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Thermal conversion of pineapple crown leaf waste to magnetized activated carbon for dye removal



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G R A P H I C A L A B S T R A C T



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ABSTRACT

Pineapple crown leaf was successfully converted to the magnetized activated carbon (MAC) as an attractive solution to overcome separation problems. The activated carbon (AC) was produced by an innovative method combining KOH activation and microwave heating while the magnetization process was prepared by a co-precipitation method. In this sense, the activation stage was studied at different impregnation ratio. The resulted magnetic adsorbent was further tested its feasibility for methyl violet dye removal. The result shows that MAC consists of both micropores and mesopores with more oxygen-containing functional groups, indicating it can be used to remove dye from contaminated water. The increase of impregnation ratio led to an increase in the MAC porosity and a decrease in the magnetic property. The adsorption behavior of methyl violet dye onto MAC was well described by the Redlich-Peterson isotherm model.

1. Introduction

Pineapple (*Ananas comosus*), a herbaceous perennial plant, belongs to the family of Bromeliaceae and grows in tropical countries including Indonesia. A large number of pineapple crown leaves are generated by households and food industries and become abundantly available biomass waste. Pineapple crown leaf has a high content of cellulose (70–80%), lignin (5–12%), and hemicellulose (Weng et al., 2009) containing carbonyl, carboxyl, and hydroxyl groups, that can be used as a precursor in the preparation of activated carbon (AC) (Mahamad et al., 2015).

In the preparation of AC, the precursor (e.g. biomass) is thermally

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decomposed through carbonization followed by activation. The activation can be carried out via physical activation using steam or carbon dioxide (Cansado et al., 2018; Chang et al., 2015), or chemical activation using chemicals (Suhas et al., 2016), to develop pore network and improve adsorption performance. In comparison with physical activation, chemical activation has several advantages such as greater yield and lower process temperature (Liew et al., 2018). In this process, the precursor is mixed with activator agent such as potassium hydroxide (KOH) (Elmouwahidi et al., 2012), sodium hydroxide (NaOH) (Norouzi et al., 2018), zinc chloride (ZnCl₂) (Hong et al., 2019), phosphoric acid (H₃PO₄) (Sun et al., 2016), potassium hydroxide (KOH)-sodium hydroxide (NaOH) mixture (Liew et al., 2018), and ferric chloride (FeCl₃)-zinc chloride (ZnCl₂) mixture (Tian et al., 2019). Among those, the use of KOH has several advantages including the development of micropores and the formation of oxygen functional groups (Foo and Hameed, 2012). In this sense, the heating method during activation process affects pore structure and adsorption performance. In general, conventional heating using furnace is adopted (Beltrame et al., 2018, Mahamad et al., 2015). In conventional heating, a heat source is located outside the material bed and energy is transferred to the bed interior through convection, conduction and radiation mechanism. It generates a thermal gradient from the hot surface of the material bed to its interior until the steady state condition is reached. To overcome the thermal gradient problem, a slower rate of heating is used. It increases energy consumption.

Recently, microwave heating becomes a viable alternative to replace conventional heating using a furnace (Foo and Hameed, 2012). In contrast to the conventional heating, microwave heating is both internal and volumetric which means it takes place in the whole volume of material. Electromagnetic energy is converted to the thermal energy at a molecular level, through dipole rotation and ionic conduction. It provides several advantages such as selective heating, shorter time and uniform temperature distribution, resulting in more uniform pores (Kazmierczak-Razna et al., 2015; Ao et al., 2018; Chen et al., 2019).

Although AC has been widely applied to remove organic pollutants from wastewater (Wen et al., 2019; Wang et al., 2018), it is still hard to separate and recover the used AC from the effluent, particularly in the powdered form. The idea of combining AC and magnetite (Fe₃O₄) is considered to be able to overcome the separation problems and provides a quick way for practical applications (Altintig et al., 2017; Wong et al., 2016). The loading of magnetite into AC lead to polarity on the AC surface, further it can be trapped by magnetic fields. However, it creates another problem due to most pores of AC are filled by magnetite, leading to a decrease in surface area and adsorption ability (Juang et al., 2018).

