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Optimization of Microwave-Assisted Inorganic Salt Pretreatment for Production of Fermentable Sugars from Spent Coffee Ground

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ABSTRACT

Spent coffee ground (SCG) is a solid waste that is generated in the coffee brewing process for coffee beverage production. SCG hold a great potential in reducing sugar production as it consists of high amount of carbohydrates. However, SCG is a lignocellulosic biomass (LCB) which requires pretreatment to degrade the lignocellulosic structure and enhance enzyme accessibility during saccharification process. Hence, this research aims to study the performance of microwave-assisted inorganic salt pretreatment for generation of reducing sugars. Different concentrations of NaCl was applied to determine their effects on reducing sugar produced as well as pH, and solid recovery. Pretreatment with 3% NaCl was found to yield the highest reducing sugar concentration of 43.56 mg/mL, hence it was selected for the subsequent optimization study. Process optimization was designed by using the Response Surface Methodology approach (RSM) with Central Composite Design (CCD), based on three pretreatment parameters; solid to liquid ratio (1:50 - 8:50), microwave power (300W – 800W) and irradiation time (1-10 minutes). The optimized conditions were achieved at solid to liquid of 8:50, microwave power of 800 watt and irradiation time of 10 minutes for a maximum response of 40.89 mg/mL. Moreover, it was observed that microwave-assisted NaCl pretreatment had significantly caused surface morphological changes of the SCG and the removal of functional groups in lignin, resulted in increment of the crystallinity value. In conclusion, microwave pretreatment is a promising green technology for fermentable sugar production from SCG.

Keywords: Spent coffee ground, Microwave pretreatment, Reducing sugars, Inorganic salt.

1. INTRODUCTION

Food processing industries has generated a huge amount of waste every year. Coffee is the second profitable traded food commodities in the world (Atabani *et al.*, 2019). According to a report released by the International Coffee Organization, 167.26 million of coffee has been consumed in the years of 2020 to 2021 (International Coffee Organization, 2021). Therefore, coffee industry generates large amount of residues causing environmental pollutions. Spent coffee grounds (SCG) is the one of the major unwanted solid residues produced when roasted coffee beans are ground into powder and treated with hot water during instant coffee production. Almost 50% of coffee industries in the world produced instant coffee and 650 kg of SCG are produced from 1000 kg of the green beans (Leow *et al.*, 2021).

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Coffee grounds contain high value of sugar, oil, phenolic compounds and other components after brewing (McNutt & He 2018). However, they are usually burned and disposed as waste to the environment due to no commercial value. The untreated SCG can release greenhouse gases leading to climate change due to improper waste management (La Scalia *et al.*, 2021). This has raised the awareness to reduce such pollution from industrial activities. Hence, researchers have studied and explored on SCG to be fully utilized in other industrial applications to achieve sustainable development goals (SDG).

However, the recalcitrant structure of SCG can inhibit the hydrolytic action which is the important step in reducing sugar production. Pretreatment process is required to degrade the recalcitrant structure of SCG for the accessibility of hydrolysis process. Recently, microwave pretreatment has become an alternative method due to its ease of use and high heating capacity, which could help to reduce reaction time compared to the conventional heating (Saleem *et al.*, 2015). Most importantly, it can destabilize the structure of cellulose and reduce the formation of inhibitor during pretreatment process under low energy consumption (Kumar & Sharma 2017). Microwave-assisted inorganic salt pretreatment can lead to a higher sugar recovery (Moodley & Gueguim Kana 2017), but has not been tested on SCG. Therefore, this research was carried out to investigate the most suitable inorganic salt concentration in microwave pretreatment that can produce a higher yield of reducing sugar from SCG.

2. MATERIALS AND METHODS

2.1 Sample Collection and Preparation

SCG was collected from Sanctuary Café at Kangar, Perlis. The samples collected were dried in an oven at 80°C for 48 hours to prevent growth of microorganisms (Ravindran *et al.*, 2017). The dried SCG were sieved to obtain particles sized between 0.25mm to 0.5 mm. The samples were stored in the freezer at -20°C until further use.

