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Characterisation of water hyacinth with microwave-heated alkali pretreatment for enhanced enzymatic digestibility and hydrogen/methane fermentation

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HIGHLIGHTS

- Microwave-heated alkali pretreatment (MAP) was effective to pretreat water hyacinth.
- MAP resulted in a deconstructed lignocellulose matrix and swollen surface.
- Crystallinity decreased from 16.0 to 13.0 after MAP due to cellulose amorphisation.
- The energy conversion efficiency was enhanced to 49.5% by methane fermentation.

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ABSTRACT

Microwave-heated alkali pretreatment (MAP) was investigated to improve enzymatic digestibility and H_2/CH_4 production from water hyacinth. SEM revealed that MAP deconstructed the lignocellulose matrix and swelled the surfaces of water hyacinth. XRD indicated that MAP decreased the crystallinity index from 16.0 to 13.0 because of cellulose amorphisation. FTIR indicated that MAP effectively destroyed the lignin structure and disrupted the crystalline cellulose to reduce crystallinity. The reducing sugar yield of 0.296 g/gTVS was achieved at optimal hydrolysis conditions (microwave temperature = 190 °C, time = 10 min, and cellulase dosage = 5 wt%). The sequentially fermentative hydrogen and methane yields from water hyacinth with MAP and enzymatic hydrolysis were increased to 63.9 and 172.5 mL/gTVS, respectively. The energy conversion efficiency (40.0%) in the two-stage hydrogen and methane cogeneration was lower than that (49.5%) in the one-stage methane production (237.4 mL/gTVS) from water hyacinth with MAP and enzymatic hydrolysis.

1. Introduction

The ever-growing energy demands and rapid consumption of non-renewable fossil fuels emphasise the significance of developing a sustainable alternative energy source. Hydrogen has elicited special attention because of its renewable, carbon-neutral and environment-friendly characteristics (Christopher and Dimitrios, 2012; Guo et al., 2010; Guwy et al., 2011). Biological hydrogen production from renewable resources (e.g., lignocellulosic biomass and waste materials) has drawn increasing attention compared with conventional hydrogen production technologies (e.g., steam reforming and water electrolysis) (Cheng et al., 2011a; Kırtay, 2011; Liu et al., 2014; Rai et al., 2014). As an aquatic plant, water hyacinth has emerged as a major invasive weed in the tropical and subtropical regions of the world because of its high reproduction rate. Water hyacinth reproduces sexually by seeds and vegetatively by budding and stolon production. Daughter plants sprout from the stolons, and the doubling times have been reported of 6–18 days. Under favourable conditions, the vegetative propagation of water hyacinth is very fast and the edge of mat can even enhance by 60 cm/month (Malik, 2007). However, water hyacinth may also be a sustainable resource for biofuel production because of its abundance, low cost and availability. Biofuel production from water hyacinth greatly depends on the disruption of its complex lignocellulosic structure, which is recalcitrant to biodegradation. The organic components of lignocellulosic structure mainly contains of cellulose, hemicelluloses and lignin (Hendriks and Zeeman, 2009). Cellulose is an unbranched polymer chain, constituted by glucose units, which are linked by β-1,4-glycosidic bonds.

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Hemicellulose is a group of different branched polysaccharides that comprise both pentoses (e.g., xylose and arabinose) and hexoses (e.g., glucose, mannose and galactose). Lignins are regarded as complex, amorphous, branched polymers that comprise different phenylpropane units, which give the structural support. Therefore, effective pretreatment methods for disrupting the lignocellulosic structure must be devised to improve the enzymatic digestibility and subsequent biofuel production from water hyacinth.

Effective pretreatment methods include the preservation of pentose (hemicellulose) fractions, avoidance of fermentative production inhibitors, minimisation of energy demands and savings in process costs (Binod et al., 2012). Several pretreatment methods have been developed, such as mechanical pretreatment, microwave irradiation, alkali or acid pretreatment, steam explosion, ammonia fibre explosion, hot water treatment, supercritical CO_2 treatment and biological pretreatment (Moretti et al., 2014; Zhang and Wu, 2014; Zhao et al., 2014; Zheng et al., 2014). Recent studies indicated that microwave-assisted pretreatment of sugarcane bagasse (Chen et al., 2011, 2012), rice straw (Cheng et al., 2011b; Ma et al., 2009) and switchgrass (Hu and Wen, 2008) greatly enhanced the bioaccessibility of biomass and biofuel production. A 5-min microwave pretreatment significantly destroyed the lignocellulosic structure of bagasse (Chen et al., 2011). The microwave pretreatment of sugarcane bagasse removed lignin, maintained its cellulose structure and improved enzyme hydrolysis (Moretti et al., 2014). Alkali pretreatments performed by using sodium, potassium, calcium and ammonium hydroxides as bases can effectively alter the structure of lignin and subsequently increase the enzymatic accessibility to cellulose and hemicelluloses (Hendriks and Zeeman, 2009). They lead to the saponification of the uronic bonds between hemicelluloses and lignin, swell the fibres and increase pore size, and facilitate the diffusion of the hydrolytic enzymes. Thermo-alkali pretreatment and enzymatic hydrolysis of sunflower stalks increased the hydrogen production to 59.5 mL H_2/gTVS (Monlau et al., 2013). Alkali hydrogen peroxide pretreatment significantly improved the enzymatic digestibility of cashew apple bagasse (Correia et al., 2013).

