Egypt. J. Chem. **Vol. 64,** No. 6 pp. 2819 - 2825 (2021)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Characterization of Hydrogel and Fly Ash from Biomass

Nursafika Bahira Binti Juli, Norhayati Talib*, Syarifah Rysmalia Maya Yusoff Abas, Normadyzah Ahmad, Azil Bahari Alias*

Faculty Chemical Engineering Univeriti Teknologi Mara (UiTM) Shah Alam, Malaysia

Abstract

This study aims to produce an efficient adsorbent derived from 4 different biomass and to study the characterization of blending hydrogel from 4 different biomass. Type of material used to produce biochar is corn husk, rice husk, sugarcane bagasse, and sawdust. These four materials are blending with fly ash with different ratios. For hydrogel preparation, Acrylamide (AAm) is used as the monomer, N, N' – methylenebisacrylamide (MBA) as a crosslinker, and ammonium persulfate (APS) as an initiator. This hydrogel – biochar is then characterized by Brunauer – Emmet – Teller (BET) surface area analysis, Thermo Gravimetric Analysis (TGA), and swelling test analysis. Seven samples are analyzed for each raw material: fly ash hydrogel and corn husk hydrogel. For example like SW: FA (1.0:0), SW: FA (0.8:0.2), SW: FA (0.6:0.4), SW: FA (0.5:0.5), SW: FA (0.4:0.6), SW:FA (02:08) and lastly SW:FA (0:1.0). Repeated with the same ratio for the other biomasses. For BET surface area analysis, samples with large surface areas and high pore volumes are suitable for the adsorbent. SW: FA (0.8:0.2) has the largest surface area, which is 6.9966 m^2/g, while the total pore volume is the highest compared to the other samples. In a proximate analysis, Thermogravimetric Analysis (TGA) determined the moisture content, ash content, fixed carbon content, and volatile matter content. A sample with the high volatile matter, high carbon content, and low ash content is more economically attractive. Sample of SW :FA (0.8:0.2) has high moisture content, fixed carbon, volatile matter, and has the lowest ash content among all. All the samples showed a positive impact on the swelling test. Therefore, a sample of SW: FA (0.8:0.2) is the best and suitable to use as an adsorbent.

Keywords: Biochar, Activated Carbon, Rice Husk, Corn Husk, Sugarcane Bagasse, Sawdust, Fly Ash, Hydrogel

1. Introduction

Agricultural activities are now a large growing sector and have contributed a great deal of revenue to the Malaysian economy. The activity will also provide the citizen with employment opportunities. To ensure that agricultural activities contribute, measures have been taken to protect sustainability, such as maintaining soil fertility. Superabsorbent polymer is a material that can absorb a huge amount of water while retaining its original shape without the loss of water that had been absorbed earlier. The addition of acrylamide in acrylic acid can increase the porosity of the absorbent polymer [15].

There is currently much hazardous gas released into the atmosphere, which leads to pollution, thinning the ozone layer, and affecting people's health. The inorganic sulfur compound like CS_2, H_2S, or SO_2 is dangerous to the environment and human health. The biochar is relatively low in price rather than the activated carbon that has inveterate in various applications such as gas adsorption. Usually, the material used to manufacture biochar is from biomass. Moreover, biochar is applicable for adsorption is because of the large, microscopic surface area [2]. Activated carbon, or other names as activated coal or activated charcoal, is a processed carbon acquired from the organic material containing a large amount of carbon content like coal [11].

According to Promraksa & Rakmak (2020), thermal decomposition is also known as pyrolysis, in which the process occurred at moderate temperatures. The biomass is heated at high temperatures without the oxygen gas or air to produce a mixture of gases, condensable liquids (bio-oil), and biochar. During the pyrolysis process, there are two operating conditions, which are fast and slow pyrolysis proses. At fast pyrolysis, the degradation occurred at high

*Corresponding author e-mail: norhayati0653@uitm.edu.my (Norhayati Talib)

Receive Date: 27 December 2020, Revise Date: 27 January 2021, Accept Date: 21 March 2021

DOI: 10.21608/EJCHEM.2021.55464.3171

temperature and high heating rates with short residence time rather than slow pyrolysis [5].