2.2 Microwave-Assisted Inorganic Salt Pretreatment

Microwave pretreatment was carried out in a microwave oven (Electrolux EMS21400W, Sweden) at 90W-800W, with frequency of 2.45GHz. Five g of dried SCG was loaded with 50 mL of NaCl with concentrations of 1%, 2% and 3% (Jamsai *et al.*, 2019). The pH of the solutions were measured using a pH meter. These samples were mixed thoroughly using magnetic stirrer and heated in the microwave at 300 W for 3 minutes (Jamsai *et al.*, 2019). The pH was measured again after pretreatment. The pretreated samples were then filtered using a filter paper. The solid residues were washed with distilled water and dried in the oven at 60°C for 24 hours (Jin *et al.*, 2020). The total solid loss was determined after the SCG was dried. The dried SCG were used in the saccharification process. Each experiment was run in triplicates.

2.3 Optimization of Microwave-Assisted Pretreatment of SCG

Response surface methodology (RSM) with CCD (Design Expert version 11, Stat-Ease Inc, Minneapolis, Minnesota) was used for the optimization of the selected microwave-assisted pretreatment in this study. The parameters used for the optimization were solid to liquid ratio (1:50 - 8:50) (Cao *et al.*, 2019, Norazlina *et al.*, 2021), microwave power (300W – 800W) (Sombatpraiwan *et al.*, 2019) and irradiation time (1-10 minutes) (Fatriasari *et al.*, 2017, Tiwari *et al.*, 2019), with reducing sugar concentrations as the response. Analysis of variance (ANOVA) was applied to test the fitness of the model and determine the p- and F-values. Three-dimensional graphs and contour plot were generated from the regression models.

2.4 Saccharification

In enzymatic saccharification, 10% (w/v) of dried pretreated SCGs solids and 10 FPU/g of cellulase were added into a 50 mL of Erlenmeyer flask which contained 7.5 mL of 0.1 M citrate buffer (Jin et al., 2020) at pH 4.8 with working volume of 15 mL (Ríos-González *et al.*, 2021). The flask was incubated at 50°C with agitation speed of 225 rpm in an incubator shaker for 72 hours (Passadis *et* *al*., 2020). Lastly, the samples were centrifuged at 8000 rpm for 10 minutes to analyze the supernatant for reducing sugar concentrations.

2.5 Sample Analysis

2.5.1 Determination of Reducing Sugar Concentration

Supernatants collected from the saccharification process were analyzed using the DNS analysis for reducing sugar content. First, 0.5 mL of DNS reagent was added into the test tubes containing 1 mL of supernatants, and mixed well using a vortex mixer. The test tubes were placed in boiling water bath at 95°C for 5 min, and cooled in iced water. Then, 4.5 mL of distilled water was added into the test tubes and mixed well. Sufficient amount of solution was added into the cuvette and placed in UV-vis spectrophotometer at 540nm. The reducing sugar concentration was obtained by substituting the absorbance into the equation of a standard curve (Jin *et al*., 2020).

2.5.2 Determination of Surface Morphology

The surface morphology of raw and pretreated SCG were analyzed using a scanning electron microscope (SEM) (JEOL JSM-IT 300LV, USA). The sample was placed on the conductive tape and observed at magnification of 500X (Jamsai *et al*., 2019).

2.5.3 Determination of Functional Groups

Fourier transform infra-red spectroscopy (FTIR) (Perkin-Elmer, USA) was used to determine the functional groups of the raw and pretreated SCG to observe the changes in functional groups after pretreatment. One mg of dried sample was added with 100 mg of potassium bromide, pelletized and analyzed at wavelengths between 600 cm^{-1} to 4000 cm^{-1} (Jamsai *et al*., 2020). The functional groups were compared by identifying the spectrum peak of each sample.

