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Production of magnetic biochar derived from durian's rind at vacuum condition for removal of methylene blue pigments from aqueous solution

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Abstract— Durian, originating from the Durio Zibethinus genes is one of the widely consumed fruits in South East Asia especially in Malaysia, Indonesia, Thailand, Singapore and Philippines. Durian's rind was found to be abundantly available in Malaysia due to the high consumption of durians by the locals. Durian rinds were opted to produce magnetic biochar in the presence of iron oxide solution by employing the pyrolysis process in a muffle furnace at a pyrolysis temperature of 700°C and pyrolysis time of 20 minutes. The pyrolysis process was carried out in a condition of absence of oxygen in the muffle furnace by generating a vacuum condition without utilizing any carrier gas. Magnetic biochar which were produced with a surface area of 790 m^2/g successfully provided a 95% removal of 30 mg/L methylene blue from aqueous solution with a maximum adsorption capacity of 87.32 mg/g at an optimum condition of pH 9 of stock solution, adsorbent's dosage of 0.5 gram, agitation speed of 120 rpm and contact time of 45 minutes. Langmuir and Freundlich adsorption isotherm model were opted to analysis the adsorption of methylene blue by magnetic biochar from aqueous solution which provided a Langmuir constant, K_L value of 0.0910 L/mg and Freundlich constant, K_F 4.395 $mg^{1-n}L^n$/g. Results obtained acknowledge the discovery behind the transformation of waste material into an innovative substance for a cleaner and healthier environment.

***Keywords*— magnetic biochar, durian's rind, methylene blue, adsoprtion, pyrolysis**

I. Introduction

The advance of technology and economy is growing in a tremendously fast pace in which an innovative idea or material is being produced every single day. On that note, the growth in a process industry leaves a negative impact in terms of harmful waste materials being released to the environment. The idea of reusing or treating these waste materials before discharging into the environment has received a good response from the society. On that account, Malaysia, being one of the well grown countries in terms of technology and economy, produces 2 million agricultural wastes annually which either being dumped or burned in an open area [1]. In refer to this statement, the "king of fruits", Durian which originated from genus *Durio* were found to be one of the highly consumed fruits in Malaysia in which the *Durio*,*D.Zinbenthinus* species were found to be the only species commercially grown to provide fruits in a great intensity [2]. Durian is generally available in round shape and comes with a strong pungent smell with a semi-woody rind exterior consisting of sharply pointed thorns and spike-like spine [3]. However, the rapid growth of durian related industry has been obstructed by the accumulation of durian residues consisting of its seeds, peels, shell and rinds which is not handled in proper method [4]. Due to the environmental regulations which got more stringent, conversion of these materials into biochar turns out to be a remarkable solution.

Biochar, which can be produced in the absence of oxygen was initially discovered due to its ability to increase the nutrient intake in soil which resulted in a growth rate of plants three times higher compared with normal soil [5, 6]. The application of biochar has expanded from that to a wide range of application such as increasing the fertilizer's retention time in soil [7, 8], as a dopant in semiconductor to increase its electrical conductivity [9] and as a good adsorbent removing heavy metals and organic substance from aqueous solution [10-12]. Despite its good outcome in various type of application, biomass based biochar faced certain pullbacks which required further improvement such as the difficulties faced during the separation of biochar particles after adsorption experiment or the prior activation by oxygen plasma method process required for the application as dopant in semiconductor [9, 13]. This problem was overcome by the discovery of magnetic biochar, an innovative type of biochar which were impregnated with metal ion solution prior the pyrolysis process. A typical modified furnace or microwave oven were employed with the flow of carrier gas such as nitrogen to achieve a zero oxygen condition during the pyrolysis process for the production of magnetic biochar. These magnetic biochar which were produced from waste material provided a better adsorption of heavy metal ions from the polluted water source, leading to the acknowledgment of the idea of recycling waste materials for a fresh and harmless environment [14, 15].

In this study, magnetic biochar were produced by a novel method in which a vacuum condition were attained in a muffle furnace without the supply of any type of carrier gas to ensure a zero oxygen condition in the muffle furnace. Durian's rind of the *D.zibenthinus* species were opted as the raw material and sonicated with iron (III) oxide, Fe_2O_3 prior the pyrolysis process. The effect of process parameter such as pH of aqueous solution, agitation time, agitation speed

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and adsorbent's dosage on adsorption of methylene blue (MB) by magnetic biochar was studied along with its adsorption isotherm.