A different method is used to increase the efficiency of the adsorbent. Usually, the heating of biomass used equipment like microwave, but this time it used furnace to heat up the biomass to become biochar. There are two parameters in the pyrolysis process: the flow rate and temperature of gas supplies. Other than that, the biomass properties such as ash content, chemical component, and particle size are significant to get an effective blending of hydrogel biochar. In this study, the hydrogel biochar is prepared using four different biomass types: corn husk, sugarcane bagasse, rice husk, and sawdust. These four biomasses will be blended with fly ash with different ratios to produce hydrogel biochar.

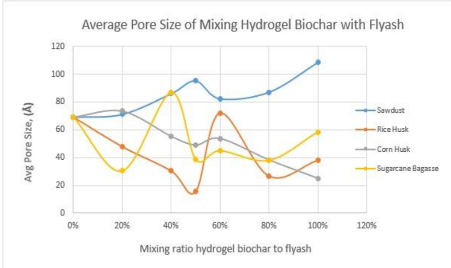
2. Materials and Method

2.1. Preparation of biochar

Cornhusk, sugarcane bagasse, and sawdust were collected from the nearest market, while rice husk was collected at BERNAS. All 4 different biomass were dried under the sun for at least 2 days to make sure it is fully dried. Dried corn husk, sugarcane bagasse, sawdust, and rice husk were filled in earthenware and then put inside the Front-Loading Furnace. The whole body of earthenware was wrapped with aluminum foil, and the dried biomass was put in a large amount to avoid oxygen from entering inside. The pyrolysis reaction occurred at 500˚C for 1 hour. Then, the biochar was cooled down for 3 hours.

2.2. Preparation of hydrogel biochar

To prepare hydrogel biochar, the biochar that dried would be activated with zinc chloride ($ZnCl_2$) solution in 1.0 to 1.0 ratio, which is in this experiment, 25 g of $ZnCl_2$ was dissolved in 150 g of distilled water, and 25 g of the biochar was mixed and kept for 24 hours to activate the process. Then, 0.1 mol of HCl was used to wash the biochar and to obtain a neutral pH. It was washed using distilled water until the pH is 7. After that, it was dried in an oven for 50℃ in 1 day. Acrylamide (AAm) was used as the monomer, N, N'–methylenebisacrylamide (MBA) as a crosslinker, and ammonium persulfate (APS) as an initiator. First, 1.0 gram of AAm was dissolved in 1.0 mL of distilled water. Then, 0.6 g of biochar and 0.01 g of MBA were added to the AAm solution. Then, the mixture was mixed thoroughly before the initiator was added. Next,



0.2 mL of 0.1 g aqueous solution of APS was added to initiate the polymerization steps. To make sure the polymerization and cross linking is completed, the hydrogel precursor solution was placed into a small container, and then it was left for a few minutes at room temperature. The elimination of unwanted monomers by washed with distilled water and keeping the lowest hydrogel's lowest molecular weight was cut into mini size. After that, to keep the moisture content, the hydrogel was kept in a desiccator.

2.3. Brunauer-Emmet- Teller (BET) surface area method

The nitrogen static physical adsorption was used to measure the relationship between adsorption and desorption isotherms at 77 K with 3000 surface area of Micromeritics Tristar and analyze pore. Based on nitrogen adsorption-desorption studies, the samples were degenerate at 150 ˚C for at least 12hours to remove the impurities [1].

2.4. Proximate analysis

The analysis is carried out using a Thermogravimetric Analyzer (TGA), which used about 10 mg of sample. The sample was being heated at a heating rate of 20 °C per minute at room temperature until 600 °C with a nitrogen flow rate of 30ml/min. The nitrogen gas will switch to air for a temperature 600 °C until 1000 °C.

3. Result and discussion

3.1. Brunauer-Emmet- Teller (BET) surface area method

BET analysis's function is to determine the surface area, pore volume, and pore size of the sample. For BET surface area analysis, surface area and the hydrogel's porosity – biochar is determined by N_2 adsorption. Static nitrogen physisorption was used to measure nitrogen adsorption-desorption isotherms with a surface area and pore analyzer of Micromeritics Tristar 3000 at 77 K [14]. The samples were degassed at 120 ℃ for 24 hours based on nitrogen adsorption-desorption studies Nurul et al. (2018). The specific surface area was calculated using the BET equation multipoint. The procedure for BET analysis is shown below. The total pore volume was estimated by single point N_2 adsorbed at N_2 relative pressure of 0.99. The way solids react, burn, and dissolve with other materials can be determined by their surface area. It can be seen from figure 1 that the sample of 80:20 ratio of sawdust and fly ash has the highest surface area value of 6.9966 m^2/g when compared to the other ratios for sawdust, while the smallest surface area is at the ratio of 0:100.