2.5.4 Determination of Crystallinity Index

X-ray diffractometer (Bruker, D2, USA) was used to determine the crystallinity of the raw and pretreated SCG. The SCG sample were loaded in the shallow well of the sample holder with diameter of 25mm. A round surface of glass was used to pack the sample into the well. The native and pretreated SCG was determined at scan range of $5° < 2\theta < 60°$ (Sindy 2019). The X-ray was emitted from the copper tube with λ= 0.154 nm at 30 kV and 10 mA. The crystallinity index (Crl) can be calculated by using Equation 1 (Jamsai *et al*., 2019).

$$Crl(\%) = \frac{(I_{002} - I_{am})}{I_{002}} \times 100\% \tag{1}$$

3. RESULTS AND DISCUSSION

3.1 Effects of NaCl Concentration on pH, Solid recovery and Reducing Sugar Production

Figure 1 shows the comparison of reducing sugar produced at different NaCl concentration in microwave pretreatment of SCG. In general, reducing sugar concentration increased with the concentration of NaCl. It was observed that 3% NaCl solution showed the highest reducing sugar concentration which was 43.56 mg/mL, while 2% NaCl and 1% NaCl resulted in 38.51 mg/mL and 25.11 mg/mL, respectively. The result obtained was in agreement with the previous studies by Jamsai *et al*., (2019) and Moodley & Gueguim Kana (2017).

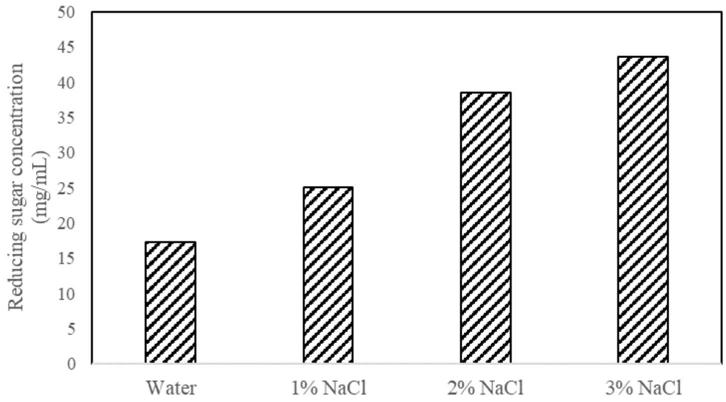


Figure 1. Production of reducing sugar in microwave pretreatment of SCG at different NaCl concentrations

Lignin was one of the components contained in SCG that can hinder the enzyme hydrolysis process as lignin adsorbed the enzyme to form lignin-enzyme complex, leading to inactivation of enzyme. NaCl is a metal chloride salt where it can form metal cation to remove the lignin. The metal cation attach to lignin by forming metal-lignin complex, and it can increase the enzyme accessibility (Kamireddy *et al*., 2013). Therefore, more reducing sugar can be produced. Besides that, metal chloride salt was characterized as Lewis acid where it can degrade the hemicellulose by breaking down ether bonds to release monomer sugar (Moodley & Gueguim Kana 2017). The reducing sugars obtained in microwave-assisted water pretreatment was 17.32 mg/mL, lower than those treated with NaCl. This was probably due to NaCl ions induced more heat compared with water leads to degradation of LCB structure (Xu 2015). Since 3% NaCl produced the highest reducing sugar, hence this concentration was applied in the subsequent optimization work. Table 1 shows the pH of the liquor before pretreatment and after pretreatment.