II. Materials and methods

A. Preparation of biomass

Dried durian's rinds were collected, chopped into small pieces and washed thoroughly to remove any fungus prior drying it in a vacuum oven for 5 days at 105˚C. Dried durian's rind were then grinded by a ball mill grinder at Forest Research Institute Malaysia (FRIM) to obtain particle size of less than 20µm. The grinded durian's rind were then sonicated with 200mL of 1.0M iron (III) oxide, Fe_2O_3 along with 150mL of 1.0M nitric acid, HNO_3 and 50mL of 1.0M potassium permanganate,$KMnO_4$, in the ratio of 3:1 [16] for optimum oxidation process. This mixture were sonicated for 5 hours at 40°C with 50% vibration energy in a Elmasonic P, modelled sonicator and the obtained biomass were dried for 5 days continuously at 70°C in vacuum oven.

B. Synthesis of magnetic biochar

A programmable muffle furnace modelled WiseTherm, FP-03, 1000˚C, 3.Lit were used for the pyrolysis of the metal ion – durian rind biomass in a vacuum condition. 30g of biomass was transferred into a closed crucible and kept in the middle of the muffle furnace and the door was closed tightly prior the pyrolysis process. A vacuum pump which was connected to the syngas effluent's tip at the top of the furnace sucked out air from the muffle furnace until a constant reading of pressure is obtained at pressure gauge, indicating a vacuum condition is attained in the muffle furnace. The control valve was then closed tightly and the pyrolysis process was carried out at 700˚C and 20 minutes (mins). Crucible was removed from the muffle furnace and the magnetic biochar produced were rinsed with distilled water until a pH7 is obtained. Neutralized magnetic biochar were dried in vacuum oven for 5 days at 70°C.

C. Batch adsorption experiment

Batch adsorption experiment were carried out by agitating 100 mL of 30 mg/L of MB, $C_{16}H_{18}N_3SCl$ with varying dosage of magnetic biochar along with other manipulated parameters as listed in Table 1 which were further statically approached via the design of experiment (DOE) obtained from Design Expert, version 9.0. The required pH of MB aqueous solution was altered by adding few drops of 1.0M hydrochloric acid, HCL or 1.0M of sodium hydroxide, NaOH solution into the 100mL of 30 mg/L of MB solution. On the other hand, adsorption isotherm experiment were executed by agitating 0.5 gram of magnetic biochar in 250mL of 30 mg/L, 40 mg/L and 50 mg/L of MB aqueous solutions of pH 9 for 2 hours.

D. Characterization of magnetic biochar

Field-emission scanning electron microscopy (FESEM, Zeiss, Model Auriga) were opted to study the physical morphology of the durian's rind derived magnetic biochar.

TABLE I. OPERATING PARAMETER FOR BATCH ADSORPTION EXPERIMENT

Parameter	Variation Range
pH of aqeuous solution	pH5 to pH9
Agitation time	15 to 45 mins
Agitation speed	60 to 120 rpm
Adsorbent's dosage	0.1 to 0.5 g

Besides that, the Fourier Transform Infrared (FTIR, Bruker, Model IFS66v/S) spectroscope was employed to determine and analyse the surface functional group present on the surface of magnetic biochar. The specific surface area of the magnetic biochar was measured by nitrogen adsorption at 77K using BET analyzer (Quanta Chrome Autosorb 6B).

III. Results and Discussion

A. Characterization of magnetic biochar

1) Field Emission Scanning Electron Microscope

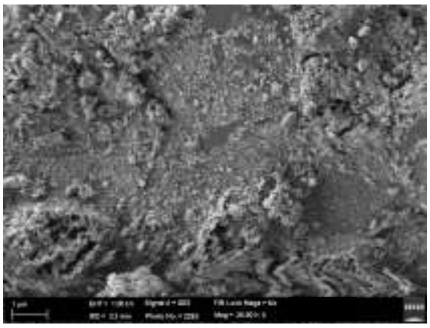
Fig. 1 (a) and (b) indicates the images of raw durian's rind and the prepared magnetic biochar through the pyrolysis process in a vacuum condition. Based on Fig. 1 (a), it can be seen that the surface texture of raw durian's rind is slender and there are not many pores formed on the durian's rind. After the pyrolysis process, the surface of the durian's rind were found to be more porous structure as per in Fig. 1 (b). The oxidation process of durian's rind with HNO_3 and $KMnO_4$ has removed the impurities and widened the pores to achieve a mixture of meso and micropores in the structure while removing the impurities on the surface as well [17].

2) Fourier Transform Infrared Spectroscopy

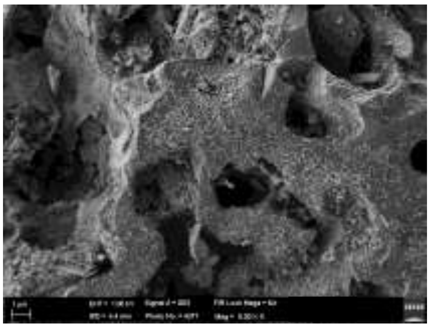
Fig. 2 (a) and (b) indicates the FTIR results for the surface functional groups of the durian's rind and magnetic biochar in which it can be seen that there were no functional groups present on the surface of raw durian's rind. On the other hand, Fig. 2 (b) indicates that there are few successful attachment of functional group on the surface of magnetic biochar such as the C=H alkenes at 650 to 100 cm^{-1} band, C ≡N nitriles group at 2210 to 2260 cm^{-1} band, H-C=O aldehydes group at 2695 to 2830 cm^{-1} band and O-H hydroxyl group at 3200 to 3500 cm^{-1} band [14]. This functional groups present on the surface of magnetic biochar acknowledge the sonication process carried out with HNO_3 and $KMnO_4$ as agreed by other researches as well [16].