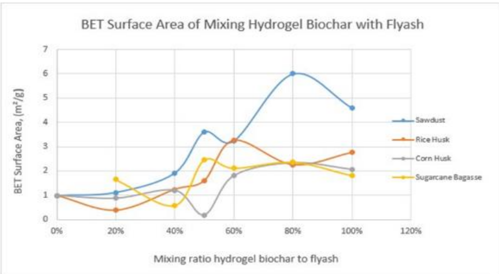


Fig 1: BET surface area of mixing hydrogel biochar.

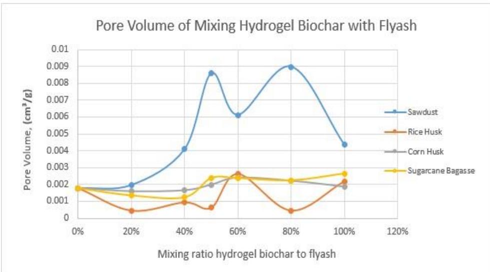


Fig 2: Pore volume of mixing hydrogel biochar

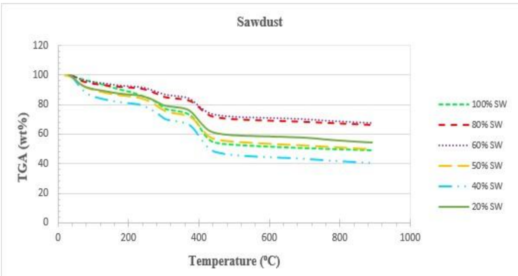


Fig 3: Average pore size of mixing hydrogel biochar.

Generally, as the surface area increases, the sample's adsorption capacity also increases [6]. Moreover, the total pore volume at the ratio of 80:20 for sawdust has the highest value, which is 0.018974 compared to the other ratios for sawdust. Fly ash is familiarized as the economical adsorbent in several adsorption processes, such as the NOx and Sox adsorption, organic compounds, and mercury in the air. In addition, the unburned carbon residual in the fly ash particles can be refined by activating it that will then contribute to the main surface area and the adsorption. The micropore volume shows the same trend as the BET surface area in which the hydrogel biochar sample of 80:20 (SW/FA) shows the highest pore volume compared to other samples. For the soil improvement application, this higher volume can improve the moisture content in the soil.

Consequently, fly ash is mixed with biochar to increase the adsorption capacity. Generally, the surface area increases the adsorption capacity of the sample also increases. This is proven in figure 4. The pore structure and the functional group are used to identify the effectiveness of the adsorption

The specific area of the surface of the fly ash obtained usually varies from 250 to 850 m^2/g. A good adsorbent's characteristics are high pore volume because an adsorbent with high pore volume can absorb more particles. Other than that, the pore size of the sample also can affect the effectiveness of the adsorbent. In this case, the hydrogel biochar mixing with fly ash of sawdust at the ratio of 80:20 has a value of 87.0471Å for pore size. The Barrett-Joyner-Halendar (BJH) and Dollimore Heal (DH) adsorption are the techniques used to determine the effect of surface porosity of the hydrogel biochar [16]. According to the trend is shown by Barrett- Joyner-Halendar (BJH) adsorption, the results seem to follow the trend of BET surface area.

In this experiment, it can be concluded that the ratio of 80:20 (HB/FA) in the hydrogel biochar contained pores at the maximum size compared to other ratios. Therefore, according to literature written by Karakoyun, who had studied the hydrogel biochar by using other biomass for phenol adsorption had verified that the hydrogel biochar is very effective as an adsorbent for removal of toxic organic species from an aqueous environment. Moreover, a hydrogel that can adsorb highest capacity particles and sensitive to the environmental condition as the hydrogel is capable of swelling or de-swelling reversibly in solution and able to retain the swollen state with the changes of the environment condition.

