MJFAS MALAYSIAN JOURNAL OF FUNDAMENTAL AND APPLIED SCIENCES
PRINT ISSN: 2289-5981 | ONLINE ISSN: 2289-599X

RESEARCH ARTICLE

Chemical composition in sugarcane bagasse: Delignification with sodium hydroxide

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Article history
Received 17 April 2018
Revised 17 April 2018
Accepted 27 July 2018
Published Online 14 April 2019

Abstract

Sugarcane bagasse is a cheap agro-based waste material. These biomass materials have a lot of potential to be converted into useful products such as carbon. Sugarcane bagasse was extracted by sodium hydroxide. Several characterizations has been done to analyse the chemical properties of sugarcane bagasse after extraction by sodium hydroxide including FTIR, XRF, HPLC and SEM-EDS. SEM showed an increase in internal surface area of the lignocellulose particles and weakening of the structural, while EDS showed 60.59 % content of carbon. HPLC results showed some peaks at different retention times. The organic compound could be observed by retention time at 9.611 minute with 66.428 % of height and it was identified as schaftoside. FTIR showed that the peak was shifted from 1096 cm^{-1} to 1638 cm^{-1}, indication the presence of H-O-H (water adsorption). The element with the highest concentration that found by using XRF in untreated sugarcane bagasse was water, H_2O (98.5 %), followed by sodium, Na (0.669 %) and sulfur, S (0.638 %). The concentration of each element was decreased (except H_2O) after being treated with NaOH. Sugarcane bagasse which treated with alkaline solution was more suitable to be applied in the industry compared to acidic solution. This was due to the high reactivity of acidic solution that might damage the entire structural compounds of sugarcane bagasse.

Keywords: Sugarcane bagasse, sodium hydroxide extraction, chemical characterization, retention time, organic compound

INTRODUCTION

About 32% of bagasse is produced from every ton of sugarcane (Sahiron *et al.*, 2017). The total plantation area of sugarcane bagasse in Malaysia is nearly 34 500 acres (Mohan *et al.*, 2012). Based on the statistic reported by Food and Agriculture Organization (FAO), in 2014, there are about 9 147 tons of sugarcane have been produced in Malaysia.

Agricultural industry is rapidly increasing in Malaysia, but the waste of this industry is not well managed. The huge numbers of organic waste have not been fully utilized (Saska *et al.*, 1995). Baharuddin in 2007 reported that natural organic waste has a potential as an alternative method for creating paper, partition material and channel. Since there is an increase in the proportion of recyclables in the waste stream such as organic wastes, it is compulsory to take action for better recovery and reuse (Baharuddin, 2007). In relation to waste management issues, it is recommended that eco-friendly solutions should be considered before sending the organic wastes for disposal by optimize the MSW (municipal solid waste).

Sugarcane bagasse is a waste residue which produced in a large quantity from many industries. In fact, one metric ton of sugarcane bagasse generates 280 kg of bagasse, the fibrous by-product that remained after sugar extraction from sugarcane (Walford, 2008). Nevertheless, the utilization of sugarcane bagasse is still limited and mainly used as a fuel to power sugar mill (Daud *et al.*, 2007).

Sugarcane is used as a main source in producing sugar for food and beverages (R. Bodîrlău & C.A. Teacă, 2007). In sugar and alcohol industry, sugarcane bagasse is generated as a waste. This bagasse can be a pollutant to the environment if it is just disposed without treatment. Generally, the biomass is composed of cellulose, polyoses, lignin, hemicelluloses, small amounts of extractives and mineral substances (Mohan *et al.*, 2012). In the cell wall of biomass, it consists of lignin, hemicelluloses and cellulose. The sugars are linked together in long chains called polysaccharides, forming the structural portion of plant cell walls (Showalter, 1993).

Rezende et al., in 2011 reported that alkali treatments are initially used to increase biomass digestibility for animal feeding. Lignocellosic cell walls may be distrupted by using diluted alkaline solutions which will be dissolved the hemicellulosee, lignin and silica on hydrolizing uronic and acetic acid esters by swelling cellulose as well (R. Bodîrlău & C.A. Teacă, 2007). The most promising method is alkaline treatment with sodium hydroxide (NaOH). Suksombat in 2004 has use sodium hydroxide, as a strong alkali in his research as recalcitrant material like sugarcane bagasse (Suksombat, 2004).

