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Enhancement of hydrolysis of lignocellulose waste pulp and paper mill sludge through different heating processes on thermal pretreatment

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ABSTRACT

Different heating processes were applied to pretreat the pulp and paper mill sludge to enhance the hydrolysis stage. Hot air oven, autoclave, microwave and water bath were used for comparison. Chemical analyses exposed that all the pretreatment methods have shown improvement in solubilisation of organic matter. Among the pretreatments studied, heat transfer through hot air (80 °C for 90 min) mode had the highest impact on sludge solubilisation. There was an increase in cellulose ($P = 0.0096$), acid soluble ($P = 0.0053$) and insoluble lignin ($P = 0.0012$), but decrease in hemicellulose ($P = 0.0009$) content after pretreatment. The XRD and FT-IR spectroscopic characterisation shows the development of aliphatic, unsaturated and carbonyl carbon functionalities in the pretreated samples at higher severities. FESEM picture also confirms the change in structure after pretreatment. Thus, pretreatments contribute to disruption of the lignocellulosic structure making the cellulose easily accessible to acidogenic microorganisms.

1. Introduction

Growing and increasing worldwide energy demand have led to the development of alternative energetic sources such as lignocellulose biomass and its waste (Rubin, 2008). There have been produced a wide range of lignocellulose organic waste material such as agricultural and forestry residues, municipal solid waste, animal manure, and industrial wastes. Because of a continuous production in the industry, there is an increased need of energy at an industrial level but also a copious availability of waste material serve as a potential feedstock. Special attention has been focused to anaerobic digestion, which is an alternate management method for waste reduction with energy (Elliott and Mahmood, 2012). Anaerobic digestion is a biological process absent from oxygen in which organic matter could be transformed and decomposed mainly to methane (CH_4) and carbon dioxide (CO_2) by a diverse group of microorganisms.

Inherent recalcitrant characteristics of lignocellulose content, turns hydrolysis step into a rate-limiting stage in the anaerobic digestion process. Lignocellulose material consist of three biopolymers: cellulose, hemicellulose, and lignin, which together form a rigid and complex structure (Zheng et al., 2014). Cellulose is the main component and consists of a linear polysaccharide polymer of cellobiose strongly linked by β-1,-4 glycosidic linkages. The hydrogen bonds and Van der Waals forces forms the interlinking of cellulose chain, resulting in the high tensile strength of microfibrils (Ha et al., 1998). Cellulose microfibrils are attached to each other by hemicellulose, and covered by lignin complexes. These specialized and complicated structures make cellulose resistant to chemical and biological attacks. Hemicellulose polymers are random, amorphous, and branched heterogenic polysaccharides formed by hexoses, pentoses, and acids. Short and branched chains of hemicellulose combined with network of cellulose microfibrils interact with lignin leading to a rigid cellulose-hemicellulose-lignin matrix. The different form of inter-unit linkages, such as β-O-4, β-β, β-5, β-1, 4-O-5, etc. are combined to build the heterogeneous and highly cross-linked lignin component (Sasaki et al., 2013). Palmqvist and Hahn-Hägerdal (2000) reported that lignin plays the role of cement rigid three dimensional structure by forming the cross-linking between cellulose and hemicellulose as shown in Fig. 1.

Owing the complexity and variability of the lignocellulose chemical structure, the optimal pretreatment conditions will depend on the content of lignocellulose. The main goal of

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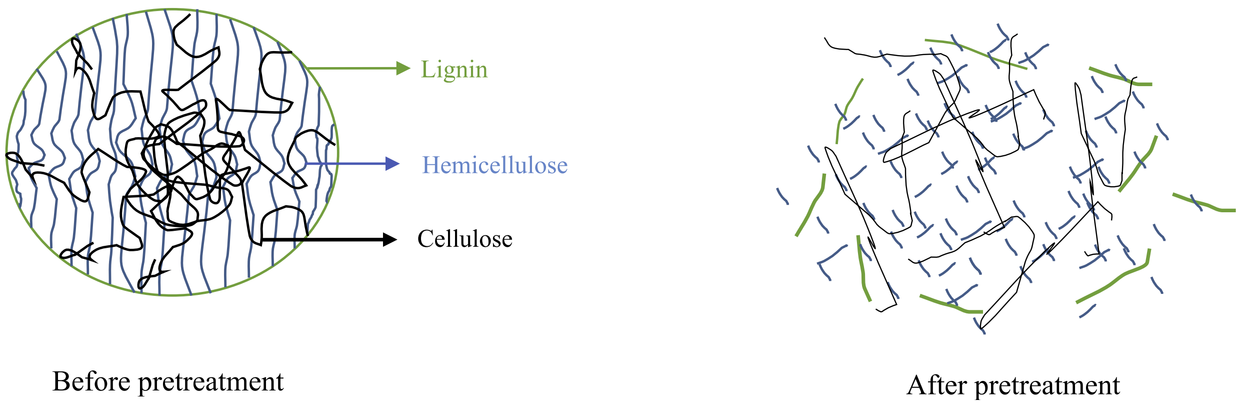