To remove organic pollutants including dyes from wastewater more effectively, it is desired to develop magnetized activated carbon (MAC) having a relatively high surface area. In this sense, the use of Fe_3O_4 nanoparticles has been recommended (Juang et al., 2018). In addition, the cellulose content of precursor and the activation method are also considered to affect pore structure and magnetic properties of MAC produced. It provides motivation for this study, which was performed to prepare MAC from pineapple crown leaf with emphasis on the utilization of KOH as an activating agent coupled with microwave heating. Pineapple crown leaf was chosen as precursor due to its abundance in Indonesia, high cellulose content and very limited studies reported on the use of pineapple crown leaf as a precursor in the MAC production. The effect of impregnation ratio toward pore structure and magnetic properties was investigated with the intention to explore the potential of microwave heating to improve the quality of MAC produced.

The MAC was further evaluated for its feasibility as an adsorbent to remove methyl violet dye, for potential use in wastewater treatment. Methyl violet represents a synthetic dye that is used in ink, textile, paint, leather, and paper industries as a coloring agent (Astuti et al., 2017). As a cationic dye, methyl violet is toxic, mutagenic and carcinogenic (Astuti et al., 2016). Therefore, it is urgent to remove the dye

from industrial effluent before being discharged into the stream.

2. Material and methods

2.1. Pretreatment of pineapple crown leaf-waste

The pineapple crown leaf used as a precursor in this study was obtained from the traditional market in Gunungpati, Semarang, Indonesia. Before any treatment, the leaf was chopped into smaller pieces with a size of 1 cm, washed with distilled water, and dried at 105 °C for 24 h. The dried sample was further milled to the powder and sieved to obtain a uniform size of less than 150 μ m.

2.2. Preparation of activated carbon

A two-step approach (i.e. carbonization using an electric furnace and chemical activation using a microwave oven) was performed to prepare AC from pineapple crown leaf (Liew et al., 2018). In contrast to the one-step approach where carbonization and activation process simultaneously performed in one process, a two-step approach could produce activated carbon with a higher specific surface area. It is due to the majority of volatile matter can be removed during the carbonization process to create pores, while the activation process led to the formation of more pores and the widening of existing pores.

The carbonization of pineapple crown leaf was carried out by loading 100 g of dried material into an electric furnace (Model FB1310M-33 Thermolyne, Thermo Scientific, USA), which was further heated at 500 °C for 90 min in limited air (Gao et al., 2013). The yield of the resulting char was found to be around 27%. The char was further mixed with KOH and 10 mL of distilled water. The weight ratio of KOH/ char was set at 1, 2, and 3 and the resulting ACs were denoted as AC-1, AC-2, and AC-3, respectively. The mixture was mixed properly for 120 min and dried at 105 °C for 24 h before the activation process (Mohammed et al., 2015). In the activation process, the sample was placed in a quartz reactor installed in the microwave cavity. The activation process was conducted in a 2.45 GHz microwave oven (Model ME731K, Samsung, Malaysia) at 600 W, under a stream of N₂ with a flow rate of 0.250 L/min, for 6 min. After cooling to ambient temperature, the sample was washed sequentially with 0.1 M HCl and distilled water until the pH of the filtrate was around 7. The wet sample was further dried at 105 °C for 12 h.

2.3. Preparation of magnetized activated carbon

MAC was prepared by co-precipitation method (Altıntıg et al., 2017) with a few modifications. First, 1.14 mol of $FeCl_3$ · $6H_2O$ and 0.57 mol of $FeSO_4$ · $7H_2O$ were dissolved in 300 mL of distilled water. The mixture was stirred and heated at 65 °C for 20 min. Then, 10 g of AC was added to the solution and stirred continuously. While stirring, NaOH solution (1 M) was added drop-wise to increase pH to 12 and precipitate iron (II) hydroxides from the aqueous solution. After cooling, the magnetite-loaded activated carbon was washed with distilled water until the pH of the filtrate was around 7 and dried in an oven at 98 °C for 2 h. MACs obtained from AC-1, AC-2, and AC-3 were denoted as MAC-1, MAC-2, and MAC-3, respectively.