Although high-temperature alkali pre-treatment was fast and effective (Rezende *et al.*, 2011), it still possessed high-energy demanding process that requiring heat and corrosion-resistant equipment. Lignin decomposition is usually attributed to the cleavage of the α-aryl ether bonds from its polyphenolic monomers, while hemicellulose dissolution and cellulose swelling are a consequence of

hydrogen bond weakening. A 3-4 folds increase of the initial digestibility value is achieved by applying 5-6% of solid NaOH to the materials on a dry matter basis (Suksombat, 2004).

Cellulose microfibrils consist of a crystalline structure of thousands of strands, each of which contains hundreds of glucose sugar molecules. These microfibrils are wrapped in a sheath of hemicelluloses and lignin. These sheaths protecting the cellulose from microbial attack. Hemicelluloses are relatively easy to break down using the pretreatment step. It also disrupts the hemicelluloses or lignin sheath around the cellulose, making the cellulose to be accessible to further hydrolysis. Fig. 1 below shows the structure of cellulose microfibrils.

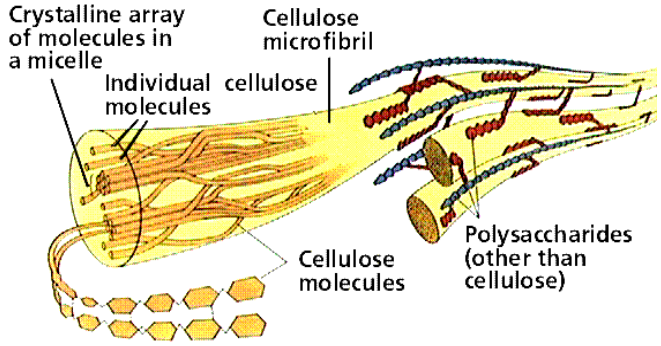

Fig. 1 The structure of cellulose microfibrils. (This image was copyright Dennis Kunkel at www.Dennis Kunkel.com, used with permission).

Low ash content will enhance the enzymatic hydrolysis process. Sugarcane bagasse ash, a by-product of sugar and alcohol production, is a potential pozzolanic material to be used as partial replacement of Portland cements in mortars and concrete as they are low ash content (Pandey *et al.*, 2000b).

A lot of studies have been done on treating the bagasse into more valuable end products such as sugar, fuel, and alcohol. From previous studies, bagasse was found to be a fuel source as it could produce more heat energy to supply in sugar and alcohol industries (Carvalho, 2015). Sugarcane bagasse is a cheap and abundant raw material which can be used for this purpose. The sugarcane industry generates considerable amount of residues during harvesting. Cane green tops are collected by the laborers for harvesting them to be used as animal fodder. Meanwhile, the remaining dry portion is mixed with animal manure and left to decompose. Decomposition of the dry cane tops with manure leads to emissions of greenhouse gases such as methane and loss of organic content of the cane tops that can be utilized as fodder or fertilizer (Nakhla & Haggar, 2014).

This research would determine what was the main organic compound contained and produced from sugarcane bagasse. Thus, this research is needed in order to develop the baggase's potential usage.

EXPERIMENTAL

Materials

The starting materials were comprised of sodium hydroxide (1.0 M), nitric acid (1.0 M), sodium silicate, sodium sulphate, toluene, diethyl ether, chloroform and hexane. The sugarcane baggase (SB) was collected from the market and local farmer in Kelantan. All other chemicals and reagents used were of the highest commercially available purity.

Sample preparation

The sugarcane waste, bagasse (30 g) was dried under sunlight to reduce the moisture content in bagasse. The dry bagasse was ground with a grinding machine and placed in electric furnace. The two types of sugarcane bagasse were SB-Original (sugarcane bagasse without any chemical treatment) and SB-NaOH (sugarcane bagasse that was treated with NaOH solution). The organic compounds were extracted with two methods using three different types (SB-Original and SB-NaOH) of sugarcane bagasse. For solvent extraction method, only one type of sugarcane bagasse (SB-NaOH) was used in the reaction. The aqueous sodium silicate was obtained by stirring 1.0 M of NaOH with the sugarcane bagasse for 24 hours. NaOH solution was acted as an extracting agent by hydrolyzing the organic compounds from the sugarcane bagasse.

