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The effect of surfactant-assisted ultrasound-ionic liquid pretreatment on the structure and fermentable sugar production of a water hyacinth

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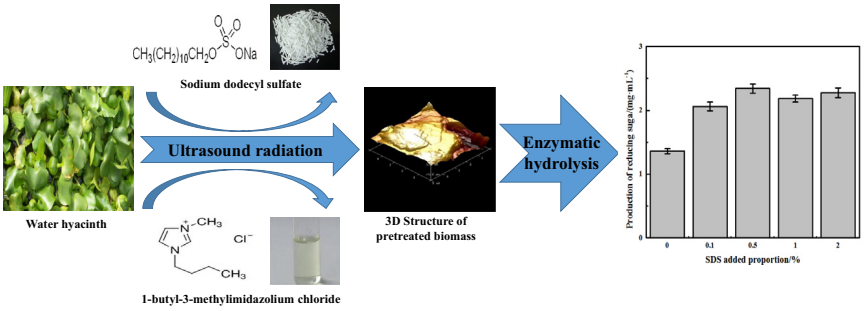
HIGHLIGHTS

- SDS was firstly utilized with US-IL for the pretreatment of WH.
- The cellulose conversion rose by 58% after adding the SDS.
- SDS addition increased delignification by 21% compared with US-IL pretreated WH.
- The hydrophilic ability of WH was improved by the addition of SDS.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated the possibility of enhancing the disruption of water hyacinth (WH) in an ultrasound-ionic liquid (US-IL) pretreatment assisted by sodium dodecyl sulfate (SDS). 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) was used to dissolve the WH. The optimum concentration of SDS for the highest production of reducing sugar was also determined. Compared to the US-IL pretreatment, the production of reducing sugars, cellulose conversion and delignification were increased by 72.23%, 58.74% and 21.01%, respectively, upon addition of 0.5% SDS. Moreover, the enhancement of SDS in the US-IL pretreatment was confirmed by the analysis of structural features, which demonstrated that the SDS increased the removal of lignin and decreased the cellulose crystallinity.

1. Introduction

Water hyacinth is a non-native and invasive aquatic weed and has an extraordinary adaptive ability in various water bodies, covering the surfaces of lakes and rivers due to its remarkable growth rate and high reproductive capacity. Currently, it is recognized as a nuisance to water quality and aquatic ecosystems owing to the depletion of dissolved oxygen in the water as a result of its growth spurts (Rezania et al., 2015). However, some studies have indicated that WH is promising lignocellulose resource for the production of biofuel, given its high carbohydrate content and propagation rate (Das et al., 2015; Rezania et al., 2015; Xu et al., 2016). Therefore, this may prove to be an efficient way not only to dispose of the WH biomass at low cost after collection from the water but also to abate the environmental problems caused by the uncontrolled growth of the problematic weed.

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Unfortunately, the rugged structure of natural lignocellulose prevents the enzyme from accessing the polysaccharides which decreases the sugar yield of enzymatic saccharification. Thus, pretreatment to disrupt the sturdy construction is required to enhance the efficiency of enzymatic hydrolysis. Ionic liquid (IL), which was first reported to be capable of dissolving cellulose in 2002, has been widely applied in biomass pretreatment (Gao et al., 2013; Swatloski et al., 2002; Xu et al., 2016). The dissolution of cellulose is based on the breakdown of inter- and intra-molecular hydrogen bonds of cellulose chains and the formation of new hydrogen bonds between the hydroxyl present in cellulose and the anions of the IL (Badgujar and Bhanage, 2015). After adding the anti-solvents, such as water, the dissolved cellulose can be easily regenerated from the IL-cellulose mixture. This dissolution-reprecipitation process effectively breaks down the matrix of a cross-linked three dimensional polysaccharide network by removing the lignin and increasing the porosity of the cellulose.

