Characterisation of Microwave-assisted Pretreatment for Spent Coffee Grounds

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Abstract:

Spent coffee grounds (SCGs) is the natural waste from industry and cafe. It mainly composes of cellulose, hemicellulose, and lignin. The pretreatment process could alter the structure and composition of pretreated materials. This study was to characterise the pretreated SCGs based on microwave irradiation assisted NaCl. The process was carried on the various concentration of NaCl (1, 2 and 3 % w/v) and time of irradiation (1, 2 and 3 min). The power consumption of microwave was 300 W for all treatments. The morphological changes of SCGs residue from pretreatment process was characterised by Scanning Electron Microscopy (SEM), the functional groups of main components by Fourier transform infrared spectroscopy (FTIR), and crystallinity index by X-ray diffraction (XRD) methods. The pretreated SCGs with microwave and NaCl showed clear changes in structural surface with rougher and pores when increasing the NaCl concentration and irradiation time. The hemicellulose and lignin in SCGs residues were reduced after the pretreatment process with observation by the different FTIR spectra profiles between before and after SCGs treatment. After pretreatment with microwave power at 300 W for 3 min, the crystalline index was reduced to 31.20, 24.89, 23.39 and 21.82% with increased the NaCl concentration of 1, 2, and 3 % (w/v), respectively. However, the crystalline region was decreased with an increase in the amorphous region. These results could enhance the hydrolysis step and apply in the cellulose conversion process.

Keywords: Pretreatment, Spent coffee grounds, Microwave

Introduction

The production of energy from waste materials is an attractive alternative to replace the conventional process. Coffee is one of the most popular drinks around the world. Spent coffee grounds (SCGs) are products through the process of instant and fresh coffee productions. These processes are related to pretreatment methods with steam, hot water and high pressure that conduct coffee powder to be treated [13, 14]. The chemical composition of SCGs mainly of cellulose, hemicelluloses and lignin [15]. The cellulose composes of crystalline domains (highly ordered microfibrils) and amorphous domains (randomly ordered microfibrils) [2]. The pretreatment steps involved in a reduction in biomass size, depolymerization, and separation of the major components of biomass [16]. There are various pretreatment methods, such as physical, chemical, biological methods, and the combination of physicochemical method. The aim of pretreatment is to produce high sugar yield with the mild condition [18]. The use of inorganic salts as a catalyst to pretreat the lignocellulosic biomass has non-toxicity and low-cost [20]. Moreover, the catalytic activity of inorganic salts has been shown higher than that of acids [19]. Moreover, salts have unique characteristic activities when exposed to an electromagnetic field, owing to their Lewis acid nature [8]. The combination of Microwave-inorganic pretreatment is a promising green methodology in the cellulose production due to its unique characteristics of rapid volumetric heating, increased reaction rates, and energy saving, compared with other conventional heating methods [17]. Effect of microwave irradiation has been reported to change the chemical structure in the lignocellulosic materials [25]. Microwave irradiation has benefits in creating the thermal hot spots, accelerating the collision of ions with neighbouring molecules, and higher heat power than conventional heating method [8]. Therefore, this work aims to alter the structural cellulose of spent coffee grounds by applying microwave and sodium chloride in a pretreatment step. The pretreatment process could reduce the crystalline region and enhance chemical accessibility during the hydrolysis.

Table 1 Validation of the optimized pretreatment on different lignocellulosic residues and crystallinity index.

Sample	Pretreatment method	% Crystallinity	Reference
Rubber wood fibers	Laccase enzyme 70 U/g, at 40-55°C for 8 h + sodium chlorite at 75°C for 45 min + potassium hydroxide (3% w/w) at 80°C for 2 h + potassium hydroxide (6% w/w) at 90°C for 2 h	65	[1]
Dissolving pulp	Sulfuric acid (65% w/w) at 45°C for 1 h + ultrasonicated for 45 min	67	[2]
Paper	Ball milling + sulfuric acid (47 wt%) at 45°C for 1.5 h	89	[3]
Para rubber wood sawdust	Sodium hydroxide (1% w/v) at 80°C for 2 h + sodium sulfide (1% w/v) at 80°C for 1.5 h + bleached by sodium chlorite (0.7% v/v) at 80°C for 1.5 h + hydrolyzed sulfuric acid (64% w/w) at 45°C for 3 h	70.2	[4]
Lime residues	Autoclaving at 120°C for 2 h + homogenization	50.35	[5]
Sugarcane bagasse	Sodium hydroxyl (1% w/v) at 90°C for 1.5 h + ionic liquid 130°C for 2 h at 400 W of microwave + homogenization	36%	[6]

Materials and methods

Microwave-NaCl pretreatment

The SCGs was obtained from the Amazon Cafe in Maha-sarakham province, Thailand. The SCGs was dried at 60°C until the weight was constant and stored in a desiccator. The SCGs pretreatment was carried out in a household type microwave (Samsung, ME81KS-1/ST, Korea). The output power range of the equipment was 100–800 W (Microwave test procedure IEC-705) with an operating frequency of 2450 MHz. The power consumption was subjected to 300 W for 1, 2 and 3 min. The sodium chloride (NaCl) concentration of 1, 2 and 3 % w/v was applied on SCGs with solid loading 1:10 (g/mL). After pretreatment, SCGs was thoroughly washed with distilled water and air-dried. The dried SCGs residue was used for further studies.