Method of solvent extraction

30 g of the sample (SB) was stirred with 750 ml of 1.0 M NaOH solution for 24 hours. The sugarcane bagasse and the aqueous solution (sodium silicate) were separated after being treated with NaOH. Next, the aqueous solution was titrated with 1.0 M nitric acid (HNO_3) to pH 3, 7 and 13. The solutions were left for 4 days for the aging process until the silica gel was started to form. The solution was centrifuged at 4000 rpm for about 10 minutes. The liquid portion was extracted in equal amount of 50 ml for every solvents such as hexane, chloroform, diethyl ether, and toluene. The supernatants were filtered. The solution obtained from the previous step was dried over anhydrous sodium sulfate, evaporated and filtered at room temperature while the remaining liquid was collected. HPLC was used in order to analyze the organic phase.

Characterization of sugarcane bagasse

A morphological analysis of the untreated sugarcane bagasse (SB-Ori) and sugarcane bagasse treated with NaOH (SB-NaOH) were performed at the materials laboratory of University Malaysia Kelantan Jeli Campus. For this analysis, a JEOL® scanning electronic microscope (SEM) model JSM-5800LV was used. Initially, the bagasse sample was subjected to dry in an oven at 60 °C/24 h. This assembly was maintained in a vacuum-desiccator prior to the analysis. The sample was then placed on metallic cylindrical holders called "stubs", measured at 10 mm in diameter and secured with double-sided adhesive tape. The sample in the stubs was then coated with gold and placed in the SEM. The acceleration voltage was set at 1.5kV, 1.8kV or 2.0kV depended on types of sample.

Analytical method by using HPLC

The chemical compositions of sugarcane bagasse, both treated (SB-NaOH) and untreated (SB-Ori) were determined by using HPLC. The hydrolysate was also analyzed by HPLC to determine carbohydrate, organic acid, furfural and hydroxy-methylfurfural contents. HPLC determinations were performed in a Shimadzu LC-10AD chromatograph equipped with refractive index and PDA detectors. LiChrospher column (100 RP-18, 125.0 × 4.0 mm, Hewlett-Packard-Palo Alto, CA, USA) was operated with a mobile phase containing acetonitrile to water ratio of 1:8 (v/v) at a 0.8 mL/min flow rate and 25 °C.

Fourier transform infrared spectroscopy (FTIR) analysis

The properties of the reaction products were characterized by FTIR using a Digilab Fourier Transform Infrared spectrophotometer, Model Excalibur FTS2000. The samples of sugarcane bagasse with pH values of 7 and 11 were passed into a disk for FTIR measurement. The spectra were recorded in the frequency range of 4000-600 cm^{-1} with a resolution of 4 cm^{-1}.

X-ray fluorescence (XRF) analysis

The samples of treated and untreated sugarcane bagasse (liquid) were poured into special cups with supporting films. Diluents were sometimes added to obtain sufficient samples. The samples could not be measured in vacuum because they would evaporate, causing the measurement in air was possible. However, the air could absorb much of the radiation, making it impossible to measure light elements. The spectrometer chamber was therefore filled with He gas. The samples would not evaporate and hardly any radiation was absorbed.

RESULTS AND DISCUSSION

Morphological analysis of sugarcane bagasse

The morphology of SB fibers was investigated using SEM to determine the change of fiber surface and morphology during extraction processing, as showed in Fig. 2. Fig. 2. and Fig. 3 showed the morphology of untreated and treated SB fibers, respectively. The surface of untreated SB fibers presented the smooth surface due to the

presence of oil and waxes (Qi *et al.*, 2017). The images obtained by scanning electron microscopy on the surfaces of the untreated sugarcane bagasse showed two morphological features which were pith and fiber structures (labelled as P and F, respectively) in Fig. 2(b) (Maung *et al.*, 2015). The fiber surface was formed by parallel stripes and partially covered with residual material. The pith was more fragile and fragmented structure containing pits, which were small pores connecting neighboring cells on the surface of the walls *(*Rezende *et al.*, 2011). The electron micrograph of cross section of untreated bagasse showed a large void and loose packing of the fibres and the wall of untreated fibres was intact (Ahmed *et al.*, 2012).