2.4. Characterization of adsorbent

The surface morphology of the char, AC and MAC were examined by Scanning Electron Microscope (SEM) (Phenom Pro X Desktop, UK) equipped with Energy Dispersive X-Ray (EDX) at a fixed current of 18 mA. The samples used were covered by Au-Pd using mini sputter coater quorum SC7620. Crystal structure of MAC was determined through X-ray diffraction type D8 Advanced (Bruker, United Kingdom) with Cu K α radiation. While the surface organic structures of the adsorbents were analyzed by Fourier Transform Infra-red Spectroscopy (FTIR) (Spectrum 100, PerkinElmer, USA) recorded between 400 and 4000 cm⁻¹ with the KBr disc method. The pore structure of AC and MAC were characterized through adsorption-desorption of N₂ at 77 K using an automated gas sorption apparatus (NOVA 1200, Quantachrome, USA), where specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method, pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method while the Dubinin-Radushkevich (DR) method was used to evaluate micropore volume. The magnetic property of the MAC was analyzed by vibrating sample magnetometer (VSM) type Oxford VSM 1.2H, while the particle size of AC and MAC were characterized using particle size analyzer (Model SZ-100, Horiba, Japan).

2.5. Adsorption studies

Methyl violet in chemical grade was obtained from U.D. Indrasari, Semarang, and used as adsorbate without further purification. The methyl violet solution was prepared by dissolving methyl violet powder with distilled water to the required concentration for adsorption experiments.

For pH study, about 50 mL of methyl violet solutions (concentration of 20 mg/L) and 0.3 g of AC-3 or MAC-3 were added into six Erlenmeyers (100 mL size). The pH was adjusted with the addition of 0.1 N NaOH or HCl to an appropriate pH (pH range of 1, 3, 5, 7, 9, 11). The Erlenmeyers were sealed and shaken with a speed of 120 rpm for 180 min to reach equilibrium. After 180 min, the suspended solid was filtered and the filtrate was analyzed to determine methyl violet concentration using a UV–visible Spectrophotometer (Model Genesys 10 UV, Thermo Scientific, USA) at λ_{max} of 581 nm.

To investigate the effect of contact time, 0.3 g of AC-3 or MAC-3 was put into ten Erlenmeyer (100 mL size) containing 50 mL of methyl violet solutions (concentration of 20 mg/L). All the suspensions were maintained at pH 5 using 0.1 N HCl or 0.1 N NaOH. The Erlenmeyers were sealed and shaken with a speed of 120 rpm for 10–180 min. Afterward, suspended solid was filtered and the filtrate was analyzed for residual methyl violet using a UV–visible spectrophotometer (Model Genesys 10 UV, Thermo Scientific, USA) at $\lambda_{max} = 581$ nm.

To investigate the adsorption capacity of AC and MAC, 0.3 g of AC-3 or MAC-3 and 50 mL of methyl violet solutions (concentration of 10–500 mg/L) were prepared in a series of 100 mL Erlenmeyer. The initial pH was adjusted to pH 5 using 0.1 N HCl or 0.1 N NaOH. The Erlenmeyers were sealed and shaken with a speed of 120 rpm for 180 min. Afterward, suspended solid was filtered and the filtrate was analyzed for residual methyl violet using a UV–Visible spectrophotometer (Model Genesys 10 UV, Thermo Scientific, USA) at $\lambda_{max} = 581$ nm. The amount of methyl violet adsorbed per unit mass of AC or MAC at equilibrium, q_e (mg/g) was expressed by Eq. (1) as follows (Dawood et al., 2017):

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

with C_o is the initial concentration of methyl violet (mg/L), C_e is the concentration of methyl violet in solution at equilibrium (mg/L), V is the volume of methyl violet solution (L) and m is the adsorbent mass (g). While the percentage of methyl violet adsorbed was expressed by Eq. (2) as follows (Altintig et al., 2017):

methyl violet adsorbed (%) =
$$\frac{(C_o - C_t)}{C_o} \times 100$$
 (2)

where C_t is the concentration of methyl violet in solution at the time *t* (mg/L).