To accelerate the dissolution of cellulose in IL, several studies have combined ultrasonic irradiation with the IL pretreatment (Montalbo-Lomboy and Grewell, 2015; Ninomiya et al., 2015; Yang and Fang, 2015). Ultrasound (US), which consists of mechanical acoustic waves over a frequency range of 20 kHz to 500 MHz, imparts high energy to the reaction medium by acoustic cavitation and secondary effects. The acoustic effect is the phenomenon of the production of numerous micro-bubbles in the medium, which causes rarefaction, or a negative pressure, to be applied to the liquid. The collapse of bubbles leads to microjets that move at a high speed towards solid surfaces and local hotspots with extremely high temperature and pressure, which facilitate mass transfer and chemical reactions (Luo et al., 2014; Montalbo-Lomboy and Grewell, 2015). Recently, Yang and Fang (2015) combined IL with ultrasonic bath processing in rice hulls, whereas Ninomiya et al. (2015) have reported that ultrasonically treated bamboo powder using sonotrode exhibited a lower crystallinity than powder treated using conventional heating. To achieve further reductions in the pretreatment time for the ultrasonic process, Montalbo-Lomboy and Grewell (2015) used a bench scale ultrasonic unit with a maximum power of 2.2 kW to pretreat switchgrass in IL. The results showed a delignification of 50.8% for the ultrasonic assisted sample using a 160 μm amplitude over 4 min, which was slightly lower than 53% delignification achieved for a 24 h heated sample. Although the US-IL combination has the advantages mentioned above, the most important challenge is how to balance the acoustic power delivered to the reaction medium. It is difficult to cause cavitation for low power levels, whereas high energy loading can cause partial degradation of the IL, making it difficult to implement the recycle process (Chatel and MacFarlane, 2014). Therefore, it is necessary to determine another way to enhance the reaction associated with the US-IL pretreatment.

Other studies have shown that liquid with a low surface tension can produce favorable conditions for cavitation (Luo et al., 2014; Montalbo-Lomboy and Grewell, 2015). Interestingly, surfactants containing both hydrophobic and hydrophilic groups can decrease the surface tension between the two phases (Sindhu et al., 2013). Some studies have also demonstrated that cavitation in aqueous solutions exposed to an ultrasound field will increase after adding a surfactant, such as sodium dodecyl sulfate (SDS), Triton® X-10 and NCW®-1002 at certain concentrations (Keswani et al., 2013; Lee et al., 2005). However, this also results in synergistic effects between the surfactants and IL in dissolving the lignocellulose (Chang et al., 2016; Sindhu et al., 2013). To the best of our knowledge, there have been no reports on the combination of surfactants and the US-IL treatment to enhance subsequent enzymatic hydrolysis.

Here, we describe a novel pretreatment technique that uses SDS as an additive reagent to assist the US-IL pretreatment to degrade WH. The optimum pretreatment conditions were also determined as part of the study. Moreover, to investigate mechanisms that may improve the process efficiency, the structural features of WH treated with or without SDS as part of the US-IL pretreatment method and conventional heating were analyzed using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and atomic force microscopy (AFM).

2. Materials and methods

2.1. Lignocellulosic material and reagents

Water hyacinth stems and leaves were obtained from the higher education Mega center in Guangzhou, Guangdong province, China. These stems and leaves were washed with tap water to remove any accumulated dirt, dried at 60 °C for 48 h, pulverized (Taisete FW100, China) and passed through a size 40 mesh. The ionic liquid [BMIM]Cl (purity ≥ 99%) and SDS (purity ≥ 65%) were purchased from Monils Chem. Eng. Sci & Tech. Co. Ltd., China, and China Titans Eng. Tech. Group Co. Ltd., China, respectively. All the experiments except pretreatment were performed in duplicate under the same conditions with the average values reported here.

2.2. Ionic liquid pretreatment

A mass of 0.25 g of WH power was added to a 20 mL corning tube containing 5 g of [BMIM]Cl. The WH/IL mixture in the tube was then heated to 130 °C in an oil bath using continuous magnetic stirring (Yuhua DF-101S, China) for 0–120 min.

2.3. Ultrasound-Ionic liquid pretreatment

Masses of 0.25 g of WH powder, 5 g of [BMIM]Cl and 0–2% (W/W, based on the weight of [BMIM]Cl) SDS were mixed in the tube same with the IL pretreatment. The tube was submerged in an oil bath at a temperature maintained at 120 °C (Yuhua DF-101S, China). Immediately, a titanium probe tip (3 mm in diameter) ultrasonic processor (Scientz JY88-IN, China) was inserted to a half height depth into the mixture. The solution was sonicated for 15–60 min at a frequency of 20 kHz, an emission power of 100 W and a pulsing cycle of 15 s on/15 s off. All pretreatment mentioned above were repeated for three to six times to prove its repeatability and generated enough samples for following analysis.