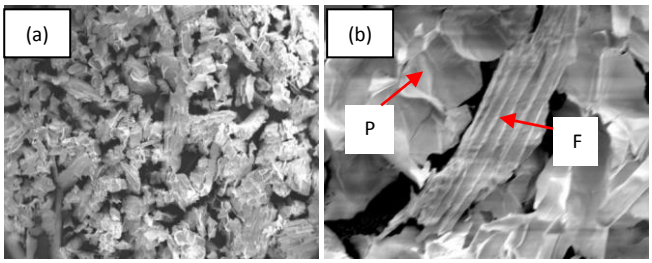

Fig. 2 Morphology of the untreated sugarcane bagasse by SEM analysis with magnification 30k (a) and 200k (b).

Alkaline treatment also has a remarkable effect on the bagasse morphology, especially on the fibre bundles. The images obtained from fiber surfaces of the samples under 1.0 M concentration of NaOH were presented in Fig. 3. After being treated with NaOH, the bagasse bundles were started to dismantle and the fibers were detached from the others. Alkaline pretreatment by adding NaOH solution could cause a swelling of the biomass, which would result in the increase of the internal surface area of the lignocellulose particles, as well as the weakening of the structural integrity of the lignocellulose and breaking of bond linkages between lignin and the other carbohydrates (cellulose and hemicellulose), causing in greater accessibility and digestibility of the cellulose fraction, and thus, it could be depolymerized into fermentable sugars (Maryana *et al.*, 2014).

Table 1 Elements found in the sugarcane bagasse (untreated and treated) as indicated in the spectrum in Fig. 5.

Element	Untreated Sugarcane Bagasse		Sugarcane Bagasse Treated with 1.0M NaOH	
	Weight %	Atomic %	Weight %	Atomic %
C	60.59	68.41	52.46	61.94
O	33.53	28.42	33.46	29.66
Na	2.49	1.47	10.10	6.23
Mg	1.55	0.87	2.10	1.23
Si	1.50	0.73	1.88	0.95

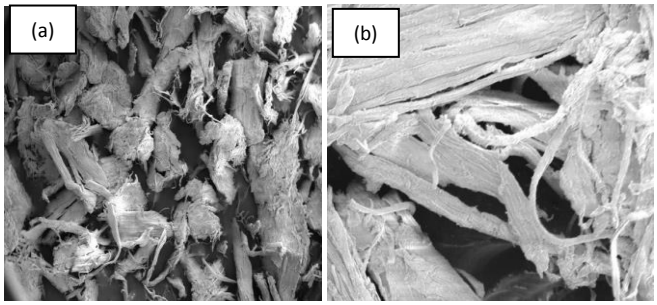

Fig. 3 Morphology of the sugarcane bagasse treated with NaOH by SEM analysis with magnification 30k (a) and 200k (b).

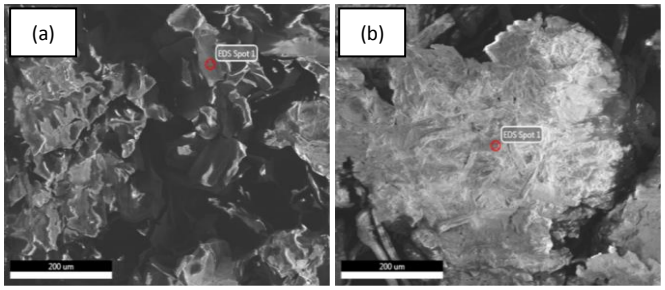

Fig. 4 SEM-EDS spot taken from the untreated sugarcane bagasse (a) and sugarcane bagasse treated with NaOH (b).