3. Results and discussion

3.1. Characterization of magnetized activated carbon

In contrast to the conventional heating in which the heat energy target is everything within the furnace chamber, microwave irradiation offers a selective heating mechanism in which the main target is char bed. In this sense, the interaction between the microwave and the char need to be considered. When high frequency voltage of microwave is applied, molecules having permanent dipole moment or induced dipole change their orientation to be opposite to the applied field. Furthermore, the synchronization of their orientation to the applied field generates heat in the char interior. Heat energy can be absorbed by alkali metal atom such as potassium (K) impregnated in the char matrix thus become energized atom. It can insert or migrate into the internal structure of char and widen the existing pores. It is known as intercalation process. Further heating expels the potassium atom from the intercalated system, thus produces AC having high porosity. According to Tseng et al. (2008), the development of porosity by KOH activation was associated with Cf-KOH reactions as follows:

 $2\text{KOH} \rightarrow \text{K}_2 \text{ O} + \text{H}_2 \text{O} \tag{3}$

 $C_f + H_2 O \rightarrow H_2 + CO \tag{4}$

$$CO + H_2 O \rightarrow H_2 + CO_2 \tag{5}$$

$$K_2 O+ C_f \rightarrow 2 K+ CO$$
 (6)

$$K_2 O+ H_2 \rightarrow 2 K+ H_2 O \tag{7}$$

$$K_2 O+ CO_2 \rightarrow K_2 + CO_2 \tag{8}$$

Eqs. (6)–(8) are parallel reaction mechanism. Concurrently, K_2CO_3 produced from the reaction in Eq. (8) was reduced under an inert condition to form CO, CO₂, K₂O, and K as a final product, according to the following reactions (Foo and Hameed, 2011):

$$K_2CO_3 + 2C_f \rightarrow 2 K + 3CO \tag{9}$$

$$K_2 CO_3 \rightarrow K_2 O+ CO_2 \tag{10}$$

$$K_2 O+ C_f \rightarrow 2 K+ CO$$
 (11)

According to Eqs. (9)-(11), it is deduced that the potassium (K) element was produced after a serial of reactions in the activation process with KOH. The activation temperature was around 800 °C, while the boiling point of potassium is 759 °C (Tseng et al., 2008). As a result, potassium would lose in a large amount at further heating after the intercalation process through vent and exhaust of microwave oven, as previously explained. It was indicated by the absence of potassium in the EDX results. Therefore, it can be concluded that the diffusion of potassium compound into the internal structure of char matrix caused both the widening of the existing pores as previously explained, and the formation of new pores, due to the reaction of a fraction of char (i.e. C_f) with potassium compound. Accordingly, the porosity of the AC increased with the increase in the impregnation ratio from 1 to 3 (Table 1). In contrast to the AC, the char surface was constricted, blocked and covered by tar substances obtained from the carbonization process. Surface morphologies of char and AC evaluated using Scanning Electron Microscope (SEM) are shown in Supplementary Material.

When magnetite was loaded on the AC, the surface of AC partially covered by magnetite. As previously explained, the increase of impregnation ratio led to the higher porosity. When the AC having higher porosity (i.e. MAC-3) was soaked in the iron solution, a large amount of magnetite diffused to the interior of AC and the AC surface was covered by magnetite incomplete. As a result, the surface was dominated by O and C substance, as can be seen in the EDX results (Supplementary Material). On the contrary, when the AC having lower porosity (i.e. MAC-1) was soaked with an iron solution, a small amount of magnetite diffused to the interior of char and the AC surface covered by magnetite

Table 1

Surface physical characteristics of char, AC and MAC.

Surface physical parameters	char	AC-1	AC-2	AC-3	MAC-1	MAC-2	MAC-3
Particle size, µm	4.44	6.77	6.03	5.91	1.93	0.69	0.64
BET surface area (m^2/g)	17.03	71.75	128.94	383.17	95.11	155.01	314.08
Total pore volume (cm ³ /g)	0.0242	0.027	0.0402	0.1193	0.1056	0.1315	0.1098
Micropore volume (cm ³ /g)	0.0025	0.0039	0.0049	0.0549	0.0153	0.0229	0.0715
Micropore volume (%)	10.33	14.44	42.71	46.02	14.20	17.41	65.11
Pore radius (nm)	2.34	2.32	2.01	1.79	2.04	1.96	1.58
Micropore volume (cm ³ /g) Micropore volume (%) Pore radius (nm)	0.0025 10.33 2.34	0.0039 14.44 2.32	0.0049 42.71 2.01	0.0549 46.02 1.79	0.0153 14.20 2.04	0.0229 17.41 1.96	0.0715 65.11 1.58