Table 1. pH and solid recovery following microwave-assisted NaCl pretreatment

NaCl concentration	Initial pH	Final pH	Solid recovery (%)
Water (Control)	4.99 ± 0.01	4.97 ± 0.04	85.96
1%	4.70 ± 0.03	4.51 ± 0.03	87.51
2%	4.63 ± 0.01	4.45 ± 0.03	90.70
3%	4.61 ± 0.00	4.38 ± 0.02	92.93

The initial and final pH in the liquor of microwave-assisted NaCl pretreated SCG were measured to identify the presence of inhibitors and destruction of sugar component (Ethaib *et al*., 2016). From Table 1, the pH of the liquor has dropped after microwave-assisted NaCl pretreatment, as well as in Control. The percentage of pH decrement was 4.03% when SCG was treated with 1% of NaCl in the microwave. The pH of liquor in 2% and 3% of NaCl also showed pH reduction of 3.89% and 4.99%, respectively. For microwave-assisted with only water (Control), the pH was slightly dropped from 4.99 to 4.97. This might be due to the formation of organic acids such as acetic and lactic acid during microwave pretreatment, leading to reduction in pH as the acetyl group in hemicellulose has been hydrolyzed (Hoekman *et al*., 2011, Loow *et al*. (2015). Besides that, the solid recovery of microwave-pretreated solid SCG was also investigated. The lowest solid recovery was achieved by the Control with 85.96%. The solid recovery of microwave-assisted NaCl pretreatment was found to be increased with increased NaCl concentration. Pretreatment with 3% NaCl showed the highest solid recovery, 92.93% followed by 2% NaCl with solid recovery of 90.70% and 1% NaCl with 87.51%. The destruction of lignin and hemicellulose can lead to the increase in cellulose content in SCG (Thiamngoen *et al*., 2022). This may be due to exposure of cellulose after degradation of lignin and hemicellulose. Low solid recovery has significant effect on the reducing sugar yield due to the cellulose has been degraded with hemicellulose and lignin in the pretreatment process (Obeng *et al*., 2019). However, several studies have shown that the solid recovery is inversely proportional to the concentrations of chemicals such as acid, alkaline and inorganic acid as the pretreatment process solubilized lignin, hemicellulose and amorphous region leads to solid loss in biomass (Ethaib *et al*., 2016, Kang *et al*., 2013, Obeng *et al*., 2019).

3.2 Optimization of the Pretreatment Condition

In the present work, RSM was employed to optimize the microwave pretreatment parameters which are solid to liquid ratio, microwave power and irradiation time using CCD. Table 2 presents the result of each run at different combination of parameters.

Table 2. Experimental design for reducing sugar production from microwave-assisted NaCl pretreated SCG.

Runs	Factor 1 A: Solid to liquid ratio	Factor 2 B: Microwave power (Watt)	Factor 3 C: Irradiation time (minutes)	Reducing sugar concentration (mg/mL)
1	4.5: 50	550	5.5	38.08
2	1: 50	550	5.5	35.67
3	4.5: 50	550	10	38.79
4	8: 50	800	10	40.89
5	1: 50	800	10	35.87
6	4.5: 50	800	5.5	38.91
7	4.5: 50	300	5.5	35.43
8	1: 50	300	1	30.73
9	8: 50	550	5.5	38.86
10	8: 50	800	1	34.67
11	4.5: 50	550	1	36.03
12	8: 50	300	10	36.93
13	8: 50	300	1	33.46
14	4.5: 50	550	5.5	37.50
15	1: 50	800	1	34.39
16	4.5: 50	550	5.5	37.11
17	1: 50	300	10	31.98

The highest reducing sugar concentration of 40.89 mg/mL was obtained at solid to liquid ratio of 8:50, microwave power of 800 Watt and irradiation time of 10 minutes. In contrast, the lowest reducing sugar concentration of 30.73 mg/mL was obtained at solid to liquid ratio of 1:50, microwave power of 300 Watt and irradiation time of 1 minute. Based on the ANOVA in Table 3, F-value of the model was 33.71 and p-value was <0.0001, which indicated that the model was statistically significant. Lack of fit is used to indicate the inadequacy of model by comparing the residual error with model prediction (Breig & Luti 2021). The lack of fit of F-value and p-value obtained were 1.71 and 0.4083, respectively. This implied that the model was not significant to pure error and fits well. The individual variables, solid to liquid ratio (A), microwave power (B), irradiation time (C) and quadratic variables A^2, B^2, C^2 were found significant due to the p-value being less than 0.05. The interaction between variables AC has significant effect to reducing sugar production. However, interaction variables AB and AC were not significant as the p-value was larger than 0.05. The data obtained fitted in the second order polynomial as given by Equation 2.