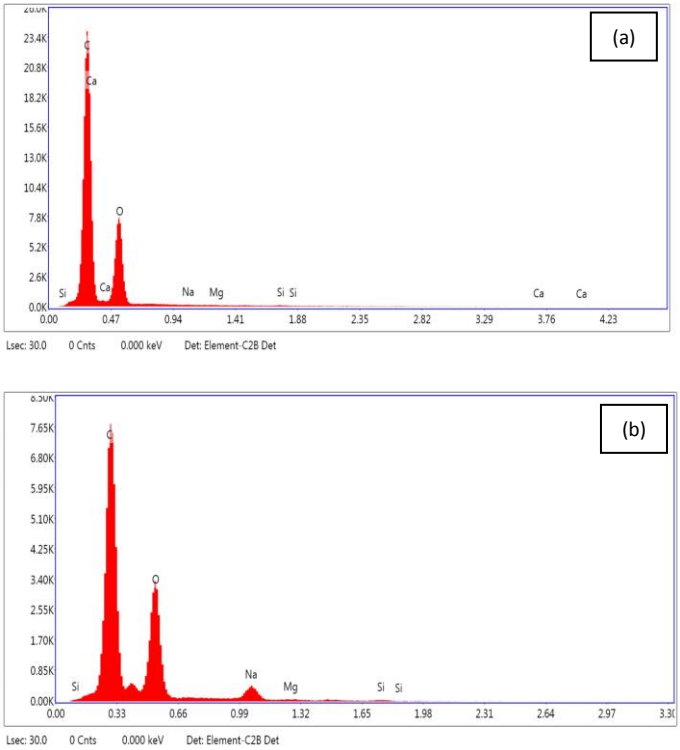

Fig. 5 Spectra of SEM-EDS analysis of the untreated sugarcane bagasse (a) and suagarcane bagasse treated NaOH (b).

Sugarcane bagasse has low nutritional value, which occurred with other lignocellulosic residues and was rich in cell wall matter (da Penha *et al.*, 2012). In this study, the result from SEM-EDS showed that untreated sugarcane bagasse has 1.50% content of silica and 60.59% content of carbon. This result was confirmed with the previous research in the literature review that sugarcane bagasse was suitable as absorbant due to its high quantity of carbon.

Analytical method by using HPLC

Fig 6 and 7 show the chromatograms of untreated and treated sugarcane bagasse that were obtained from HPLC test. The data from both figures were tabulated in Table 2 and 3. The total peak of the untreated sugarcane bagasse (Table 2) was 9 and it was reduced to 7 peaks as shown in Table 3 (after being treated with NaOH). This might be due to the removal of the organic compound in the sugarcane bagasse after treatment with NaOH. From Table 2 (untreated sugarcane bagasse), the highest peak which was peak 9, observed at retention time of 10.09 minute with 62.745% height. The previous research showed that at this highest peak (peak 9), the organic compound was identified as isoschaftoside (Vila *et al.*, 2008). From Table 3 (treated sugarcane bagasse), the highest peak which was peak 7 observed at retention time of 9.611 minute with 66.428% height. The organic compound at this retention time was identified as schaftoside which was found by (Colombo *et al.*, 2009) in the previous study.

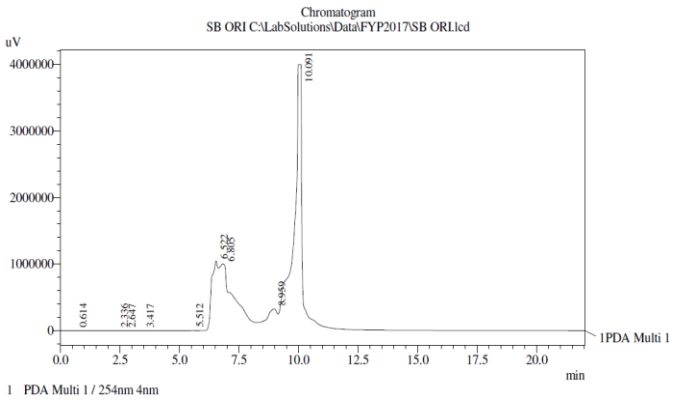

Fig.6 Chromatogram showing retention time (RT) in minutes of untreated sugarcane bagasse.