B. Statistical analysis on removal of MB pigment from aqueous solution by magnetic biochar

Fig. 3 (a) to (c) represents the 3-dimensional plot for the adsorption of MB based on 4 different operating parameters as in Table 1. Fig. 3 (a) indicates that as the dosage of



(a)



(b)

Figure 1. FESEM images of (a) raw durian's rind and (b) magnetic biochar

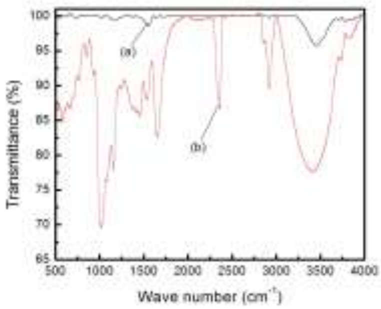
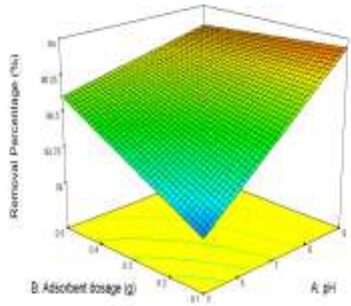
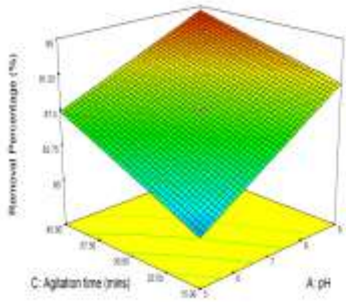


Figure 2. FTIR adbsorption spectra (a) raw durian's rind and (b) magnetic biochar

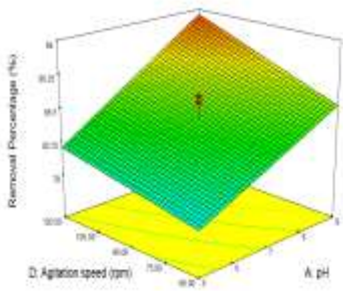
magnetic biochar increases, the removal percentage of MB pigment increases as well due to the increase in the availability of surface of magnetic biochar for the chemisorption process of MB pigment from aqueous solution. On the other hand, Fig. 3 (b) indicates that the removal percentage of MB pigment from aqueous solution increases as the agitation time and pH of the MB aqueous solution increases. As the agitation time increases, the interaction between the MB pigments and the magnetic biochar's surface increases leading to a higher removal percentage. On the other hand, at lower pH, the surface of magnetic biochar may get positively charged leading to competition of H^+ ions with MB pigment cations causing a lower removal percentage of MB pigment. On the other hand, at higher pH, the surface of magnetic biochar gets more negatively charged, encouraging the electrostatic attraction between the MB pigment cation and negatively charged surface of magnetic biochar. Fig. 3 (c) demonstrates that the removal percentage of MB pigment increases as the agitation speed increases as well. This is due to the



(a)



(b)



(c)

Figure 3. A 3-D interaction plot representing the removal of MB dye cation from aqueous solution employing magnetic biochar, (a) interaction of adsorbent dosage (g) and pH of aqeous solution, (b) agitation time (mins) and pH of aqeous solution, (c) interaction between agitation speed (rpm) and pH of aqeous solution

enhancement of interaction and collision's frequency between the surface of magnetic biochar and the MB pigment's cations which leads to a higher adsorption capacity of magnetic biochar.

C. ***Adsorption Isotherm Study***

Langmuir and Freundlich isotherm model were applied to determine the adsorption capacity of magnetic biochar. Langmuir isotherm model (1) provides a relationship between solid phase adsorbate concentration, q_e and the adsorbate to the equilibrium concentration, C_e;

$$q_e = (q_m K_L C_e) / (1 + K_L C_e) \quad (1)$$

where q_e (mg/g) represents amount of adsorbed MB pigment's concentration per unit weight while C_e (mg/L) represents adsorbed MB pigment's concentration in aqueous solution at equilibrium level. The Langmuir constant, K_L(L/mg) defines the affinity of binding sites while q_m defines the maximum adsorption capacity of magnetic biochar. A graph of C_e/q_e against C_e was plotted to determine the K_L and q_m value based on the slope and intercept obtained from the graph.