The effectiveness of using fly ash as the material for biochar blending is supported by Beiyuan et al. (2016) which stated that the fly ash is chosen to blend with the rice husk because of its ability as an aluminosilicate source which contains porous geopolymers monoliths showing distinct pore structures and considered as the good adsorbent of heavy materials. Since the rice husk contained rich constituted parts of silica, aluminum, magnesium, potassium, and iron, the porosity change is affected by these components in the rice husk. Therefore, the blending of rice husk and fly ash showed a good mixture of biochar to adsorb the toxic gas via the pores structure on the surface of the components.

As for sugarcane bagasse, the way the solids burn, react, and dissolve with other materials can be determined by its surface area. It can be seen from the data above that the sample of 50:50 ratio of sugarcane bagasse and fly ash have the highest surface area compared to the other samples.

3.2. Proximate Analysis

In this characterization, each sample's fixed carbon content, moisture content, volatile matter, and ash content are determined. Based on figure 4, all the samples analyzed' moisture content, ranging from 3.33% to 7.98%, which stated that the least moisture content is at a 20:80 ratio of sawdust and flash.

Adsorbents with high volatility, fixed carbon, and low ash content were reported as a promising property of the precursor [4]. The percentage of the ash content indicates the presence of minerals as impurities in the carbon. To have the most active sites on the adsorbent surface, samples with the lowest ash content are preferred. The high content of ash ultimately reduces the percentage of fixed carbon.

As for ash content, the value gradually decreases with the increment of the fly ash ratio. It can be assumed that the content of ash in the bagasse is lower after undergone the pyrolysis process. Some of the volatile matter present in the biomass should be decomposed into vapors during the pyrolysis process, thus reducing the percentage of volatile matter in the biochar. The unburnt gaseous happens because of a high content of volatile matter, leading to carbonaceous components in fine particles [10].

Fixed carbon is a solid combustible residue left after the pyrolysis process, and the volatile matter is decomposed. Therefore, in the fixed carbon term, the higher value of fixed carbon is desired for the sequestration of carbon as an adsorbent [13]. The HB (80:20 SW) sample has a high fixed carbon value, which is 29.07%. This is parallel with the BET surface area where HB (80:20) has the highest value.

The experiment was performed at temperature started from 30°C until 900°C with a heating rate 10 °C per minute, and nitrogen flow was constant at 100 mL per minute. For the first peak from figure 5, it shows that there is weight loss due to removing moisture content from the sample. The loss is due to a moisture content that can occur at a temperature below 200^{o}C. The huge weight drop is due to a large amount of cellulose, hemicellulose, and lignin. According to Šantek et al. (2016), the corn husk is a type of lignocellulosic material that contains 39% cellulose, 26.5% hemicellulose, and 11.6% lignin. At the second peak from figure 5, it can occur at 200 °C to 360 °C. A good adsorbent should have excessive moisture content, high volatility, and containing low ash. The ratio of 80:20 has the highest moisture content value, which is 7.98% while the least value for moisture content is at the ratio of 20:80, which is 3.33%.

As the temperature increase above 350 °C a huge amount of weight loss has been detected, which shows that the decomposition of highly bonded lignin residue in the sample can be said as the removal of ash from the sample temperature. Next, in figure 6, it shows the result for sugarcane bagasse. The ratio of 40:60 tends to have low degradation compared to the ratio of 100:0, which has the highest degradation. Adsorbents with a high content of volatile matter, fixed carbon, and low ash content were reported as a promising property of the precursor. The percentage of the ash content indicates the presence of minerals as impurities in the carbon.

To have the most active sites on the surface of the adsorbent, samples with the lowest ash content are preferred. The high content of ash ultimately reduces the percentage of fixed carbon. As for ash content, the value gradually increases with the increment of the bagasse ratio. It can be assumed that the ash content in the bagasse is excessive after undergone the pyrolysis process. Some of the volatile matter present in the biomass should be decomposed into vapors during the pyrolysis process. Thus, it can reduce the percentage of the volatility of biochar. The high content of volatile matter happens because more unburnt gaseous organic compound leads to carbonaceous components in fine particles.