2.4. Enzymatic hydrolysis

A total of 1% (W/V) pretreated and untreated WH was suspended in 0.05 M sodium citrate buffer (pH 4.8) with 0.02% sodium azide, a cellulose complex (Novozyme NS220086, 250 FPU mL^{-1}) enzyme load of 50 FPU/g-solid substrate and a β-glucosidase (Novozyme NS221118, 320 CBU mL^{-1}) enzyme load of 40 CBU/g-solid substrate, respectively. The regenerated WH was hydrolyzed in a horizontal shaker incubator for 48 h at a constant temperature of 50 °C and an agitation rate of 150 rpm. A sample was collected at 0 h and 48 h, boiled at 100 °C for 5 min and centrifuged (10000 rpm). The reducing sugar was determined via the 3,5-dinitrosalicylic acid method (Miller, 1959).

3. Result and discussion

3.1. Effect of pretreatment time on enzymatic hydrolysis

As shown in Fig. 1, the production of reducing sugar increased with the pretreatment time from 0 to 45 min during the IL and US-IL pretreatment. However, it remained constant or slightly decreased after 45 min, likely because most of the easily dissolved

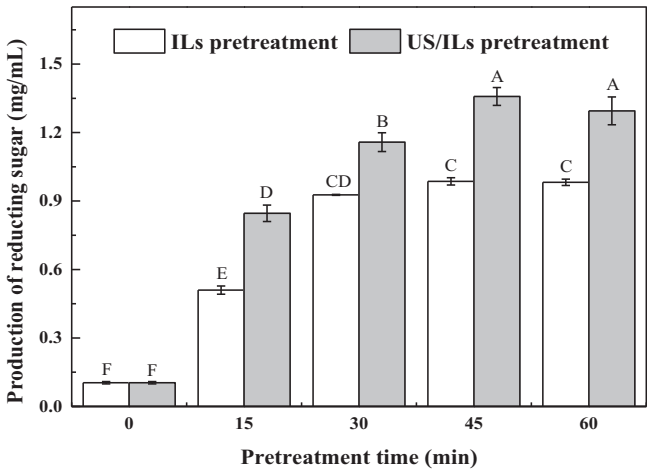

Fig. 1. The effect of time on enzymatic hydrolysis of the water hyacinth during the IL or US-IL pretreatments. *The different letters above the bars in figure indicate significantly difference at $P \leq 0.05$.

lignocellulose reacted with the IL under the examined conditions. Moreover, the US-IL pretreatment has a higher sugar yield than for the IL, with improvements in the range from 27.73% to 65.88% for 15 to 60 min. To confirm the enhancement associated with the ultrasound irradiation, a 120 min pretreat process with [BMIM]Cl was also conducted. The results showed that the sugar content after hydrolysis is approximately 1.233 mg mL^{-1}, which is 6.5% higher than for the 30 min US-IL pretreatment, but still 9.2% less than the 45 min pretreatment. This finding indicated that IL pretreatment assisted by ultrasound has a positive effect on sugar production during enzymatic hydrolysis compared to the conventional thermal pretreatment with stirring and heating. Ninomiya also reported this result during the pretreatment of kenaf powder using the same method, but at different conditions (Ninomiya et al., 2015). Additionally, the temperature of the WH/IL mixture increased to 130–133 °C after 15–60 min sonication (data not shown).

