



Cellulose extraction from *Zoysia japonica* pretreated by alumina-doped MgO in AMIMCl



Le Liu, Meiting Ju*, Weizun Li, Yang Jiang

College of Environmental Science and Engineering, Nankai University, Tianjin 300071, PR China

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ABSTRACT

In this study, alumina-doped MgO was produced as a solid alkali for lignocellulose pretreatment. Pretreatment with alumina-doped MgO disrupted the lignocellulose structure and significantly reduced the lignin content of the *Z. japonica*. After pretreatment, *Z. japonica* showed significant solubility in 1-allyl-3-methylimidazolium chloride (AMIMCl). The similar high solubility of pretreated *Z. japonica* samples by original alumina-doped MgO and used alumina-doped MgO also proved that alumina-doped MgO had strong stability, which can be recycled and used repeatedly. The regenerated cellulose was similar to microcrystalline cellulose according to FTIR and NMR analyses. Compared to microcrystalline cellulose, only the crystallinity of the regenerated cellulose decreased.

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1. Introduction

In China, the “National Long-Term Science and Technology Development Plan (2006–2020)” points out that agricultural biomass is one of the key development areas. Plants, which produce 100 billion tons of cellulose through photosynthesis annually (Zhu et al., 2006), are regarded as an inexhaustible and renewable resource. Plant-derived cellulose is widely used in the textile, chemical, pharmaceutical, and energy industries because it does not contribute to pollution and is biocompatible, biodegradable, and abundant (Zhang, Lv, & Luo, 2011). Moreover, agricultural solid wastes can be used as important lignocellulosic feedstock (Heinze & Liebert, 2001; Zhu et al., 2006). Although the biochemical conversion of biomass into energy and industrial raw materials has significant technical and economic potential, lignocellulosic biomass is naturally resistant to chemical degradation. This resistance is due to various physical and chemical factors, such as the presence of lignin, the crystallinity of cellulose, and the presence of covalent cross-linkages between lignin and hemicelluloses in the plant cell wall (Li et al., 2010). Cellulose is a linear homopolymer of $\beta(1\rightarrow4)$ -linked D-glucopyranose units that may aggregate to form a highly ordered structure. The chemical constitution and spatial conformation of cellulose account for its aggregation tendencies

(Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998; Oh et al., 2005).

Various pretreatment techniques were used to enhance the breakdown of lignocellulosic biomass. However, these technologies commonly use soluble acidic or basic chemicals and result in pollution. Therefore, these chemicals must be recycled, and complex waste-water treatment systems are indispensable in this process. To solve these problems, a novel pretreatment method with a recoverable solid alkali was studied. In the present process of biomass utilization, the removal of lignin is a key step. Cellulose and some hemicellulose are separated from the lignocelluloses through the removal of lignin, and then are hydrolyzed and transformed. But the present methods of lignin removal mainly use chemicals to provide an alkaline condition. These chemicals will result in pollution. Therefore, this study tries to use an insoluble Mg-based solid alkali instead of the soluble alkali to provide a new delignification medium condition. Many types of solid alkalis have been investigated in trans-esterification reactions in the biodiesel or other industries (Sun et al., 2010), including alkali and alkali earth metal oxides (Ebiura, Echizen, Ishikawa, Murai, & Baba, 2005), calcined hydrotalcites (Cantrell, Gillie, Lee, & Wilson, 2005; Xie, Peng, & Chen, 2006), zeolites (Peterson & Scarrah, 1984) and anion exchanged resins (Leclercq, Finiels, & Moreau, 2001). Solid alkali was used for lignocellulosic materials pretreatment in recent years. In 2002, Pang et al. introduced a novel method of cooking corn stalk with solid alkali and active oxygen for pulp production (Pang et al., 2012). Studies also reported that solid alkali was used as a catalyst for lignin degradation and polyurethane synthesis (Sun, 2012; Wang, 2012).

* Corresponding author at: College of Environmental Science and Engineering, Nankai University, 94 Weijin Street, Tianjin 300071, China. Tel.: +86 13672031215.
E-mail addresses: jumeit@nankai.edu.cn, yingying0913@126.com (M. Ju).

Ionic liquids, known as low-temperature molten salts or designable solvents, have been recognized to comprise a new kind of green solvent (Deng, 2003). They offer various advantages that allow them to be widely used in chemical synthesis, extraction and separation, materials preparation, and other fields. Ionic liquids consist solely of cations and anions that are present in liquid form at or near room temperature. Ionic liquids have unique physical and chemical properties, such as low melting point (up to 173 K), higher solubility, and designable selective dissolution (Benoit, Peter, & Moreau, 2004). In 2002, Rogers et al. first reported the solubility of natural cellulose in a series of ionic liquids such as 1-butyl-3-methylimidazolium chloride (BMIMCl) (Swatloski, Spear, Holbrey, & Rogers, 2002). BMIMCl is a nonvolatile, strong solvent for cellulose and is easily recovered after processing. These attributes prompted further research on the regulation and design of cation–anion structures to obtain new types of ionic liquids with superior properties. In 2003, Ren et al. introduced the allyl group to the cationic structure of an ionic liquid to prepare 1-allyl-3-methylimidazolium chloride (AMIMCl), which has excellent solvent properties (Ren, Wu, Zhang, He, & Guo, 2003).

In the present study, alumina-doped MgO is used as a solid alkali, having a weak solubility in water, which can be reused by calcinations after recycling from the cooking effluent. *Zoysia japonica* was pretreated by alumina-doped MgO in a stainless reactor. We focused on the dissolution of pretreated samples in AMIMCl upon ultrasonic treatment. The regenerated cellulose was characterized by Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) analyses. This paper provides the necessary theoretical basis for the application of solid alkali for utilization of biomass feedstock resources.