completely. As a result, the surface was dominated by Fe. The lower of AC porosity led to a large amount of Fe in the AC surface, resulting in an increase in magnetic properties. Wong et al. (2016) had been reported that the surface of magnetite-loaded palm shell waste activated carbon was dominated by O and C substance, while Altintig et al. (2017) created that Fe and O substances dominated the magnetite-loaded acorn shell activated carbon surface. In this case, the activation process using $ZnCl_2$ with the impregnation ratio of $ZnCl_2$:char = 3:1, so the existence of Fe and O substances in the AC surface were only obtained from magnetite compound. However, the effect of impregnation ratio on the chemical composition of the MAC surface was not explained.

The N_2 physisorption is one of the standard procedures for pore textural properties determination of carbonaceous materials. From Fig. 1(a), it could be deduced that the adsorption-desorption profile of char belongs to the Type III isotherm according to the Brunauer's classification (Inglezakis et al., 2018), indicating unfavorable equilibrium in that the interaction of adsorbate molecules with an adsorbed layer is greater than the interaction of adsorbate molecules with the adsorbent surface (i.e. adsorbate-adsorbent interaction is weak). The result (Fig. 2) detected peaks at a pore radius between 2.14 and 6.04 nm



Fig. 2. The pore size distribution of char, AC-3, and MAC-3.



Fig. 1. The adsorption-desorption isotherms of N2 at 77 K for (a) char, (b) AC-3, and (c) MAC-3.

with an average pore radius of 2.34 nm, showing the majority of pores within the mesoporous range. After the activation process (i.e. AC-3), the isotherm exhibited hysteresis loops and appear to become a combination of Type I and IV isotherm according to Brunauer's classification (Fig. 1(b)). It could be concluded that the material consists of both micropores and mesopores. Fig. 2 shows that the main peak was centered at around 1.79 nm and most pores were less than 3.24 nm. The ratio of micropore volume to total volume increased from 10.33 to 46.02% after the activation process (Table 1), indicating the activation stage developed a microporous structure, as previously reported by Zhu et al. (2014). The addition of magnetite to activated carbon seems to slightly change the shape of the N₂ adsorption-desorption isotherms, where the isotherm plot becomes more distinctly Type I (Fig. 1(c)). indicating MAC-3 consists of more micropores. The result (Fig. 2) detected the main peak centered at around 1.58 nm and most pores were less than 3.14 nm. The ratio of micropore volume to total volume increased from 46.02 to 65.11% after the addition of magnetite (Table 1).

As previously explained, the pore development mechanism was suspected through three stages, including the opening of blocked pores, widening of the existing pores and formation of new pores. According to Table 1, an increase in the impregnation ratio led to an increase in the BET surface area and microporosity. Therefore, it could be deduced that the new pores formation mechanism was thought to be more dominant for the activation process using KOH. BET surface area and total pore volume of AC-3 were higher than those of MAC-3 (Table 1), indicating a fraction of pores on the MAC-3 was blocked by magnetite particles, as previously explained.

The particle size of AC-3 and MAC-3 was $5.91 \,\mu\text{m}$ and $0.64 \,\mu\text{m}$, respectively (Table 1). The results showed the increase in impregnation ratio led to smaller particle size due to a large amount of magnetite diffused to the interior of AC and the AC surface was covered by magnetite incomplete. As a result, the particle size was smaller (Table 1). The particle size distribution of MAC-3 can be seen in Fig. 3.

The magnetic property of MAC-3 was measured by a VSM at room temperature. The VSM magnetization curve showed the existence of a characteristic hysteresis loop indicating ferromagnetic behavior of the MAC with the value of specific saturation magnetization (*Ms*) of 15.0 emu/g. The value was higher than that of magnetically separable adsorbent (i.e. Ni-AC) studied by Gorria et al. (2006) (4.4 emu/g). As a result, MAC was attracted toward magnet when a bottle containing an aqueous dispersion of MAC particles was placed near a magnet.

