaction scheme of DNBZ-Cl with the hydroxyl groups of xylan in ionic liquids and the adsorption mechanism of creatinine.

Sun, 2010, Petzold, Schwikal, Günther, & Heinze, 2005), oleoylated hemicelluloses (Sun, Sun, & Sun, 2004), lauroylated hemicelluloses (Ren, Xu, Sun, Peng, & Sun, 2008), acetylated hemicelluloses (Fang, Sun, Fowler, Tomkinson, & Hill, 1999; Ren et al., 2007), ε-caprolactone-grafted hemicelluloses (Zhang, Chen, Liu, & Sun, 2014). These xylan-based materials have been found to have a variety of applications as functional biomaterials. Particularly, the biological activity of xylan-type hemicelluloses has attracted great attention in medicine and biology fields. It is reported that xylan-type hemicelluloses can inhibit cell mutation and have some functions such as detoxification, anti-inflammatory and anticancer (Barbat et al., 2008; Oliveira et al., 2010). Xylan-type hemicelluloses are not degraded in the stomach and the small intestine of the body, but can be degraded in the colon (Oliveira et al., 2010). Those striking features of xylan provide the high availability for the preparation of medicinal materials with biological activity. However, there are few reports on xylan-based medicine materials.

Creatinine is one of the primary toxins in patients with chronic renal failure (CRF) (Dietrich, Marletta, & Kenyon, 1980). Oral adsorbent can reduce the creatinine concentration in gastrointestinal tracts. It is significance for biomass adsorption to replace the conventional technologies to remove creatinine. Currently, many different kinds of biomass adsorption have been developed (Wang & Yu, 2003; Yu, Wu, Wang, & Ma, 2007; Yu & Yang, 2003a, 2003b). However, there has been no report about xylan-based adsorbent to removal creatinine in the medical application.

In view of these facts mentioned above, in this study, the homogeneous acylation of xylan-type hemicelluloses with 3,5-dinitrobenzoic acid chloride (DNBZ-Cl) in 1-butul-3-methylimidazolium chloride ([BMIM]Cl) ionic liquid firstly were discussed and the resulting products (xylan 3,5-dinitrobenzoate) were employed as new adsorbents for the removal of creatinine (Scheme 1). The effects of reaction conditions including reaction time, temperature and the molar ratio of 3,5-dinitrobenzoyl chloride to anhydroxylose units in xylan on DS of xylan 3,5-dinitrobenzoate were discussed. The physicochemical properties of obtained products are characterized by elemental analysis, Fourier transform infrared (FTIR) and ^{13}C nuclear magnetic resonance (NMR) spectroscopies. The surface morphological differences were monitored by scanning electron microscopy (SEM). The adsorption capacity of xylan 3,5-dinitrobenzoate for creatinine was investigated by varying the adsorption conditions such as contact time, contact temperature, initial concentration of creatine and pH value. In addition, isotherm and thermodynamic studies were conducted to evaluate their adsorption capacity.

2. Experimental

2.1. Materials

Xylan (M_w of 130,000 g mol^{-1}) from beech wood with xylose residues of greater than 90% was obtained from Sigma–Aldrich (Taufkirchen, Germany). [BMIM]Cl ionic liquid was obtained from Lanzhou Greenchem ILS, LICP. CAS (Lanzhou, China). 3,5-Dinitrobenzoic acid chloride (DNBZ-Cl) and creatinine were obtained from Aladdin Reagent Co. (Shanghai, China). Silver nitrate was provided by Shenzhen Bolinda Technology Co., Ltd. (Shenzhen, China). Absolute ethyl alcohol was provided by Guangzhou Chemical Reagent Factory (Guangzhou, China). All chemicals were analytically pure and used without further purification.

2.2. Preparation of xylan 3,5-dinitrobenzoate in [BMIM]Cl ionic liquid

A series of xylan 3,5-dinitrobenzoate was prepared in [BMIM]Cl by varying the ratio of DNBZ-Cl to xylan, reaction temperature and time (Table 1). 0.33 g of dry xylan (0.005 mol of hydroxyl groups in xylan) and 10.0 g of [BMIM]Cl were added into a 250-mL three-neck flask. The mixture was stirred at 90 °C for 5 h to get a homogeneous solution under the nitrogen atmosphere. A required quantities of DNBZ-Cl was added, followed by heated to the temperatures in a range of 90–110 °C for a desired time. The mixture obtained was precipitated with 100 mL of 80% (v/v) ethanol aqueous solution under stirring for 60 min and then centrifuged at 3000 rpm for 20 min. The precipitate was washed repeatedly by stirring in 100 mL of 80% (v/v) ethanol aqueous solution until there was no