Based on figure 6, at the ratio of 60:40, which is sugarcane bagasse char to fly ash have the highest value of moisture content among other ratios, which is the value is 10.5705%. It can be observed that the ratio of 60:40 has the highest value of volatile matter and have the lowest value for ash content, which is 15.1239%. A good adsorbent should have high moisture content, volatile matter, and fixed carbon. At the same time, the ash content for a good adsorbent should below.

Lastly, in figure 7, all the samples analyzed' moisture content, ranging from 2.694% to 9.735%, stated that the least moisture content is at the ratio of 50:50 rice husk and flash. While the ash content at ratio 80:20 has the lowest value compared to other ratios, which is 35.056%. The ash will be produced for rice husk when the temperature reaches 600°C and above, and the residue is mainly non-combustible silica. The higher ash content might contribute to fouling and slagging, in which direct combustion can happen [12]. This is because the silica content of rice husk ash is very abrasive, and it will form alkali silicates, which fade away and melt at low temperatures and initiate the growth of slag clinker. As the heating value increases, it will increase the percentage of volatility and decreasing the ash content.

3.3. Swelling Analysis

Initially, the mixture of 1.0 gram of hydrogel biochar for four different feedstocks (sawdust, rice husk, corn husk and sugarcane bagasse) mixed with flyash at different ratios was added the container 30 ml of distilled water in it. The swelling properties were compared by using 24 hours of the degree of swelling. Q is the degree of swelling between the weight of the swollen (Ws) and the 1.0g dry gel (Wd). To know how much water had been absorbed into the hydrogel, another calculation must be calculated in percentage where the difference of weight after, must be minus with the total weight before getting to know how much water had been absorbed.

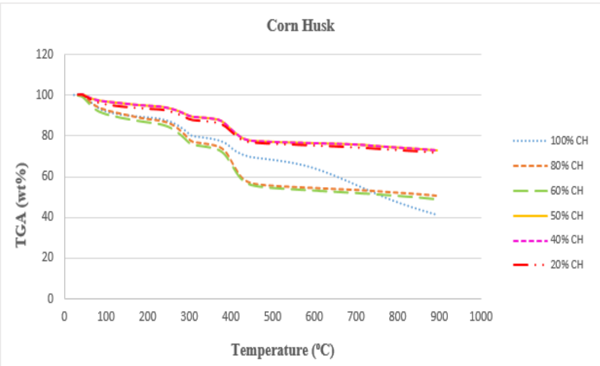


Fig 4: The value of the proximate analysis of sawdust.

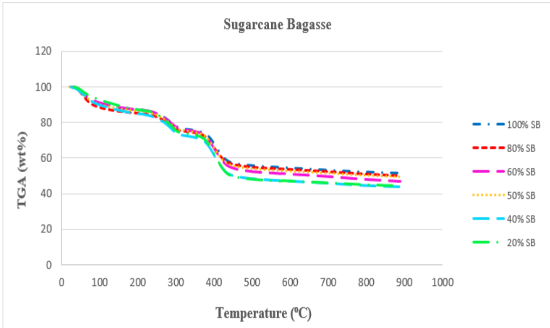


Fig 5: The value of the proximate analysis of corn husk.

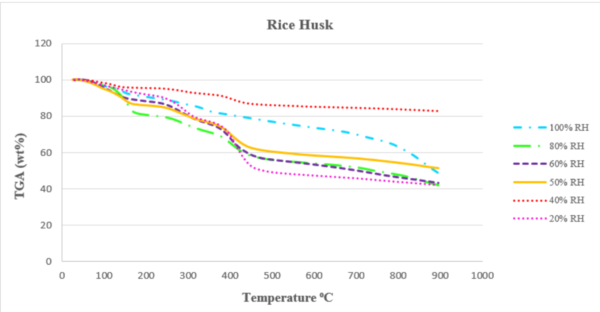


Fig 6: The value of the proximate analysis of sugarcane bagasse.

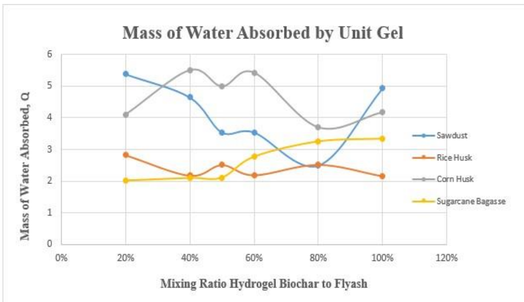


Fig 7: The value of proximate analysis of rice husk

Table 1: Result of sawdust.