Table 2 Peak table for untreated sugarcane bagasse.

Peak	Ret. Time	Height	Area %	Height %
1	0.614	1284	0.008	0.020
2	2.336	269	0.002	0.004
3	2.647	451	0.003	0.007
4	3.417	387	0.004	0.006
5	5.512	1634	0.006	0.026
6	6.522	1046247	10.789	16.414
7	6.805	1001774	25.607	15.716
8	8.959	322630	6.330	5.062
9	10.091	3999473	57.251	62.745

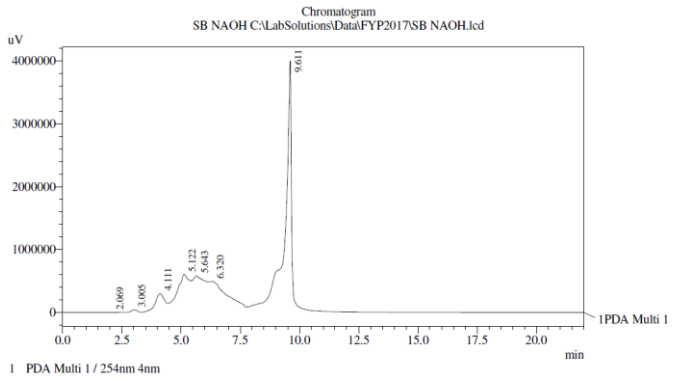

Fig.7 Chromatogram showing retention time (RT) in minutes of treated sugarcane bagasse.

Table 3 Peak table for sugarcane bagasse treated with NaOH.

Peak	Ret. Time	Height	Area %	Height %
1	2.069	98	0.001	0.002
2	3.005	41856	0.463	0.695
3	4.111	297045	5.178	4.932
4	5.122	604524	13.914	10.038
5	5.643	582874	14.027	9.678
6	6.320	495486	16.027	8.227
7	9.611	4000575	50.390	66.428

Fourier transform infrared spectroscopy (FTIR)

The main differences in respect to functional groups of the treated and unteated sugarcane bagasse might be observed from the FTIR spectra presented in Fig 8 and 9. The functional group of the molecules was represented by the absorption bands in the range of 600 cm^{-1} to 4000 cm^{-1}. According to the spectrum, wavenumbers between 600 cm^{-1} to 4000 cm^{-1} were represented for the functional groups of Si, O and H. The patterns of the result obtained was almost the same and only differred at the spectrum pattern.

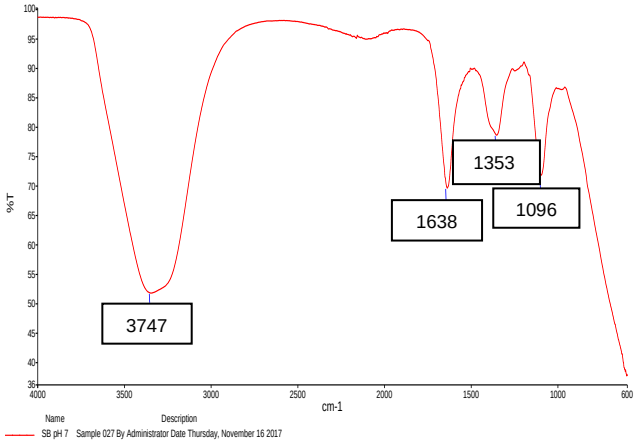

Fig. 8 FTIR spectrum of Untreated Sugarcane Bagasse (SB-Ori).

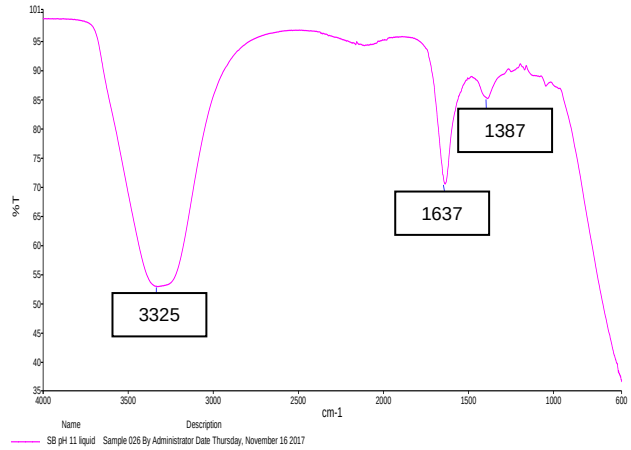

Fig. 9 FTIR spectrum of Treated Sugarcane Bagasse (SB-NaOH).