Characterization of microwave-NaCl pretreated

SEM analysis

The morphological changes of SCGs before and after microwave-NaCl pretreatment was analysed by scanning electron microscopy (SEM, JEOL JSM-5600, Japan). The surface of SCGs residue was observed at magnification 1000X. The specimens were mounted on conductive tape and coated with gold palladium.

FTIR analysis

Fourier Transform Infrared spectroscopy (Bruker, TENSOR27, USA) was used to analyse the changes in functional groups that occurred by pretreatment. FTIR spectrum was recorded between 4000 and

600 cm^{-1} using a Shimadzu Spectrometer with a detector at 4 cm^{-1} resolution and 25 scans per sample. Samples were prepared by mixing 1 mg of the dried sample with 100 mg of KBr (Spectroscopic grade) in the hydraulic pump with 10 Mpa pressure.

XRD analysis

The crystallinity of SCGs was analysed by XRD (Bruker, D8, USA) Advance data collection in two dimensions, 2Theta (2θ) and Gamma (γ) angular range 360°. The instrument was set at 40 kV, 40 mA; radiation was Cu K□ (□=1.54 Å), and grade range between 5 and 40° with a step size of 0.03°. Crystallinity of cellulose was calculated according to the empirical method proposed by Segal et al. [21]

$$CrI\ (\%) = [(I_{002} - I_{18.0^{\circ}})/I_{002}] \times 100$$

CrI is the crystalline index, I_{002} is the maximum intensity of the (002) lattice diffraction, and $I_{18.0^{\circ}}$ is the intensity diffraction at 18.0°, 2□.

Results and discussion

SEM analysis

Figure 1(a-d) illustrates the surface features of untreated SCGs and microwave-NaCl treated SCGs by using the scanning electron microscopy (SEM). The untreated and treated SCGs were comparatively observed which pretreated SCGs surface was clearly ruined and exposed the inner surface. The untreated SCGs surface presented a contiguous and smooth surface since the fibres were all intact. All of pretreat SCGs were loosening of fibres and cellular distortion that due to the microwave irradiation combined with NaCl. Moreover, increasing the incubation time from 1 to 3 minutes could enhance pore size and number. This occurrence revealed that the SCGs had the structural changes after microwave-NaCl pretreatment. This result is consistent with those reports in microwave-inorganic salt pretreatment by P. Moodley and E.B.G. Kana (2017) [8]. The highly fractionated-surface appearance was observed when pretreated SCGs with microwave-NaCl (300 W, 3%, for 3 min).

FTIR analysis

FTIR spectroscopy was used to investigate the changes of cellulose structures after microwave-NaCl pretreatment. Figure. 2 shows the FTIR spectra of untreated SCGs, microwave-NaCl treated SCGs with 1%, 2% and 3% at microwave power 300 W. The effects of pretreatments can be analysed by changes in functional groups which relevant to the lignocellulosic biomass [9]. The FTIR spectra of 3200-3400 cm^{-1} were associated with the O-H stretching of hydrogen bonds [20].

The results showed FTIR spectra of microwave-NaCl treated SCGs that revealed the higher altered cellulose than untreated SCGs by increasing the NaCl concentration. These results were according to the spectrum at 1730 cm^{-1} and 1246 cm^{-1} these peaks indicated the changes of hemicellulose in all microwave-NaCl treated SCGs. The previous studies, the spectrum at 1730 cm^{-1} and 1246 cm^{-1} were attributed to the C=O stretching and C-O stretching vibration of hemicellulose, respectively [4, 9]. The spectrum at 1590 cm^{-1} and 1505 cm^{-1} were assigned to the aromatic parts of lignin [10]. The profiles of the FTIR spectra were different for untreated SCGs and microwave-NaCl treated SCGs. The results revealed that the lignin was decreased by pretreatment process with increasing NaCl concentration. It had been reported that the microwave irradiation enhances the saponification of intermolecular ester bonds cross-linking xylan and other components such as lignin [21]. Moreover, salts have unique characteristic activities when exposed to an electromagnetic field, owing to their Lewis acid nature [8]. The FTIR spectra for microwave-NaCl treated SCGs indicate the structural changes after microwave-NaCl treatment. These changes were according to the SEM results, which obtained from the pretreated SCGs with microwave-NaCl (300 W, 3%, for 3 min).