Fig. 1. Simplified impact of pretreatment of lignocellulose material.

pretreatment is to alter the lignin structure, reducing the cellulose crystallinity, increasing the surface area, and the degree of cellulose polymerization and hemicellulose acetylation (Zheng et al., 2014; Hendriks and Zeeman, 2009). As the hydrolysis is a rate-limiting step in anaerobic digestion of pulp and paper mill sludge (PPMS) (Veluchamy and Kalamdhad, 2017a; Elliott and Mahmood, 2012; Wood et al., 2009). Previous study by Veluchamy and Kalamdhad (2017b) reported that pretreatment is necessary to fasten the hydrolysis step in anaerobic digestion of PPMS. Hendriks and Zeeman (2009) described several pretreatment methods based on biodegradability and solubilisation of hemicellulose and lignin to improve hydrolysis efficacy. Several pretreatment studies on PPMS have been reported, such as the mechanical (Elliott and Mahmood, 2012; Saha et al., 2011), chemical (Tyagi et al., 2014; Lin et al., 2009; Navia et al., 2002), ultrasonic (Tyagi et al., 2014; Saha et al., 2011; Tiehm et al., 2001), enzymatic (Bayr et al., 2013; Lin et al., 2010) and thermal pretreatment methods (Veluchamy and Kalamdhad, 2017c; Wood et al., 2009) and a combination of different pretreatments (Bayr et al., 2013; Elliott and Mahmood, 2012; Park et al., 2012).

Within the previous enlisted pretreatments, the thermal is more effective in the degradation of hemicellulose and lignin by enhancing the hydrolysis (Veluchamy and Kalamdhad, 2017c; Nizami et al., 2009). Wood et al. (2009) compared three different pretreatment (hydrothermal, thermochemical, and ultrasonic) applied to PPMS and reported that thermal pretreatment showed increased methane production. The residence time of sludge into a biogas reactor was substantially reduced from 15 to 25 d–7 d after the thermal pretreatment (Elliott and Mahmood, 2012). Hence, an effective pretreatment is needed to produce multiple desirable effect such as changes in lignin structure, decrease in cellulose crystallinity, increase in solubilisation of cellulose and hemicellulose, and increase in surface area (Veluchamy and Kalamdhad, 2017d).

Even though there is extensive research on the effect of different pretreatment processes, the correlation between the structural and compositional properties remains unclear and contradictory. Hence, the main objective of the present study is to predict the optimal time and temperature conditions for different heating processes and to elucidate the changes produced in the structure and composition of the PPMS after pretreatment.

2. Materials and methods

2.1. Sample preparation and chemical analyses

PPMS was obtained from the Nagaon paper mill located at Jagiroad, Assam, India. PPMS was collected from the filter house of the effluent treatment plant and stored under refrigeration at 4 °C for further use. Approximately, 50 g of PPMS were mixed vigorously with 150 mL of distilled water until obtain a slurry looks.

Samples were analysed for pH, soluble chemical oxygen demand (sCOD), total solids, moisture content, and volatile solids using standard protocols according to APHA (2005). Volatile fatty acids (VFA) were analysed by pH titration method adopted by the DiLallo and Albertson (1961). Lignin was analysed using National renewable energy laboratory (NREL) procedure (Ehrman, 1996; Templeton and Ehrman, 1995). Cellulose and hemicellulose were analysed according to the protocols adopted by Updegraff (1969) and Goering and Van Soest (1975) respectively. All samples were analysed for stated above before (control) and after every heating process. The chemical characterisation and compositional analysis were shown in Table 1.

2.2. Heating processes for PPMS

2.2.1. Hot air oven

Samples were placed in conical flasks into a hot air oven (SONNU-220/230 V AC). According to conditions proposed by Wood et al. (2009), temperature was set at 70, 80, 90, 100 and 110 °C for 30 min. After evaluate the better temperature, a trial to evaluate the effect of exposure time was set with 30, 60, 90, 120, and 150 min.

2.2.2. Autoclave

Samples were placed in conical flasks into an autoclave (EQUTRON-7421SLEFA). Temperature was set at 80, 90, 100, 110, and 120 °C for 20 min according to procedure proposed by Menardo et al. (2012) and Gabhane et al. (2011). After evaluating the best

Table 1
Chemical characterisation of pulp and paper mill sludge.

Parameter	Pulp and paper mill sludge
Moisture content (%)	74.95 ± 0.36
Total solid (g/L)	25.10 ± 0.40
Volatile solid (g/L)	17.82 ± 0.65
pH	6.53 ± 0.54
Total Nitrogen (%, b.d.w[a])	1.03 ± 0.42
Organic carbon (%,b.d.w[a])	35.16 ± 1.14
Lignin (%)	5.18 ± 0.28
Hemicellulose (%)	6.53 ± 0.76
Cellulose (%)	32.57 ± 0.75
sCOD (mg/L)	1600 ± 100
VFA (mg/L)	590 ± 45

Numbers are mean ± standard deviation from three replicates.
[a] b.d.w. based on dry weight.