The most visible differences between the spectra of treated sugarcane bagasse (SB-NaOH) at pH 11 and untreated sugarcane bagasse (SB-Ori) at pH 7 were found within the region from 3500 to 3000 cm^{-1}. At peak 969 cm^{-1}, the wavenumber was represented for the Si-O-Si stretching. Both spectrums were appearred at peak 3747 cm^{-1} (SB-Ori) and 3325 cm^{-1} (SB-NaOH) that represented the peak for hydroxyl group in the sample. While peak observed at 1096 cm^{-1} to 1638 cm^{-1} was denoted to the presence of H-O-H (water adsorption).

X-ray fluorescence (XRF) analysis

The product was determined by X-ray fluorescence spectrometer (XRF) and the summarized chemical compositions of sugarcane bagasse sample were shown in Table 4. The element with the highest concentration found by using XRF in untreated sugarcane bagasse was water, H_2O (98.5 %), followed by sodium, Na (0.669 %), and sulfur, S (0.638 %). The concentration of each element was decreased (except H_2O) after being treated with NaOH. It was well known that the non-cellulosic materials like hemicelluloses and lignin were presented in the form of network that bound the fiber bundles in a composite-like structure. During the alkali treatment, hemicelluloses that have been removed would weaken this network and some lignins would become loose and remove due to this damaged network.

In this study, the bagasse was chosen as it consisted of approximately 50% cellulose and 25% each of hemicelluloses and lignin. Chemically, bagasse contains about 50% α-cellulose, 20% pentosans and 2.4% ash (da Penha et al., 2012). Because of its low ash content, bagasse offers numerous advantages in comparison to other crop residues such as rice straw and wheat straw, which have 17.5% and 11% of ash content, respectively (Pandey et al., 2000a).

Table 4 List of elements found in the treated and untreated sugarcane bagasse with concentration (%).

Element	Concentration (%)	
	Untreated sugarcane bagasse (SB-Ori)	Sugarcane bagasse treated with NaOH (SB-NaOH)
Ca	0.0359	-
Cl	0.0796	0.0718
H_2O	98.5	99.9
Na	0.669	-
P	0.0323	0.0199
S	0.638	0.0133
Sb	0.0021	0.002
Sn	0.0019	0.0018

CONCLUSION

Based on the findings of the study, the following conclusions were drawn. SEM showed an increase in internal surface area of the lignocellulose particles and weakening of the structural, while EDS showed 60.59 % content of carbon. HPLC results showed some peaks at different retention times. The organic compound could be observed by retention time at 9.611 minute with 66.428 % of height and it was identified as schaftoside. FTIR showed that the peak was shifted from 1096 cm^{-1} to 1638 cm^{-1}, indication the presence of H-O-H (water adsorption). The element with the highest concentration that found by using XRF in untreated sugarcane bagasse was water, H_2O (98.5 %), followed by sodium, Na (0.669 %) and sulfur, S (0.638 %). The concentration of each element was decreased (except H_2O) after being treated with NaOH. Sugarcane bagasse which treated with alkaline solution was more suitable to be applied in the industry compared to acidic solution.

Therefore, sugarcane bagasse which treated with alkaline solution (NaOH has been used in this study) was more suitable to be applied in the industry compared to acidic solution. This was due to the high reactivity of acidic solution that might damage the entire structural compounds of sugarcane bagasse. Besides, acidic condition could be harmful to the environment, as well as to living organisms.

ACKNOWLEDGEMENT

This work was financially supported by the Universiti Malaysia Kelantan under the Research University Grant and Ministry of Higher Education Malaysia.

REFERENCES

Ahmed, F. M., Rahman, S. R., & Gomes, D. J. (2012). Saccharification of sugarcane bagasse by enzymatic treatment for bioethanol production. *Malaysian Journal of Microbiology*, *8*(2), 97–103.