XRD analysis

Figure 3 showed the XRD patterns of untreated and pretreated SCGs. The major diffraction peaks of the cellulose crystallographic plane were identified at 2□ = 22°, signifying a highly organised crystalline region whereas the peaks at $2\theta = 18°$ indicated the less organised amorphous region [2]. The results showed that the XRD patterns of the untreated SCGs had changed after the microwave-NaCl treatment. The crystallinity index of the untreated SCGs and microwave-NaCl treated SCGs with different NaCl concentrations (1, 2 and 3 % w/v) at 300 W for 3 min were 31.20, 24.89, 23.39 and 21.82%, respectively. The crystallinity index significantly decreased because the crystalline cellulose became amorphous form after pretreatment. The amorphous structure is more easily degradable and susceptible to chemical attacks. The lignocellulosic materials, the crystalline region could be altered to the amorphous region after the pretreatment process [7]. The decreased crystalllininty in microwave-NaCl treated SCGs might be the result of removal of crystalline cellulose and hemicellulose from the biomass. A similar result was observed by J. Li et al. (2012) [6] that reported in breaking intermolecular hydrogen bonds of cellulose by using ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl). Then, the loss of hydrogen bond caused the collapse of crystal structure after pretreatment [6]. The crystallinity index of untreated SCGs was higher than microwave-NaCl treated SCGs. Moreover, the crystalline structure is less accessible to chemical attacks due to hydrogen strong interactions between the microfibers.

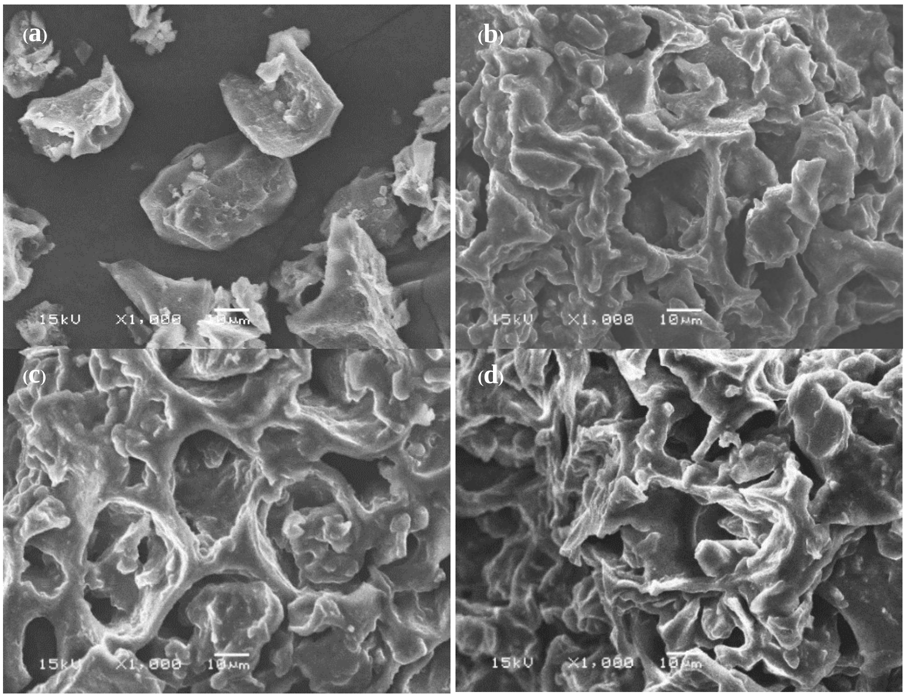

Figure 1 SEM of (a) untreated (b) 300 W, 1% for 3 min (c) 300 W, 2% for 3 min and (d) 300 W, 3% for 3 min.