$$Reducing\ sugar\ concentration = 37.98 + 1.62A + 1.62B + 1.52C - 0.295AB + 0.87AC + 0.3725\,BC - 1.03\,A^2 - 1.12B^2 - 0.8842C^2 \quad (2)$$

From Table 4, standard deviation of this model was 0.5995 and R^2=0.9774 determined that the model fitted well to the data with high correlation. This explained the model was fitted at 97.74% of the variability in response. Adjusted R^2 was 0.9485 which meant the model adequately fitted at 94.85% of data. The predicted R^2 value of 0.7786 was less than the adjusted value with difference less than 0.2, indicating that the model has high precision.

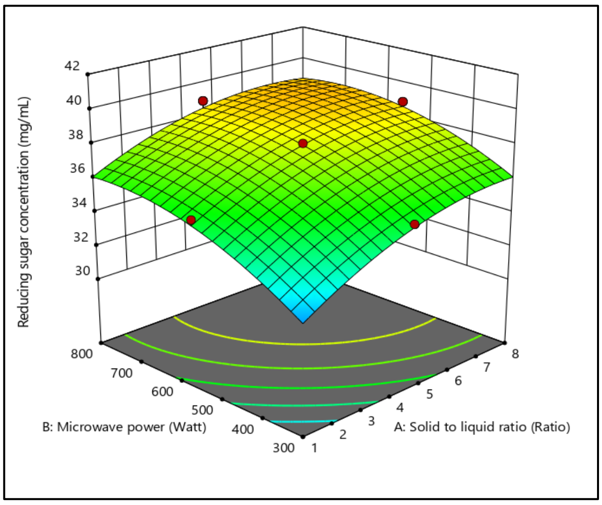
Table 3. Analysis of Variance (ANOVA) of response from microwave-assisted NaCl pretreatment of SCG.

Factor	Sum of square	df	Mean Square	F-value	P-value	
Model	109.06	9	12.12	33.71	< 0.0001	Significant
A - Solid to liquid ratio	26.15	1	26.15	72.74	< 0.0001	
B – Microwave power	26.24	1	26.24	73.01	< 0.0001	
C-Irradiation time	23.04	1	23.04	64.11	< 0.0001	
AB	0.7081	1	0.7081	1.97	0.2032	
AC	6.06	1	6.06	16.85	0.0045	
BC	1.11	1	1.11	3.09	0.1223	
A^2	2.84	1	2.84	7.90	0.0261	
B^2	3.39	1	3.39	9.42	0.0181	
C^2	2.09	1	2.09	5.83	0.0465	
Lack of fit	2.04	5	0.4079	1.71	0.4083	Not significant
Pure error	0.4765	2	0.2382			

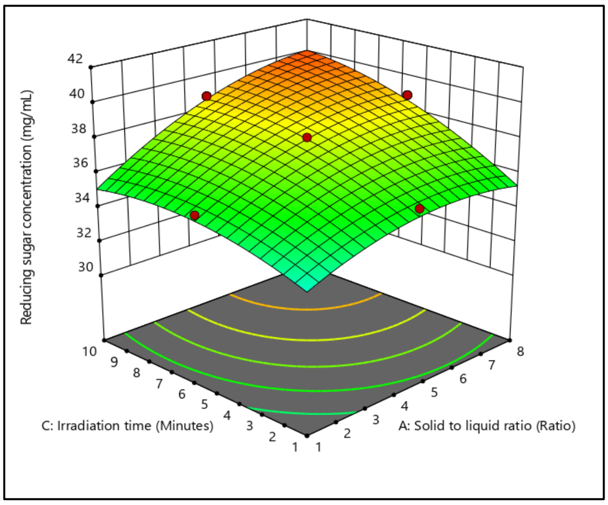
Table 4. R-squared Value for Response Parameter