Sample	Weight after (g)	After swelling test (%)	Q
HB-100%-SW	5.932	83.14	4.932
HB-80%- SW	3.490	71.35	2.490
HB-60%- SW	4.538	77.96	3.538
HB-50%- SW	4.536	77.95	3.536
HB-40%- SW	5.645	82.29	4.645
HB-20%- SW	6.378	84.32	5.378

Table 2: Result of rice husk

Sample	Weight after (g)	After swelling test (%)	Q
HB-100%-RH	3.159	68.34	2.159
HB-80%- RH	3.520	71.60	2.520
HB-60%- RH	3.191	68.66	2.191
HB-50%- RH	3.512	71.53	2.512
HB-40%- RH	3.176	68.51	2.176
HB-20%- RH	3.822	73.84	2.822

Table 3: Result of corn husk

Sample	Weight after (g)	After swelling test (%)	Q
HB-100%-CH	5.185	80.71	4.185
HB-80%- CH	4.708	78.76	3.708
HB-60%- CH	5.421	81.55	5.421
HB-50%- CH	5.991	83.31	4.991
HB-40%- CH	6.497	84.11	5.497
HB-20%- CH	5.104	80.41	4.104

Table 4: Result of sugarcane bagasse

Sample	Weight after (g)	After swelling test (%)	Q
HB-100%-SB	4.336	76.94	3.336
HB-80%- SB	4.250	76.47	3.250
HB-60%- SB	3.770	73.47	2.770
HB-50%- SB	3.112	67.87	2.112
HB-40%- SB	3.096	67.70	2.096
HB-20%- SB	3.019	66.88	2.019

From the observation in tables 1, 2, 3 and 4, the value of mass water absorbed by unit gel of all samples increased from the mass value before the swelling test. The value of mass after the swelling test for sawdust at a ratio 80:20 is 3.490 g. That means the mass of water absorbed by the gel is approximately 2.490 g. The value of sawdust hydrogel at 20:80 after the swelling test has the highest value of percentage, which is 84.32% compared to all other hydrogels. This can be seen from the table and graph in figure 6 that shows all the hydrogels from different feedstock can swell when it comes to water.

The good criteria for adsorbent have high pore volume because adsorbent with high pore volume can absorb more particles. Other than that, the pore size of the sample also can affect the effectiveness of the adsorbent. So, this definitive proof that hydrogels can swell when immersed in water after a day is 24 hours.

4. Conclusion

This research aims to produce efficient adsorbent and analyze four different biomass feedstock characteristics with different ratios of blending with fly ash: corn husk, sawdust, rice husk, and sugarcane bagasse. Their characterization analysis has been done using BET analysis to determine the samples' surface area, TGA to obtain the proximate analysis values, and swelling test, which is to determine how large the hydrogel size can be when it is immersed in water. Based on the characteristic’s analysis done, a different type of feedstock shows different characteristics. Therefore, it can be concluded that based on 4 different materials that had been characterized, sawdust is the best raw material compared to rice husk, sugarcane bagasse, and corn husk. In BET analysis, sawdust at ratio 80:20 has proved that it contained pores at maximum size, the largest value of the surface area, and high average pore size compared to other ratios. In TGA analysis, sawdust also shows the best result: the moisture content is higher than the other biomass feedstock at 80:20, and the sawdust has the lowest value of ash content compared to the other components. In the swelling test, this can be concluded that all the hydrogel biochar could swell. This shows that hydrogel biochar is a good example of an adsorbent because it can swell. All analyses' consistent results make sawdust hydrogel biochar 80:20 (SW/FA) the most suitable biomass mixed with fly ash in becoming a good adsorbent

5. Acknowledgement

The authors would like to thank the Universiti Teknologi MARA (UiTM) and Ministry of Education Malaysia for financial support. The research is conducted at the Faculty of Chemical Engineering, UiTM. Besides, the authors would also like to thank UiTM Grant 600-IRMI/5/3/LESTARI (039/2019)

6. References

[1] Abdoulmoumine, N., Adhikari, S., Kulkarni, A., & Chattanathan, S. (2015). A review on biomass gasification syngas cleanup. Applied Energy. https://doi.org/10.1016/j.apenergy.2015.05.095

