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Short Communication

Pretreatment of rice straw by ultrasound-assisted Fenton process

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HIGHLIGHTS

- Fenton's reagent can preferentially degrade hemicellulose and lignin.
- Ultrasound can degrade cellulose, hemicellulose and lignin simultaneously.
- Both ultrasound and Fenton's reagent can increase the surface area of rice straw.
- The highest concentration of reducing sugar was obtained from the U/F-RS.

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ABSTRACT

Fenton's reagent, ultrasound, and the combination of Fenton's reagent and ultrasound were used to pretreat rice straw (RS) to increase its enzymatic digestibility for saccharification. The characterization shows that compared with ultrasound, Fenton's reagent pretreatment was more efficient in increasing the specific surface area and decreasing the degree of polymerization (DP) of RS. The enzymatic hydrolysis results showed that the RS pretreated by ultrasound-assisted Fenton's reagent (U/F-RS), which exhibited the largest specific surface area and the lowest DP value, had the highest enzymatic activity, and the amount of reducing sugar released from U/F-RS at 48 h of enzymatic saccharification is about 4 times as large as that from raw RS and 1.5 times as large as that from Fenton's reagent pretreated RS. The ultrasound-assisted Fenton process provides a reliable and effective method for RS pretreatment.

1. Introduction

Bioethanol produced from lignocellulosic biomass is one of the most promising alternatives for fossil fuels. Currently, the cost of bioethanol production from lignocellulosic biomass is relatively high, largely due to the low yield and high cost of the enzymatic hydrolysis process resulting from the recalcitrant structure of lignocellulose (Zhu et al., 2015). Various pretreatment technologies have been developed to facilitate the enzyme hydrolysis of lignocellulose by converting the recalcitrant lignocellulose to reactive cellulosic intermediates (Rabemanolontsoa and Saka, 2016; Sun et al., 2016). Among the various pretreatment technologies, biological pretreatment is probably the most economical one. Researches have confirmed that in biological pretreatment microorganisms such as brown- and soft-rot fungi could produce cellobiose dehydrogenase to generate OH radicals through Fenton reaction ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^-$) for lignocellulose degradation (Arantes et al., 2012).

Although Fenton-based biological pretreatment bears the advantages of mild reaction conditions and low energy consumption, it is low efficient and time consuming, largely due to the low concentration of OH radicals generated during the pretreatment process. Therefore, intensification of Fenton-based pretreatment of lignocellulose deserve further investigation. The pretreatment of lignocellulose by directly using Fenton's reagent has received great attention recently because it is considered to be an environmentally benign process that does not require high temperature, high pressure and high concentrations of chemicals (He et al., 2015; Jung et al., 2015; Kato et al., 2014).

Recently, the ultrasonic pretreatment of lignocellulose has attracted considerable attention (Zhang et al., 2013). Ultrasound produces its effects mainly through cavitation, and the main chemical effects of cavitation include the decomposition of water molecules into extremely reactive radicals such as ${}^{\cdot}OH$ and ${}^{\cdot}H$, which can aid in cleaving lignocellulose, resulting in decreased crys-

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tallinity of lignocellulose and increased surface area (Velmurugan and Muthukumar, 2012). Cavitation can also introduce physical effects such as intense shear forces, shock waves and microjets, which can also facilitate cleavage of lignocellulose (Bussemaker et al., 2013).

Combinational lignocellulose pretreatment process presents a promising approach to overcome the drawbacks demonstrated by various individual pretreatment processes, by increasing efficiency of sugar production, decreasing formation of inhibitors and/or shortening process time (Zhang et al., 2016). Given that the lignocellulose pretreatment can be implemented by both Fenton's reagent and ultrasound, ultrasound-assistant Fenton process may provide a promising alternative pretreatment process for lignocellulose pretreatment because the process can provide a large amount of hydroxyl radicals in situ and at the same time enhance the contact between the substantial radicals and hydrocarbons in lignocellulose, thereby increasing the pretreatment efficiency. In this work, rice straw (RS), the most attractive low cost feedstock for bioethanol production, was subjected to three pretreatment procedures: Fenton's reagent, ultrasound, and ultrasound-assisted Fenton's reagent. The changes in morphology, composition and structure of RS after pretreatment were characterized and the effect of the pretreatment was evaluated by performing the enzymatic saccharification test.

2. Methods

2.1. Materials

RS from Hubei province, China was grinded to pass through a 120-mesh sieve, washed thoroughly with deionized water and then air dried at 105 °C until a constant weight. H_2O_2, $FeSO_4{\cdot}7H_2O$, H_2SO_4, NaOH, HCl, tetracycline, and citric acid monohydrate of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd. All solutions were prepared in deionized water. Commercial cellulase ($\geqslant$15,000 U/g, Sinopharm Chemical Reagent Co., Ltd.) was used for enzymatic hydrolysis.