3.2. Effect of SDS during the ultrasound-ionic liquid pretreatment on enzymatic hydrolysis

The ultrasound-ionic liquid- sodium dodecyl sulfate (US-IL-SDS) pretreatment was conducted adding 0.5–2% SDS in US-IL pretreatment. The temperature of the biomass/IL solution at different SDS concentrations is maintained at 133 °C after 45 min of sonication. The addition of the SDS enhanced the hydrolysis efficiency over the US-IL pretreatment. In particular, the addition of 0.1% SDS has a significant effect compared to not adding SDS. A total of 0.5% added SDS produced the highest sugar concentration (2.339 mg mL^{-1}), which increased by 72.24% in contrast to the US-IL pretreatment for 45 min. When the added SDS proportion was greater than 0.5%, there was not a significant improvement in the sugar production, producing 2.180 and 2.273 mg mL^{-1} reducing sugar at 1% and 2% dose, respectively. The decreased surface tension of the surfactant may enhance the cavitation effect in the IL, which leads to effective lignin removal and crystalline cellulose deconstruction (Luo et al., 2014). However, excessive surfactant may overwhelm the hydrogen bonding capacity of the IL, reducing the efficiency of the US-IL pretreatment (Chang et al., 2016; Sindhu et al., 2013).

3.3. Effect of the pretreatment method on the composition and cellulose conversion

The chemical compositions, cellulose conversion, delignification and recovery of untreated, IL-treated, US-IL-treated and US-IL-0.5% SDS-treated are summarized in Table S1. The composition analysis following another study (Jung et al., 2015), showed that the lignocellulosic composition of the raw WH was 19.63% cellulose, 33.63% hemicellulose and 26.13% lignin, which indicates that more than 20% of the composition are other substances, such as crude protein, ash, etc. Specially, the total lignocellulose content for different pretreatments increased to 84–93%, which was due to the loss of crude protein and other soluble material during pretreatment and washing. Additionally, the process also removed the hemicellulose and lignin by dissolution in the IL, which was confirmed by the decrease in the recovery %. They were 57.15%, 53.60% and 48.31% corresponding to IL-treated, US-IL-treated and US-IL-0.5% SDS-treated biomass. In addition, with the reducing sugar yield being 0.104, 0.986, 1.358 and 2.339 mg mL^{-1}, the cellulose conversion of the WH for untreated, IL, US-IL and US-IL-0.5% SDS pretreatments were 1.76%, 12.77%, 19.22% and 30.51%, respectively. The delignification based on the removal of the lignin and solid recovery was calculated as 49.11%, 57.89% and 70.05% for the IL, US-IL and US-IL-0.5% SDS processes, respectively (see Table S1). As the lignin content decrease, degree of removal difficulty increase due to the hydrophobicity of the lignin. The strong bonds between the C-O-C and C-C linkages connecting the lignin with the cellulose and hemicellulose also play a key part in further delignification. Surfactants added to the pulp as delignifying agents not only reduce the surface tension of the medium and enhance the cavitation, which may break the α-O-4 and β-O-4 linkages between the cellulose and lignin, but also decrease the amount of lignin deposited on the biomass, which induces further lignin removal (Bussemaker and Zhang, 2013; Sindhu et al., 2013). The results showed that the reducing sugar yield, cellulose conversion and delignification increased by 72.23%, 58.74% and 21.01% after adding 0.5% SDS in the US-IL pretreatment method, respectively.

3.4. Characterization of the untreated and pretreated rice straw

3.4.1. X-ray diffractometry

The cellulose crystallinity of the lignocellulose is considered to be a major factor influencing enzymatic hydrolysis. An XRD analysis was conducted to examine the crystallinity of the WH. The results showed that the untreated and treated WH samples displayed a change in the cellulose crystallinity. The intensity of the two peaks corresponding to the (001) and (002) lattice planes of the crystalline cellulose I polymorph were increased for the different pretreatments compared to the raw WH. The increase in the intensity is primarily due to the removal of amorphous components, such as hemicellulose and lignin, as well as the promotion of peeling reactions in the amorphous area (Xu et al., 2016). The increased cellulose content in treated sample listed in Table S1 also explained this result. To determine the change in the crystalline for each pretreatment, the CrI was determined using the XRD spectra. As listed in Table S2, the CrI values were 19.50%, 32.44%, 30.74% and 28.73% for the untreated sample, and the WH treated with IL, US-IL and US-IL-0.5% SDS pretreatments, respectively. These findings show that both of the applications of ultrasonic irradiation and SDS can enhance the deconstruction of the crystalline cellulose in US-IL or US-IL-0.5% SDS pretreatment.