The XRD patterns of MAC showed that MAC was approaching amorphous-like structure with the presence of some crystal structure. The peaks at $2\theta = 30^{\circ}$, 35° , 43° , 53° , 57° , and 63° were assigned to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) of cubic Fe₃O₄ crystal structure (Juang et al., 2018; Cheng et al., 2015), while the existence of crystal graphite was identified by peaks at $2\theta = 37^{\circ}$ and 40° (Cheng et al., 2015). The graphite peaks were disappeared in the MAC-2 and MAC-3 due to the graphite phase changed to amorphous phase after the

activation process. The increase of impregnation ratio led to a decrease in the intensity of magnetite peaks due to a large amount of magnetite diffused to the interior of char and the surface was dominated by C and O substance, as described previously. Thus, there was a good agreement between the result of SEM micrographs and XRD patterns.

To confirm the presence of functional groups in the adsorbent surface, FTIR analysis was conducted. The FTIR spectra of char, AC-3, and MAC-3 are shown in Supplementary Material. Char and AC exhibited similar spectra, suggesting they had similar functional groups. The spectra described the existence of several typical bands of lignocellulosic materials including aromatic, hydroxyl, carbonyl and alkene. The existence of a broad absorption peak around $3400-3700 \text{ cm}^{-1}$ was assigned to the O-H stretching vibration of the hydroxyl function groups including hydrogen bonding (Mohammed et al., 2015). The peak observed at 1500–1600 cm^{-1} may be attributed to the C=C stretching vibrations of aromatic compounds (Mohammed et al., 2015; Njoku et al., 2014), while a band at 1457 cm^{-1} reflects the C-N stretching vibration (Weng et al., 2009). Meanwhile, the bands at 792.5 cm^{-1} and its accompanying bands at 813 and 875 cm^{-1} were ascribable to aromatic and furfural -C-H- out of plane bending vibrations and can be assigned to the aromatic structures (Chowdhury et al., 2011; Gogoi et al., 2018). After activation with KOH, the position and intensity of some peaks being changed. Peak around 3400–3700 cm^{-1} was deeper which suggested the presence of more hydroxyl groups after the activation process with KOH. While the peak at 1578.46 cm^{-1} was shallower due to the reaction of a small carbon with KOH. The existence of the Fe–O group in the MAC was indicated by the presence of an absorption peak around $600 \,\mathrm{cm}^{-1}$ (Liu et al., 2018). The FTIR result shows that the AC and MAC were rich in the functional group which can help in the adsorption process.

3.2. Adsorption performance

Effect of impregnation ratio on the adsorption of methyl violet onto AC and MAC is described in Fig. 4(a). In a studied impregnation ratio range (1-3), the amount of methyl violet adsorbed by AC increased with the increasing of impregnation ratio, although the increase was insignificant. The increase may be related to the formation of more pores and active sites in the AC with higher impregnation ratio. For weight ratio of KOH/char = 1 and 2, the loading of magnetite to the AC increased surface area and adsorption uptake. In contrary, the amount of methyl violet adsorbed by magnetized activated carbon with impregnation ratio of 3 (MAC-3) was lower than that of by AC with impregnation ratio of 3 (AC-3) due to a large amount of magnetite filled the AC pores, resulting in a decrease in specific surface area and adsorption uptake. However, the advantage of magnetized activated carbon is ease of separation under the magnetic influence. The increase of impregnation ratio from 1 to 3 led to a decrease in magnetic property due to the amount of Fe in the MAC surface decreased, as previously



diameter (nm)

Fig. 3. The particle size distribution of MAC-3.



Fig. 4. Effect of (a) impregnation ratio, (b) pH of solution, (c) contact time, and (d) initial concentration toward methyl violet adsorbed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

explained. The EDX analysis showed that Fe content in the MAC surface was 89.4, 73.0, and 38.6 for MAC-1, MAC-2, and MAC-3, respectively.