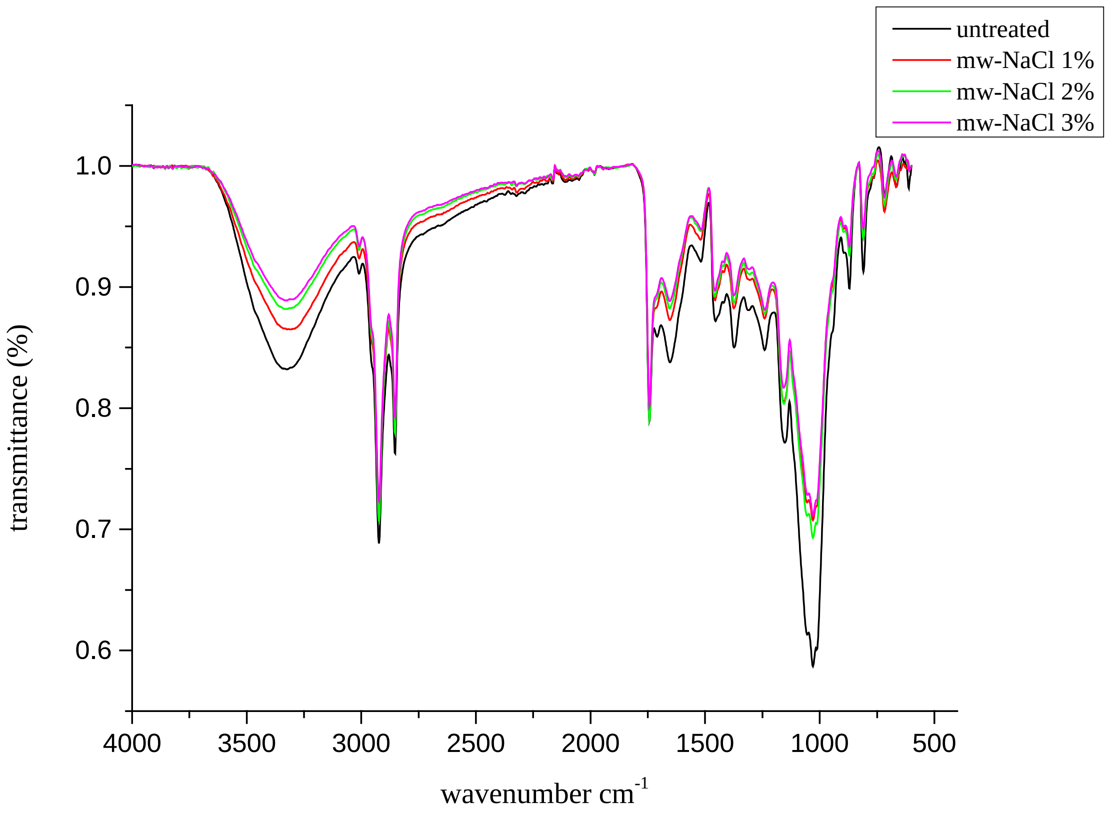

Figure 2 FTIR spectra of SCGs by using microwave-NaCl pretreatment

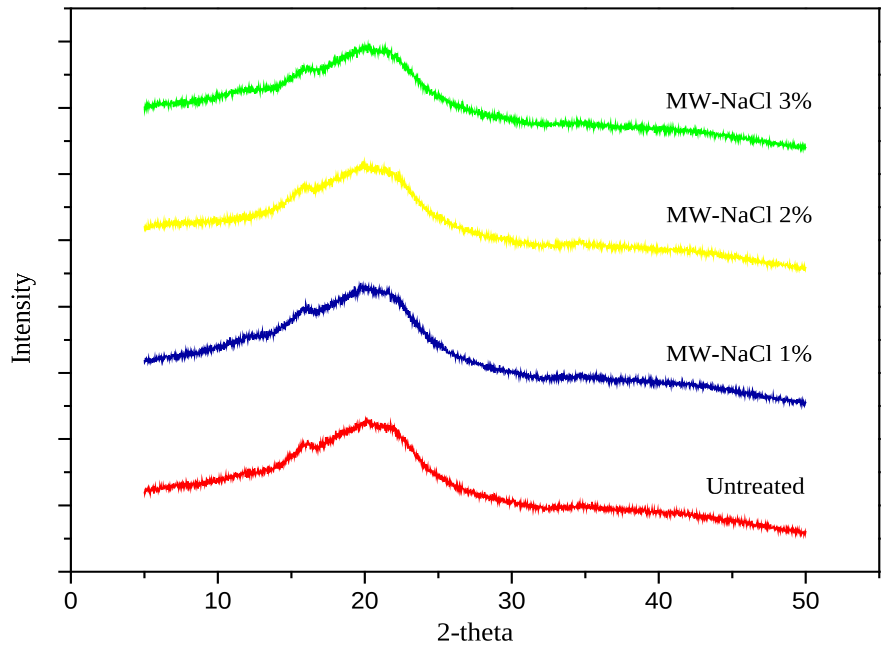

Figure 3 X-Ray diffraction of untreated and treated SCGs.

Conclusions

In this study, the pretreated microwave-NaCl SCGs was observed the changes in structural surface and crystallinity. The experiments indicated that the pretreatment of microwave-assisted 3% NaCl concentration, 300 W, 3 min obtained the crystallinity index 21.82% with more amorphous region. The morphology changes in pretreated SCGs had "sponge-puff" like appearance. This changes showed the rough surface with more porosity. Moreover, this pretreatment process can also remove lignin and hemicellulose that can be used to develop the pretreated SCGs for value-added products such as nano-carbon, nano cellulose or super capacity. These findings open up the possibility to develop SCGs into other applications.

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