Parameters	Value
Standard deviation	0.5995
Mean	36.19
R^2	0.9774
Adjusted R^2	0.9485
Predicted R^2	0.7786
Adequate precision	20.6816

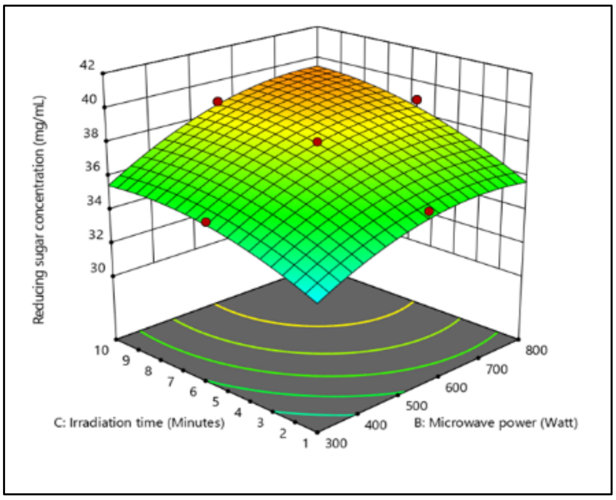
Adequate precision of 20.6816 was greater than 4 where the model showed adequate signal. Figure 2(a) showed 3D response surface plot of the effect of two variables which are solid to liquid ratio and microwave power. The reducing sugar concentration increased from solid to liquid ratio of 3:50 and microwave power of 400 watt. There was no peak in the graph and thus a wider range of solid to liquid ratio and microwave power was suggested to be used for optimization review. In Figure 2(b), the optimum region for solid to liquid ratio was 4.5:50 to 8:50, while irradiation time was 5.5 to 10 minutes. The reducing sugar concentration increased with the rise of solid to liquid ratio from 1:50 to 8:50, and irradiation time from 1 to 10 minutes. Delignification was increased with irradiation time in microwave pretreatment due to rapid molecular collision and disruption of lignocellulosic structure (Alexander *et al.*, 2020). Besides, it is noteworthy that microwave electric field induced more motion of salt ions resulting in rapid heating, causing degradation of lignocellulosic structure for enzyme accessibility (Xu 2015). Figure 2(c) showed the reducing sugar reached a maximum at 800 watt and 10 minutes. The reducing sugar concentration increased at increment of microwave power from 300 to 800 watt and irradiation time from 1 to 10 minutes. This indicated that the combination effect of irradiation time and microwave power has significantly improved the digestibility of biomass through disintegration of hemicellulose and cellulose depolymerization (Hoang *et al.*, 2021).



(a)



(b)



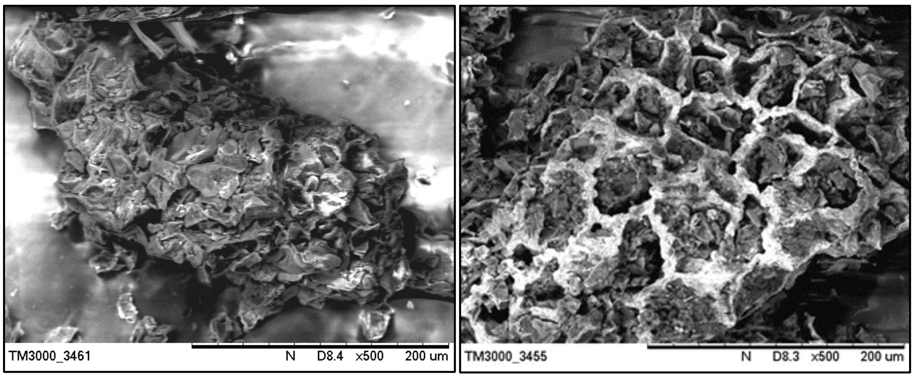
(c)

