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Mechanistic study on ultrasound assisted pretreatment of sugarcane bagasse using metal salt with hydrogen peroxide for bioethanol production

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ABSTRACT

This study presents the ultrasound assisted pretreatment of sugarcane bagasse (SCB) using metal salt with hydrogen peroxide for bioethanol production. Among the different metal salts used, maximum holocellulose recovery and delignification were achieved with ultrasound assisted titanium dioxide (TiO_2) pretreatment (UATP) system. At optimum conditions (1% H_2O_2, 4 g SCB dosage, 60 min sonication time, 2:100 M ratio of metal salt and H_2O_2, 75 °C, 50% ultrasound amplitude and 70% ultrasound duty cycle), 94.98 ± 1.11% holocellulose recovery and 78.72 ± 0.86% delignification were observed. The pretreated SCB was subjected to dilute acid hydrolysis using 0.25% H_2SO_4 and maximum xylose, glucose and arabinose concentration obtained were 10.94 ± 0.35 g/L, 14.86 ± 0.12 g/L and 2.52 ± 0.27 g/L, respectively. The inhibitors production was found to be very less (0.93 ± 0.11 g/L furfural and 0.76 ± 0.62 g/L acetic acid) and the maximum theoretical yield of glucose and hemicellulose conversion attained were 85.8% and 77%, respectively. The fermentation was carried out using *Saccharomyces cerevisiae* and at the end of 72 h, 0.468 g bioethanol/g holocellulose was achieved. Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analysis of pretreated SCB was made and its morphology was studied using scanning electron microscopy (SEM). The compounds formed during the pretreatment were identified using gas chromatography–mass spectrometry (GC–MS) analysis.

1. Introduction

Bioethanol can be produced from lignocellulosic biomass (LCB) such as crop residues (wheat straw, rice straw, corn stover, sugarcane bagasse (SCB), rice hulls, barley straw, sweet sorghum bagasse, olive stones), hardwood, softwood, cellulose wastes, herbaceous biomass and municipal solid wastes [1]. Among the various renewable energy sources, SCB is considered as an overabundant biomass because 5.4×10^8 dry tons of sugarcane is processed annually throughout the world. SCB is mainly composed of cellulose, hemicellulose and lignin. The holocellulose (cellulose + hemicellulose) recovery during the pretreatment is an important criterion, which enhances the fermentable sugar production during hydrolysis. In order to obtain high sugar yield, the protective coats around cellulose, hemicellulose and lignin need to be altered or detached without affecting the sugars during the pretreatment.

The pretreatment techniques studied include acid, alkaline, biological pretreatment, wet oxidation, organosolv, ozonolysis, ultrasound pretreatment and hydrogen peroxide with metal salts pretreatment. These methods are significantly different from one another in terms of reaction conditions, process efficiency and complexity. The ultrasonic pretreatment produces sonochemical and mechanoacoustic effects which affect the chemical and physical composition of SCB. The mechanoacoustic effect alters the surface structure of the biomass, whereas sonochemical effect produces hydroxyl radicals, which attack the components of SCB [2].

The pretreatment of SCB with metal salts and hydrogen peroxide (H_2O_2) was found to enhance the rate and yield of hydrolysis [3–5]. This method is considered as an attractive process, because the metal salts are recyclable and less corrosive than inorganic acids [4]. The decomposition of lignin occurs due to the formation of hydroxyl radicals and superoxide ions during this process [6]. The incorporation of ultrasound with this method is expected to alter the morphological structure of SCB, disrupt its structure to achieve effective hydrolytic process, and reduces the mass transfer limitations.

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In this study, SCB was pretreated with ultrasound in the presence of different metal salts (manganese sulphate monohydrate ($MnSO_4{\cdot}H_2O$), zinc oxide (ZnO), ferrous sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$), ammonium molybdate ($(NH_4)_6Mo_7O_{24}$), cobalt chloride ($CoCl_2$), titanium dioxide (TiO_2)). Based on higher holocellulose recovery and delignification, best metal salt was selected and the optimization of different process parameters such as H_2O_2 concentration, SCB dosage, ultrasound time, molar ratio of metal salt and H_2O_2, temperature, ultrasound amplitude and ultrasound duty cycle was carried out.

2. Materials and methods

2.1. Materials

The experiments were conducted using SCB collected from local sugarcane processing unit located at Chennai, India. It was washed thoroughly with distilled water to remove dust and soluble sugars, dried at 60 °C for 24 h. The dried SCB was subsequently milled, screened to a particle size of below 1 mm (>18 mesh size, ASTM standard) and stored in an air tight polyethylene bag at room temperature. The chemicals such as acetone, ammonium molybdate, 3,5-dinitrosalicylic acid, cobalt chloride and titanium dioxide, were purchased from Sisco Research Laboratory (P) Ltd., Mumbai, India. Ferrous sulphate heptahydrate and manganese sulphate monohydrate were purchased from Central Drug House (P) Ltd., New Delhi, India. Sulphuric acid was purchased from Thermo Fischer Scientific India, Ltd., Mumbai, India, Hydrogen peroxide (30%) was purchased from Merck Specialities (P) Ltd., Mumbai, India and zinc oxide was purchased from Sigma–Aldrich chemicals (P) Ltd., Bangalore, India. All the chemicals used were of analytical grade.