Carvalho, D. M. de. (2015). *Study on the structure and properties of xylan extracted from eucalyptus, sugarcane bagasse and sugarcane straw* (Doctoral dissertation, KTH Royal Institution of Technology, Stockholm). Retrieved from http://kth.diva-portal.org/smash/record.jsf?pid=diva2%3A862284&dswid=-9656

Colombo, R., Yariwake, J. H., Queiroz, E. F., Ndjoko, K., & Hostettmann, K. (2009). On-line identification of minor flavones from sugarcane juice by LC/UV/MS and post-column derivatization. *Journal of the Brazilian Chemical Society*, *20*(9), 1574–1579.

Da Penha, M. P., da Rocha Leão, M. H. M., & Leite, S. G. F. (2012). Sugarcane bagasse as support for the production of coconut aroma by solid state fermentation (SSF). *BioResources*, *7*(2), 2366–2375.

Haung, H., Yang, S.-T., & Ramey, D. E. (2003). A hollow-fiber membrane extraction process for recovery and separation of lactic acid from aqueous solution. *Applied Biochemistry and Biotechnology*, *98–100*(1–9), 311–318.

Maryana, R., Ma'rifatun, D., Wheni, I. A., K.W., S., & Rizal, W. A. (2014). Alkaline pretreatment on sugarcane bagasse for bioethanol production. *Energy Procedia*, *47*, 250–254.

Maung, Y. M., Win, T. T., & Oo, A. T. (2015). Preparation and characterization of bagasse ash. *International Journal of Technical Research and Applications*, *3*(1), 84–87. Retrieved from www.ijtra.com/download.php?paper=316

Mohan, P. R., Ramesh, B., & Redyy, O. V. S. (2012). Production and optimization of ethanol from pretreated sugarcane baggase using *Sacchromyces bayanus* in simultaneous saccharification and fermentation. *Microbiology Journal*, *2*(2), 52-63.

Nakhla, D. A., & Haggar, S. El. (2014). A proposal to environmentally balanced sugarcane industry in Egypt, 2(9), 321-328.

Pandey, A., Soccol, C. R., Nigam, P., & Soccol, V. T. (2000a). Biotechnological potential of agro-industrial residues. I: Sugarcane bagasse. *Bioresource Technology*, *74*(1), 69–80.

Pandey, A., Soccol, C. R., Nigam, P., Soccol, V. T. (2000b). Biotechnological potential of agro-industrial residues. I: Sugarcane bagasse. *Bioresource Technology*, *74*, 69–80.

R. Bodîrlău, C.A. Teacă (2007). Fourier transform infrared spectroscopy and thermal analysis of lignocellulose fillers treated with organic anhydrides. January 2007. *Romanian Journal of Physics*, *54*(1), 93-104.

Qi, G., Peng, F., Xiong, L., Lin, X., Huang, C., Li, H., Chen, X. (2017). Extraction and characterization of wax from sugarcane bagasse and the enzymatic hydrolysis of dewaxed sugarcane bagasse. *Preparative Biochemistry and Biotechnology*, *47*(3), 276–281.

Rezende, C., de Lima, M., Maziero, P., de Azevedo, E. E., Garcia, W., Polikarpov, I., Griffin, R. (2011). Chemical and morphological characterization of sugarcane bagasse submitted to a delignification process for enhanced enzymatic digestibility. *Biotechnology for Biofuels*, *4*(1), 54.

Sahiron, N., Rahmat, N., & Hamzah, F. (2017). Characterization of sodium silicate derived from sugarcane bagasse ash. *Malaysian Journal of Analytical Science*, *21*(2), 512–517.

Showalter, A. M. (1993). Structure and function of plant cell wall proteins. *The Plant Cell*, *5*(1), 9–23.

Vila, F. C., Colombo, R., De Lira, T. O., & Yariwake, J. H. (2008). HPLC microfractionation of flavones and antioxidant (radical scavenging) activity of *Saccharum officinarum* L. *Journal of the Brazilian Chemical Society*, *19*(5), 903–908.