3.4.2. Fourier transform infrared spectrometry

To further understand the mechanisms behind the increases in the enzymatic hydrolysis, changes in the molecular composition of the pretreated WH were examined using FT-IR and compared with those from the untreated WH. Almost the peaks of the samples in untreated, IL and US-IL pretreatment were same. Notably, the characteristic peaks of cellulose and hemicellulose at 1729 (C = O stretching vibration of acetyl groups in hemicellulose), 1368 (C-H bending vibration in cellulose and hemicellulose) and 1060 cm^{-1}

(C-O stretching vibration in cellulose and hemicellulose) became weaker when SDS was added to the US-IL pretreatment. The same tendency was observed from the characteristic peaks of the lignin at 1546 (aromatic skeleton C-C stretching vibration in lignin), 1318 and 1246 cm^{-1} (C-O vibration in the syringyl ring in lignin). Conversely, the peak intensity at 1460 cm^{-1} (asymmetric bending of CH_3 in lignin), which is also related to the lignin increase in the US-IL-0.5% SDS pretreatment compared to the other methods, is due to the formation of methyl that released from the deconstruction of the aromatic skeleton and the syringyl ring in the lignin (Ninomiya et al., 2012). Moreover, the peak at 895 cm^{-1} (C-H deformation vibration in cellulose) moved to lower wave number from the combination of SDS in the US-IL, which implies that the β-glycosidic linkages between the sugar units in the cellulose and hemicellulose were weakened (Zhang et al., 2012).

The TCI and LOI value were calculated based on the FTIR spectra and used for the evaluation of the overall crystallinity of the cellulose. As shown in Table S2, both of the TCI and LOI values slightly decreased in IL pretreatment after application of ultrasound irradiation. It is remarkable that the LOI values exhibited the significant reduction from 0.7133 to 0.6329 after application of SDS in US-IL pretreatment. In addition, the TCI value for WH treated by US-IL was 1.064, being higher than the value of 0.9015 for the US-IL-0.5% SDS pretreatment, which confirms that the SDS has a positive effect on decreasing the crystallinity of the cellulose. However, the TCI of the sample treated by US-IL-0.5% SDS was lower than that of the untreated sample, which was different from both that of the CrI and LOI. Consequently, it is tempting to speculate that there is a violent reaction between the medium and WH after adding the SDS in the US-IL.

3.4.3. Atomic force microscope

AFM micrographs of the untreated and pretreated WH are shown in Fig. S1. The Nanoscope Analysis Software (Version 1.40) was used to process the raw images. As shown in Fig. S1(A), the untreated WH appeared flat and even with a relatively well-oriented ultrastructure. After the US-IL and US-IL-0.5% SDS treatments (Fig. S1(B) and (C)), the surface structure of the WH were observed to be significantly rougher than the untreated sample. Moreover, the structure of the surface of the pretreated WH was uneven and non-uniformly covered with visible microfiber fragments, indicating that the fiber surface was modified after pretreatment. It is clear that after the pretreatment, many substances (i.e., lignin, hemicelluloses and other extractive) were removed from the WH. AFM phase data are sensitive to local hydrophilicity different with the hydrophilic region appearing dark in phase images. In the phase contrast image in Fig. S2, there are much brighter areas in Fig. S2(A); however, the brightness decreases and disperses in Fig. S2(B), meaning that the surface of US-IL-0.5% SDS pretreated is more hydrophilic than that of US-IL pretreated. Carbohydrates are generally more hydrophilic than lignin or extractives. Result shows that the SDS addition improved the hydrophilic ability of WH.

4. Conclusion

SDS, as an additive agent in US-IL, proved to be more effective as a WH pretreatment by increasing the degree of lignin removal and cellulose conversion. The optimal US-IL-SDS pretreatment conditions for WH were [BMIM]Cl added 0.5% SDS at 120 °C for 45 min using 100 W of ultrasonic irradiation. The subsequent enzymatic hydrolysis yielded a maximum of 2.339 mg/mL of reducing sugar. The chemical composition and structural features from the analysis also confirm that the WH pretreated using US-IL and assisted by SDS had a lower lignin content and crystallinity than using the conventional US-IL pretreatment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2017.02.044.

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