2.2. Pretreatment of rice straw

Fenton's reagent pretreatment: 50 mL of 88 mmol of H_2O_2 solution and 50 mL of 2 mmol of $FeSO_4{\cdot}7H_2O$ solution both with a pH value of 2.5 adjusted by H_2SO_4 were prepared separately. 5 g of RS was added to a magnetically stirred jacket beaker (200 mL) kept at 25 °C with circulating water, and then 50 mL of H_2O_2 solution was added to the beaker, to which 50 mL of $FeSO_4{\cdot}7H_2O$ solution was added dropwise during about 1 h.

Ultrasound pretreatment: a RS suspension (5 g in 100 mL water) in a magnetically stirred jacket beaker (200 mL) was ultrasonicated with a horn-type ultrasonic processor (VOSHIN-501D, Wuxi Voshin Instruments Co., Ltd.) operated at a frequency of 22 kHz. The ultrasonication with an on-time of 2 s and an off-time of 4 s was transferred through a titanium cylindrical horn submerged in the RS suspension. The temperature of the suspension was kept at 25 °C with circulation of water bath.

Ultrasound-assisted Fenton's reagent pretreatment: 5 g of RS in a magnetically stirred jacket beaker (200 mL) was simultaneously subjected to Fenton's reagent and ultrasound. To investigate the effect of ultrasonication power on the ultrasound-assisted Fenton's reagent pretreatment, different ultrasonication power (200, 300, 400, 500, and 600 W) was applied to the Fenton's reagent pretreatment.

In each case, after 3 h of pretreatment, the resultant suspension was filtrated and the obtained residual (pretreated RS) was washed sequentially with 5% oxalic acid solution and deionized water, and then dried at 105 °C for 48 h. Raw RS, Fenton's reagent pretreated RS, ultrasound pretreated RS, and ultrasound-assisted Fenton's reagent pretreated RS were denoted as R-RS, F-RS, U-RS, and U/F-RS, respectively.

2.3. Enzyme hydrolysis

0.0275 g of cellulase and 0.02 g tetracycline were added to an Erlenmeyer flask containing 50 mL of citric acid-NaOH buffer with a pH value of 4.8, then 1 g of the substrate (R-RS, F-RS, U-RS, or U/F-RS) was added to the above solution, which was then incubated in a shaker bath at 50 °C and 150 rpm for 48 h. During the incubation period, 1 mL of the medium was taken every 12 h by using a syringe with a 0.22-μm membrane for reducing sugar analysis.

2.4. Analytical methods

After pretreatment, the yield of the obtained residual (pretreated RS), defined as the mass ratio of the pretreated RS to the raw RS, was determined gravimetrically. The contents of cellulose, hemicellulose and acid-insoluble lignin in the raw and pretreated RS samples were determined according to the Van Soest method (Liu et al., 2014). The morphologies of RS samples were characterized by a JEOL JSM-5510LV Scanning Electron Microscope (SEM). The specific surface area and total pore volume of RS samples were determined by a Micromeritics ASAP 2460 surface area and porosimetry analyzer. The average degree of polymerization (DP) of RS was determined (25 °C) by copper ethylenediamine (CED) solution method (ISO 5351: 2010), and triplicate runs were carried out. X-ray diffraction (XRD) patterns of RS were recorded on a Bruker D8 Advance X-ray diffractometer using Cu Ka radiation generated at 40 kV and 40 mA. The crystallinity index of RS was calculated according to the conventional peak intensity method (Zhang et al., 2016). The amount of reducing sugar released by enzymatic hydrolysis was determined by the dinitrosalicylic acid (DNS) method (El-Zawawy et al., 2011) with a spectrophotometer (UV-9000S, Shanghai Metash Instruments Co., Ltd.).

3. Results and discussion

3.1. Morphology of rice straw

The SEM image (Supplementary Fig. S1) of the intact fibers of R-RS shows that the structure of which is highly crystalline and rigid. Compared with R-RS which has a relatively smooth surface, the F-RS exhibits a relatively rough surface containing voids and cracks, which can be attributed to the action of the hydroxyl radicals produced from Fenton reaction. It is recognized that hydroxyl radicals can attack the lignocellulosic cell wall constituents at close proximity, causing disruption of the lignocellulose matrix with internal cleavage of cellulose chains and lignin modification (Arantes et al., 2012). The crystalline structure of U-RS (pretreated at 400 W) fibers is disrupted and microfibrils are visible. The disrupted structure of U-RS can be attributed to the cavitation effect. Cavitation can generate high temperature and pressure, which may provide a supercritical/subcritical environment as well as extremely reactive OH radicals for RS pretreatment. In addition, cavitation can generate intense shear forces, shock waves and microjets, which can cleave RS and modify the surface structure of RS. The image of U/F-RS (pretreated at 400 W) shows that some of the covering materials on the surface of RS are removed, resulting in more open structures with visible exposure of microfibrils. The exposed surface of U/F-RS is expected to enhance the adsorption of cellulase and allow a better access of cellulase to RS.