Solution pH affects the charge of adsorbent surface and species in solution which depends on the degree of ionization. It is clear that the increase of solution pH from 1 to 5 led to an increase in the percentage removal of methyl violet (Fig. 4(b)), due to deprotonation of phenolic groups on AC and MAC surface. It creates an electrostatic attraction between negatively charged of AC or MAC with positively charged of methyl violet dye, resulting in an increase in the percentage removal of the dye. The sorption mechanism refers to the following reactions (Rai et al., 2015):

$$AC/MAC - OH \leftrightarrow AC/MAC - O^{-} + H^{+}$$
(12)

In contrary, in the strong acid medium (solution pH around 1), the AC and MAC surface becomes highly protonated. It caused electrostatic repulsion between positively charged of AC or MAC with positively charged methyl violet dye, resulting in a decrease in the percentage removal of the dye. While the increase solution pH from 5 to 11 led to a decrease in the adsorption uptake. It may be due to the formation of soluble hydroxy complexes between the dye and adsorbent in the al-kaline medium (Khattri and Singh, 2000).

Fig. 4(c) describes that the optimum contact time for methyl violet adsorption by both AC and MAC was 180 min. At the first 10 min, the removal of methyl violet increased rapidly. It was due to a large number of vacant active sites were available at the initial stage. The methyl

violet uptake tended to constant from 90 to 180 min due to a large number of methyl violet has been adsorbed and the equilibrium was reached. While Fig. 4(d) shows that the adsorption efficiency of the system decreased with the increase in the initial concentration of methyl violet solution. It may be due to there was a stronger repulsive force between methyl violet molecules on the solid and liquid phase after a lapse time.

3.3. Isotherm modeling

A number of isotherm models have been developed to describe the equilibrium of adsorbate molecules in the liquid and solid phase at a constant temperature (Inglezakis et al., 2018). For isotherm modeling, Langmuir, Freundlich, and Redlich-Peterson (R-P) isotherm models were used to the equilibrium data obtained. Langmuir is referred to the single layer adsorption on the adsorbent surface having homogeneous energy. The adsorption is assumed to be localized adsorption. Once a dye molecule occupies an active site, no further adsorption can take place on the site. In addition, the interaction between the adsorbate molecules is neglected. The Langmuir equation can be represented as (Jang et al., 2018):

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \tag{14}$$

where q_m is the maximum adsorption capacity (mg/g) and K_L (L/mg) is the Langmuir constant related to the affinity of the binding site. Eq. (14) was solved by optimizing the correlation coefficient between the value of q_e obtained from experiment and theoretically predicted from Eq. (14). The parameters (e.g. q_m and K_L) was determined using the solver add-in feature of Microsoft Excel software by minimizing the difference between the model predicted data with the experimental data.

Table 2

Isotherm parameters and values of error functions for AC-methyl violet system and MAC-methyl violet system.

Adsorbent	Langmuir isotherm	Freundlich isotherm	R-P isotherm
AC	$q_m = 31.24$ $K_L = 0.103$ $R^2 = 0.952$ SSE = 456.1 $\chi^2 = 15.25$ ARE = 24.13	1/n = 0.448 $K_F = 4.657$ $R^2 = 0.993$ SSE = 86.95 $\chi^2 = 2.109$ ARE = 4.288	$a_R = 15.11$ $K_R = 77.85$ $\beta = 0.581$ $R^2 = 0.995$ SSE = 42.13 $\chi^2 = 1.071$ ARE = 3.329
MAC	$q_m = 16.76$ $K_L = 0.183$ R^2 SSE = 1037.7 $\chi^2 = 31.503$ ARE = 17.72	1/n = 0.471 $K_F = 3.311$ $R^2 = 0.981$ SSE = 234.4 $\chi^2 = 6.811$ ARE = 8.239	$a_R = 1.503$ $K_R = 7.666$ $\beta = 0.631$ $R^2 = 0.991$ SSE = 37.97 $\chi^2 = 1.233$ ARE = 3.831

In contrast to the Langmuir isotherm, the Freundlich isotherm is an empirical equation suggested for adsorption system on the heterogeneous surface. In this sense, the enthalpy of adsorption is assumed to decrease logarithmically with the occupied area (Altintig et al., 2017). Freundlich equation is defined by Eq. (15), as follows (Altintig et al., 2017):

$$q_e = K_F C_e^{\frac{1}{n}} \tag{15}$$

where K_F (L/g) is the Freundlich constant representing the adsorption capacity, while 1/n is the Freundlich constant involving the adsorption intensity (Altıntıg et al., 2017). The parameters in Eq. (15) (e.g. K_F and n) were determined by optimizing the correlation coefficient between the value of q_e obtained from experiment and theoretically predicted from Eq. (15) using the solver add-in feature of Microsoft Excel software.