Figure 2. 3D response plot towards reducing sugar production: (a) microwave power vs. solid to liquid ratio, (b) Irradiation time vs. solid to liquid ratio, (c) Irradiation time vs. microwave power

3.3 Alteration of surface morphology, functional groups and crystallinity following pretreatment

3.3.1 Surface morphology

SEM analysis was carried out to study the surface morphology of the raw and pretreated SCG. Figure 3 shows the SEM microscopy of the raw and pretreated SCG under 500x magnification. The raw SCG had smooth surface with less porous structure. However, microwave-assisted NaCl pretreated SCG showed larger pore size and rougher surface as the fibers were loosened. This indicated that the microwave pretreatment can lead to structural changes and increased surface area of the pretreated SCG due to removal of lignin which can enhanced the accessibility for enzyme (Jamsai *et al*., 2019). The result was in agreement with the study by Moodley & Gueguim Kana (2017), where the microwave-assisted inorganic salt pretreated sugarcane leaves waste depicted cellular distortion and structural change.



(a) (b)

Figure 3. SEM microscopy of (a) raw and (b) pretreated SCG

3.3.2 Functional groups analysis

FTIR analysis was performed to analyze the changes in functional groups for the microwave-assisted NaCl pretreated SCG, and the results are shown in Figure 4.