Freundlich isotherm model (2) on the other hand presents as an exponential equation which assumes as the concentrate of adsorbate increases, the concentration of adsorbate on the surface of adsorbent increases as well;

$$q_e = K_F C_e^{1/n} \quad (2)$$

where K_F , the Freundlich constant indicates the adsorption capacity of the adsorbent while n being a constant which proves the relationship between the adsorbate and adsorbent. A graph of ln q_e against ln C_e was plotted in which the n and K_F value is determined from the slope and intercept of the plot respectively. Table 2 indicates the maximum adsorption capacity, q_m value along with other calculated value obtained from Langmuir and Freundlich isotherm model.

Fig. 4 (a) and (b) demonstrates the plot of adsorption isotherm for linearized Langmuir and Freundlich isotherm model with the respect of adsorption of MB pigment from aqueous solution.

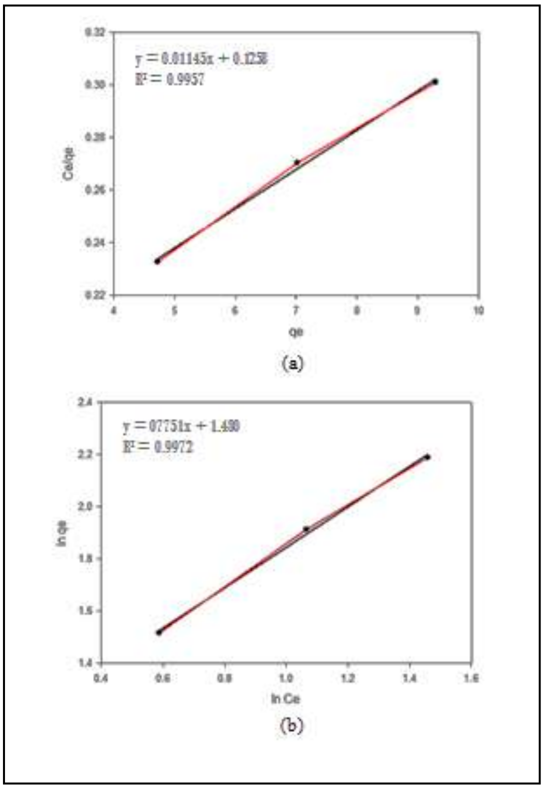


Figure 4. Langmuir (a) and Freundlich (b) isotherm model for adsorption of MB pigments from aqeuous solution by magnetic biochar

TABLE II. LANGMUIR'S AND FREUNDLICH'S ISOTHERM PARAMETERS FOR MB ADSORPTION BY MAGNETIC BIOCHAR

Langmuir Isotherm			Freundlich Isotherm		
q_m (mg/g)	K_L (L/mg)	R^2	n	K_F ($mg^{1-n}L^n/g$)	R^2
87.32	0.0910	0.9957	1.380	4.395	0.9972

As per Fig. 4 (a), the graph demonstrates that the adsorption data obtained fits well with the Langmuir isotherm model with a R^2 value of 0.9957, q_m value of 87.32mg/g and K_L value of 0.0910 L/mg. These values acknowledge the monolayer adsorption process which took place. On the other hand, Fig. 4 (b) also indicates the adsorption data obtained from this experiment fits well with the Freundlich isotherm model with a R^2 value of 0.9972, n value of 1.380 and K_F value of 4.395 $mg^{1-n}L^n/g$.

Based on the data from Table 2, Langmuir (3) and Freundlich (4) isotherm model were developed to demonstrate the relationship between MB pigment's uptake capacity by magnetic biochar, q_e to the equilibrium liquid concentration, C_e as below;

Developed Langmuir model, $q_e = 7.946C_e/(1+0.0910C_e)$ (3)

Developed Freundlich model, $q_e = 4.395C_e^{0.724}$ (4)

IV. Conclusion

Novel magnetic biochar were produced by utilizing a vacuum condition in a muffle furnace with an optimum condition of 700˚C and 20 mins. Statistical analysis proves that the overall optimized condition to attain a 95% removal of 30 mg/L MB pigment from aqueous solution would with be a condition of pH 9 of aqueous solution, adsorbent's dosage of 0.5 gram, agitation speed of 120 rpm and contact time of 45 mins. Langmuir and Freundlich adsorption isotherm model were employed to study the adsorption capacity, in which the maximum adsorption capacity, q_m calculated durian's rind based magnetic biochar was 87.32 mg/g. The respective Langmuir constant, K_L value of 0.0910 L/mg and Freundlich constant, K_F 4.395 $mg^{1-n}L^n/g$ were obtained based on the adsorption isotherm study which acknowledge the achievement behind the conversion of waste material into an innovative material to remove hazardous pollutants from the surrounding for a more fresh and clean environment.

Acknowledgment

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