Unlike the Langmuir and Freundlich isotherm which are two-parameter adsorption isotherm models, Redlich-Peterson isotherm is a three-parameter isotherm model that can be applied either in homogeneous or heterogeneous systems due to the high versatility of the equation. The model approaches the Freundlich isotherm at high concentration while it is in accordance with the Langmuir isotherm at low concentration. The Redlich-Peterson model is given by Eq. (16) as follows (Gupta and Garg, 2015):

$$q_e = \frac{K_R C_e}{1 + \alpha_R C_e^\beta} \tag{16}$$

where K_R (L/g) and α_R (L/mg) are the Redlich-Peterson isotherm constants while β is the Redlich-Peterson isotherm exponent, which lies



The sum of the square of the errors (SSE), non-linear chi-square test (χ^2) and average relative error (ARE) was used to estimate the validity of the models. In contrast to the SSE and χ^2 that are based on the square residuals, ARE considers the difference in the value of adsorption capacity obtained from the experiment and the models. The error functions equations are: (Gupta and Garg, 2015; Astuti et al., 2016):

$$SSE = \sum_{i=1}^{n} (q_{e,calc} - q_{e,meas})^2$$
(17)

$$\chi^{2} = \sum_{i=1}^{n} (q_{e,calc} - q_{e,meas})^{2} / q_{e,meas}$$
(18)

$$ARE = \frac{100}{n} \sum_{i=1}^{n} |(q_{e,calc} - q_{e,meas})/q_{e,meas}|$$
(19)

where $q_{e,meas}$ and $q_{e,calc}$ are the value of q_e measured from experiment and calculated from the models, respectively, while *n* is the number of measurements. The results are presented in Table 2.

Data in Table 2 shows that the Redlich-Peterson model best fitted to the experimental data due to it had the highest \mathbb{R}^2 value and the lowest error functions values for both AC and MAC. Redlich-Peterson isotherm is a combination of both Freundlich and Langmuir isotherms, which approaches Freundlich isotherm at high concentration and in accordance with Langmuir isotherm at low concentration. It suggests that the adsorption mechanism is hybrid. The adsorption capacity of AC was higher than MAC, as indicated by the K_R values. While, the affinity of methyl violet toward AC (15.11) was higher than MAC (1.503), as indicated by the α_R values. However, the loading of magnetite into the AC can improve separation efficiency, as explained before. Fig. 5(a) and (b) depicts the comparison of the experimental and predicted q_e for methyl violet-AC and methyl violet-MAC system, respectively.

4. Conclusion

The activated carbon (AC) was successfully produced from pineapple crown leaf. The AC surface was enlarged by KOH activation and loaded by magnetite (Fe₃O₄) to provide the magnetic property. The AC and magnetized AC (MAC) can be used as an effective adsorbent for the removal of dyes from aqueous solutions, under the optimum conditions (i.e. solution pH of 5, contact time of 180 min and the adsorbent dose of 0.3 g/50 mL). Redlich-Peterson isotherm was found the best among various isotherm models for both AC and MAC.

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Fig. 5. Isotherm adsorption for (a) methyl violet-AC-3 system, and (b) methyl violet-MAC-3 system.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2019.121426.

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Surface morphologies of (a) char and (b) activated carbon with impregnation ratio of 3 (AC-3), evaluated using SEM with magnification 1500x

Supp. 2



SEM/EDX micrographs of magnetized activated carbon with impregnation ratio of (a) 1 (MAC-1) and (b) 3 (MAC-3), magnification 1500x

Supp. 3



FTIR spectra of char, activated carbon with impregnation ratio of 3 (AC-3), and magnetized activated carbon with impregnation ratio of 3 (MAC-3)