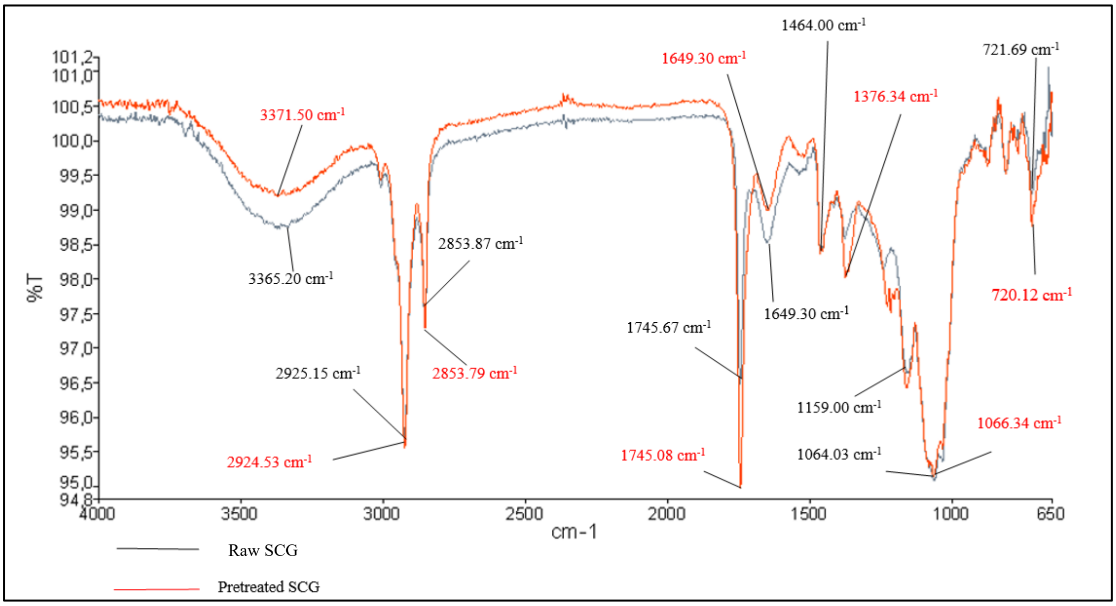


Figure 4. FTIR spectra of raw and pretreated SCG

The broad band found between 3200 cm^{-1} and 3600 cm^{-1} was attributed to the O-H stretching in hydroxyl group of cellulose (Bhaturiwala & Modi 2020). The intensity of the O-H stretching was reduced compared with the raw SCG which implied disruption of cellulose hydrogen bond after microwave pretreatment. The spectrum between 3000 cm^{-1} – 2800 cm^{-1} might be related to C-H stretching in methyl and methylene group of cellulose and lignin (Md Salim *et al.*, 2021). The C-H stretching of methyl and methylene group of cellulose and lignin slightly increased at peaks 2924.53 cm^{-1} and 2853.79 cm^{-1} after microwave pretreatment. The area between 1700 cm^{-1} and 1600 cm^{-1} represented the aromatic ring C=C stretching of the chlorogenic acid and caffeine of SCG (Ballesteros *et al.*, 2014). The reduction of intensity in the C=C stretching of the pretreated SCG implied that the lignin was ruptured. Absorption band at 1745.08 cm^{-1} which corresponded to the C=O stretching of acetyl group hemicellulose was increased after microwave pretreatment. However, the absorption band at 1464 cm^{-1} and 1159.00 cm^{-1} related to the C-H bending of the lignin and polysaccharides plane and C-O stretching of the guaiacyl in the lignin had disappeared. This result was consistent with the study of Ravindran *et al.*, (2017) as the lignin was removed during pretreatment. Also, the peak at 1376.34 cm^{-1} which represented the CH_3CH bending of cellulose, existing in the FTIR spectra of the pretreated SCG implied that the microwave pretreatment had enhanced the cellulose content (Md Salim *et al*., 2021). The peaks at 1066.34 cm^{-1} related to the C-O stretching of cellulose and hemicellulose in the pretreated SCG showed slight reduction compared to the raw SCG indicating the degradation of cellulose and hemicellulose. The increased intensity at 720.12 cm^{-1} implied the enhancement of glycosidic bond in hemicellulose and cellulose (Ballesteros *et al*., 2015). Hence, the microwave-assisted NaCl can cause lignin rupture and increase the polysaccharides content, and therefore increased the reducing sugar yield (Thiamngoen *et al*., 2022).

3.3.3 Crystallinity analysis

X-ray diffraction (XRD) analysis was used to determine the effectiveness of pretreatment by analyzing the crystallinity of the biomass. The crystallinity index (CrI) is important in analyzing the crystallinity of biomass affected by the pretreatment process through the ratio of crystalline region to amorphous region of biomass (Moodley & Gueguim Kana, 2017). The amorphous region of the LCB can be determined at X-ray signal peak of $2\theta = 15°$ whereas the crystalline region can be observed at X-ray signal peak of $2\theta = 22°$. Based on the analysis, the CrI of pretreated SCG was 23.3% higher than the raw SCG with CrI of 16.3%. This result was consistent with the research by Moodley & Gueguim Kana (2017) where the CrI of microwave-assisted NaCl of sugarcane leaves waste was 24.23%. Higher crystallinity of the pretreated SCG indicated that the lignin and hemicellulose were degraded or solubilized, hence would improve the accessibility of enzyme to cellulose molecules during saccharification.

4. CONCLUSION

SCG was successfully treated using microwave with the addition of NaCl at various concentrations in the interest to increase reducing sugar production. Application of 3% NaCl in microwave pretreatment has produced the highest reducing sugar concentration of 43.56 mg/mL, with solid recovery of 90.70%. While the optimum reducing sugar of 41.38 mg/mL was achieved at solid:liquid of 8:50 mg/mL, microwave power of 800 Watt and irradiation time of 10 minutes by using CCD. Through microscopic observation, it was found that the microwave-assisted NaCl pretreated SCG displayed high porosity and cellular distortion which indicated degradation of lignin. The disappearance of absorption peak for C-H bending and C-O stretching in FTIR spectra after microwave pretreatment supported the removal of lignin following pretreatment which enhanced the reducing sugar production. Moreover, the crystallinity of microwave-assisted NaCl pretreated SCG was higher than the raw SCG due to the removal of lignin and hemicellulose. Based on these results, it can be concluded that microwave-assisted NaCl pretreatment hold a great potential for the production of fermentable sugars from lignocellulosic biomass, particularly SCG.

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