2. Materials and methods

2.1. Materials

Samples of *Z. japonica* were collected from agricultural fields in Tianjin in northern China. After drying at 60 °C in an oven for 16 h, the grass samples were ground to particles that pass through a 0.7 mm screen. The fiber components of *Z. japonica* were analyzed according to the Van Soest method, using a FOSS Fibertec 2010 fully automated fiber analysis system. This determination revealed the following composition: lignin, 19.87% (w/w); hemicellulose, 40.86% (w/w); cellulose, 29.71% (w/w). Microcrystalline cellulose was purchased from Serva (Heidelberg, Germany). AMIMCl was synthesized from *N*-methylimidazole and allyl chloride in our laboratory (Liu, Ju, Li, & Hou, 2013). MgO powder (purity 99.95%) and Al₂O₃ powder (purity 99.997%) were purchased from Tianjin Xuanyang (Tianjin, China).

2.2. Preparation of alumina-doped MgO

MgO powder and Al₂O₃ powder were mixed in de-ionized water and then wet ball-milled to decrease the particle size. MgO powder to Al₂O₃ powder ratio was set at 1:9 (w/w). The mixture was then heated for 5 h at 105 °C to remove the water. The powder obtained as a product was isostatically pressed into a rod and then sintered at 550 °C for 6 h to produce the final sample material.

2.3. Pretreatment of *Z. japonica*

Z. japonica was loaded into a stainless reactor charged with 200 mL 50/50 (v/v) water-ethanol co-solvents and treated with alumina-doped MgO for 2 h at 160 °C. The solid alkali to *Z. japonica* ratio was set at 1:10 (w/w). Alumina-doped MgO was used 4 times for *Z. japonica* pretreatment. Measurements were recorded for each pretreatment reaction to assess the activity and stability of

alumina-doped MgO. When the reactor was cooled to room temperature, the mixture was filtered with Buchner funnel to separate pretreated *Z. japonica* from the filtrate. The pretreated *Z. japonica* was washed with deionized water, then filtered through a nylon membrane and air-dried. *Z. japonica* treated with alumina-doped MgO are denoted as follows: Z₁ (*Z. japonica* treated with original alumina-doped MgO), Z₂ (*Z. japonica* treated with solid alkali used for the second time), Z₃ (*Z. japonica* treated with solid alkali used for the third time), and Z₄ (*Z. japonica* treated with solid alkali used for the fourth time). The lignocellulose residual rate and mass loss rate of *Z. japonica* after pretreatment were calculated according to Eqs. (1) and (2):

$$R_{s,i} = \frac{M_{r,i}}{M_{o,i}} \quad (1)$$

$$R_l = 1 - \frac{M_{rZJ}}{M_{oZJ}} \quad (2)$$

where *i* represents cellulose, hemicellulose, and lignin; $R_{s,i}$ is the residual rate; $M_{r,i}$ is the mass of the residual cellulose, hemicellulose, or lignin in the *Z. japonica* sample after pretreatment; $M_{o,i}$ is the mass of cellulose, hemicellulose, or lignin in the original *Z. japonica* sample; R_l is the mass loss rate; M_{rZJ} is the mass of the residual *Z. japonica* sample after pretreatment; M_{oZJ} is the mass of the original *Z. japonica* sample.

Organic solvents in the filtrate were removed with an evaporator under reduced pressure at 40 °C and water was further evaporated at 60 °C. The remaining oily product was vacuum dried at room temperature overnight to remove the residual water and defined as degraded *Z. japonica* (DZ, water-ethanol soluble fraction).

2.4. Dissolution of cellulose

The dissolution of *Z. japonica*, pretreated *Z. japonica* and MCC samples in AMIMCl under an argon atmosphere were investigated. For the dissolution process, 2.00 g of sample was added to 50.00 g of ionic liquid (Li, Ju, Wang, Liu, & Jiang, 2013). The mixture was placed in a KQ3200DE ultrasonic oscillator with ultrasonic power 110 W at 80 °C for 30 min (Liu et al., 2013). The remaining insoluble residue was filtered under vacuum using a 60 mL G3 sand-core bush funnel. The resulting filtrate containing the cellulose was collected

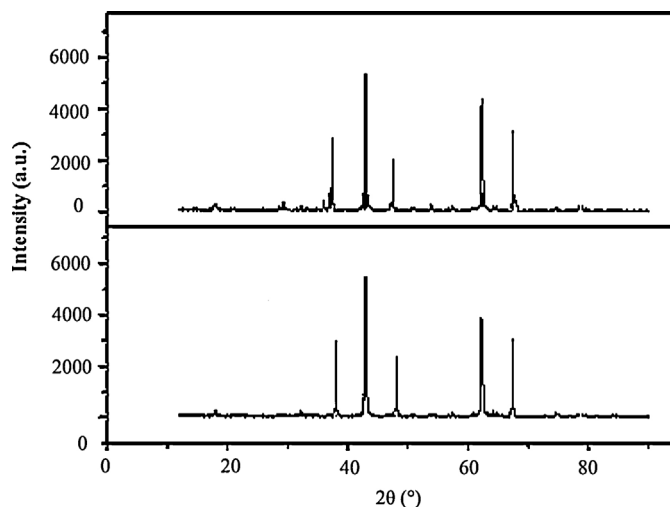


Fig. 1. XRD spectra of alumina-doped MgO (A) and the solid alkali used for the fourth time (B).

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