However, few studies discussed the effects of microwave-heated alkali pretreatment (MAP) on the physicochemical properties of water hyacinth and the following bio-hydrogen and biomethane production. In this study, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) were used to determine the physicochemical changes of water hyacinth after pretreatment. The effects of microwave temperature, time, cellulose dosage and alkali soaking time on pretreatment and hydrogen production were investigated. The water hyacinth under optimum conditions was subjected into two different fermentation processes (i.e., sequential hydrogen and methane cogeneration, as well as methane fermentation) to examine the effectiveness of the pretreatment.

2. Methods

2.1. Feedstock and bacteria

The water hyacinth collected from Fuchun River in Zhejiang Province was oven dried and powdered to 0.02 mm mesh size. The pulverised water hyacinth was stored for use in the experiments. The water hyacinth sample comprised 28.9% cellulose, 30.8% hemicellulose and 4.6% lignin. The TVS content was 78.3% and lower heating value was 17.2 kJ/gTVS.

The mixed hydrogen-producing bacteria (HPB) and methane-producing bacteria (MPB) were obtained from a biogas plant in Zhejiang Province, China. The dominating species in HPB was *Clostridium butyricum*, and the dominating species in MPB were *Methanosarcina* and *Methanothrix*. The bacteria isolation and enrichment processes have been described in previous studies (Cheng et al., 2012a; Xia et al., 2013).

2.2. Pretreatment and fermentation methods

2.2.1. Pretreatments

The optimisation of microwave-heated alkali pretreatment was conducted in a microwave digestion system (Shanghai Yiyao WX-4000, China). After presoaking in 10 mL NaOH solution (0.2 wt%) for 24 h, 0.2 g of water hyacinth was added to each polytetrafluoroethylene reactor, along with NaOH solution. To investigate the effect of microwave temperature on the hydrolysis of water hyacinth, the sealed reactors were heated to 150, 190, 210 and 230 °C for 30 min. To investigate the effect of microwave time on the hydrolysis of water hyacinth, the sealed reactors were heated at 190 °C for 5, 10, 20 and 30 min. To investigate the effect of cellulase dosages on the hydrolysis of water hyacinth, different cellulase dosages of 0, 0.5, 1, 2.5, 5, 10, 25, 50 and 100 wt% were added to the water hyacinth solutions after MAP (190 °C and 10 min).

2.2.2. Enzymatic hydrolysis

The collected water hyacinth solutions were transferred to conical flasks after the microwave pretreatments. The pH of the water hyacinth solutions was adjusted to 4.5 using 6 M HCl. Different amounts of *Trichoderma reesei* cellulase (Shanghai Boao Biotechnology Corp., China) were then added to the solutions. The conical flasks were placed in a shaker at 120 rpm and 45 °C for 24 h. The sugar contents of the water hyacinth hydrolysates before and after the enzymatic hydrolysis were then determined.

2.2.3. Sequential hydrogen and methane fermentation

The soaked water hyacinth with different times (0, 2 and 24 h) were subjected to microwave pretreatment at 190 °C for 10 min and were enzymatically hydrolysed (5 wt% cellulase). Hydrogen fermentation was performed in 300 mL glass bottles. Up to 2 g of enzymatically hydrolysed water hyacinth was added to each bottle. The initial pH was adjusted to 6.0 ± 0.1 using 6 M HCl and 6 M NaOH solutions. The bottles were then inoculated with 50 mL of HPB. Deionised water was added to adjust the solution to 200 mL. Afterwards, the bottles were sealed with rubber stoppers, purged with nitrogen gas for 10 min and maintained at 35 ± 1.0 °C during hydrogen fermentation. The pH of residual solution was adjusted to 8.0 ± 0.1 using 6 M HCl and 6 M NaOH solutions. The bottles were then inoculated with 50 mL of MPB, sealed with rubber stoppers, purged with nitrogen gas for 10 min and maintained at 35 ± 1.0 °C during methane fermentation.

2.2.4. One-stage methane fermentation

The 24 h soaked water hyacinth was subjected to microwave pretreatment at 190 °C for 10 min and then enzymatically hydrolysed (5 wt% cellulase). Up to 2 g of enzymatically hydrolysed water hyacinth was added to each bottle. The initial pH was adjusted to 8.0 ± 0.1 by using 6 M HCl and 6 M NaOH solutions. The bottles were then inoculated with 50 mL of MPB. Deionised water was added to adjust the solution to 200 mL. Afterwards, the bottles were sealed with rubber stoppers, purged with nitrogen gas for 10 min and maintained at 35 ± 1.0 °C for one-stage methane fermentation.

2.3. Analytical methods

The cellulose, hemicellulose and lignin contents in the water hyacinth were determined using a raw fibre extractor (FIWE, VELP Scientific Corp., Italy). The moisture content was determined by