2.2. Sonicator

Sonotrode H3 probe type, made up of titanium with tip diameter 3 mm and length 100 mm (Hielscher Ultrasonic Processor UP400S, Germany) was used in this study. The operating power and frequency of the sonicator were 400 W and 24 kHz, respectively. The temperature was controlled using a water bath.

2.3. Pretreatment

The schematic diagram of the experimental setup used in this study is shown in Fig. S1 (See Supplementary data). SCB was pretreated using ultrasound assisted metal salt pretreatment. Initially 2 g of SCB was placed in a 250 mL Erlenmeyer flask with desired concentration of H_2O_2 and metal salt. The contents were irradiated with ultrasound at different operating conditions. Metal salts such as manganese sulphate monohydrate ($MnSO_4{\cdot}H_2O$), zinc oxide (ZnO), ferrous sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$), ammonium molybdate ($(NH_4)_6Mo_7O_{24}$), cobalt chloride ($CoCl_2$), and titanium dioxide (TiO_2) were used. The effect of operating parameters such as H_2O_2 concentration (0.25%, 0.50%, 1% and 2% v/v), SCB dosage (1, 2, 3 and 4 g), sonication time (15, 30, 45 and 60 min), molar ratio of metal salts to H_2O_2 (0.5:100, 1:100, 2:100 and 4:100 g/mL), temperature (25, 50, 75 and 100 °C), ultrasound amplitude (30%, 40%, 50% and 60%) and ultrasound duty cycle (50%, 60%, 70% and 80%) were investigated for maximum holocellulose recovery and delignification. The performance of ultrasound assisted metal salt pretreatment was compared with ultrasound pretreatment carried out at 100 °C with 2 g SCB for 60 min. The optimization of operating parameters was done by changing one variable at a time and operating conditions were fixed based on the literature [7]. The pretreated SCB was filtered using Whatman filter paper, washed several times with distilled water, hot water and finally with acetone to remove the residual metal salt present. The filtered SCB was dried to 60 °C until constant weight was observed, and then it was subjected to dilute acid hydrolysis. The experiments were carried out in duplicate and average values were reported. The presence of reducing sugars in the liquid phase was determined by DNS method.

The % holocellulose recovery in the pretreated SCB was calculated using the following equation

$$\%\ \text{Holocellulose recovery} = \frac{HR_{PT\text{-}SCB}}{HR_{SCB}} \times 100 \quad (1)$$

where HR_{SCB} is the amount of holocellulose in native SCB and $HR_{PT\text{-}SCB}$ is the amount of holocellulose in pretreated SCB expressed in (g/g).

The % delignification in the pretreated SCB was calculated using the following equation

$$\%\ \text{Delignification} = \frac{D_{SCB} - D_{PT\text{-}SCB}}{D_{SCB}} \times 100 \quad (2)$$

where D_{SCB} is the amount of lignin present in native SCB and $D_{PT\text{-}SCB}$ is the amount of lignin present in pretreated SCB expressed in (g/g).

2.3.1. Calorimetric efficiency

The actual power dissipated into the system (calorimetric efficiency) using ultrasound probe was determined by calorimetric method. The rise in temperature of a fixed quantity of water in an insulated container for a given time was measured. Then, the actual energy (power) dissipated into the liquid was calculated from the following equation:

$$W = \frac{mC_p\Delta T}{t} \quad (3)$$

where M is the mass of solution taken in 'kg', C_p is the specific heat of liquid at constant pressure (4.180 J/kg K), ΔT is the difference between initial and final temperature during the ultrasound time in 'K', and t is the reaction time in 's' [8].

Acoustic intensity was calculated using the equation given below:

$$I = \frac{\text{Actual power dissipated (W)}}{\text{Area of horn tip (m}^2\text{)}} \quad (4)$$

For the ultrasound assisted titanium dioxide pretreatment system (UATP), the reaction mixture was subjected to ultrasound irradiation using an ultrasonic horn made up of titanium (tip diameter of 0.3×10^{-2} m) operated at 24 kHz with a rated output power of 400 W and the surface area of the ultrasound irradiating face was 7×10^{-6} m^2. The horn was operated at 50% amplitude for 60 min with 7 s on and 3 s off duty cycle. The difference in temperature during the course of the reaction was observed as 24.6 K and the corresponding power dissipation and acoustic intensity were found to be 2.856 W and 408 kW/m^2.

2.4. Hydroxyl radicals measurement

The formation of free radicals during the pretreatment of SCB using ultrasound assisted metal salt played an important role in delignification. The radicals formed were quantified using Fricke dosimetry method [9]. Fricke solution was prepared using 1 mM $FeSO_4$, 0.4 M H_2SO_4 and 1 mM NaCl and this was added into the reaction mixture containing SCB, H_2O_2 and metal salt. The reaction was carried out as per the pretreatment conditions. The samples were withdrawn at regular time intervals and the formation of Fe^{3+} during the pretreatment was determined using Elico double beam SL210 UV–Visible spectrophotometer at 304 nm. The estimation of hydroxyl radical is based on the oxidation of Fe^{2+} to Fe^{3+}.