[2] Adekola, F. A., Ayodele, S. B., & Inyinbor, A. A. (2019). Efficient rhodamine B removal using acid- and alkaline-activated Musa paradisiaca biochar. Polish Journal of Environmental Studies. https://doi.org/10.15244/pjoes/94386

[3] Beiyuan, J., Tsang, D. C. W., Ok, Y. S., Zhang, W., Yang, X., Baek, K., & Li, X. D. (2016). Integrating EDDS-enhanced washing with low-cost stabilization of metal-contaminated soil from an e-waste recycling site. Chemosphere. https://doi.org/10.1016/j.chemosphere.2016.06.030

[4] Ceylan, Z., & Sungur, B. (2020). Estimation of coal elemental composition from proximate analysis using machine learning techniques. Energy Sources, Part A: Recovery, Utilization and Environmental Effects. https://doi.org/10.1080/15567036.2020.1790696

[5] Hu, X., & Gholizadeh, M. (2019). Biomass pyrolysis: A review of the process development and challenges from initial researches up to the commercialisation stage. Journal of Energy Chemistry. https://doi.org/10.1016/j.jechem.2019.01.024

[6] Li, X., Zhang, L., Yang, Z., Wang, P., Yan, Y., & Ran, J. (2020). Adsorption materials for volatile organic compounds (VOCs) and the key factors for VOCs adsorption process: A review. Separation and Purification Technology. https://doi.org/10.1016/j.seppur.2019.116213

[7] Nurul Farhana, A., Alias, A. B., Talib, N., Abd Rashid, Z., & Ghani, W. A. W. A. K. (2018). Characteristics of rice husk biochar blended with coal fly ash for potential sorption material. Malaysian Journal of Analytical Sciences. https://doi.org/10.17576/mjas-2018-2202-19

[8] Promraksa, A., & Rakmak, N. (2020). Biochar production from palm oil mill residues and application of the biochar to adsorb carbon dioxide. Heliyon. https://doi.org/10.1016/j.heliyon.2020.e04019

[9] Šantek, M. I., Miškulin, E., Beluhan, S., & Šantek, B. (2016). New trends in the ethanol production as a biofuel. Kemija u Industriji/Journal of Chemists and Chemical Engineers. https://doi.org/10.15255/KUI.2014.032

[10] Simon, J. I., Cuzzi, J. N., McCain, K. A., Cato, M. J., Christoffersen, P. A., Fisher, K. R., … Scargle, J. D. (2018). Particle size distributions in chondritic meteorites: Evidence for pre-planetesimal histories. Earth and Planetary Science Letters. https://doi.org/10.1016/j.epsl.2018.04.021

[11] Yahya, M. A., Al-Qodah, Z., & Ngah, C. W. Z. (2015). Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production: A review. Renewable and Sustainable Energy Reviews. https://doi.org/10.1016/j.rser.2015.02.051

[12] Yao, X., Zhao, Z., Xu, K., & Zhou, H. (2020). Determination of ash forming characteristics and fouling/slagging behaviours during gasification of masson pine in a fixed-bed gasifier. Renewable Energy. https://doi.org/10.1016/j.renene.2020.06.008

[13] Yu, K. L., Show, P. L., Ong, H. C., Ling, T. C., Chen, W. H., & Salleh, M. A. M. (2018). Biochar production from microalgae cultivation through pyrolysis as a sustainable carbon sequestration and biorefinery approach. Clean Technologies and Environmental Policy. https://doi.org/10.1007/s10098-018-1521-7

[14] Zhu, B., Ma, D., Wang, J., & Zhang, S. (2015). Structure and properties of semi-interpenetrating network hydrogel based on starch. Carbohydrate Polymers. https://doi.org/10.1016/j.carbpol.2015.07.037

[15] Zohuriaan, J., & Kabiri, K. (2015). Superabsorbent Polymer Materials: A Review. (June). Bhatt, A., Priyadarshini, S., Acharath Mohanakrishnan, A., Abri, A., Sattler, M., & Techapaphawit, S. (2019). Physical, chemical, and geotechnical properties of coal fly ash: A global review. Case Studies in Construction Materials. https://doi.org/10.1016/j.cscm.2019.e00263