

LOW-COST AND EFFICIENT ADSORBENT DERIVED FROM CO₂ ACTIVATION OF *Melaleuca cajuputi* POWELL FOR COLOR REMOVAL

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Abstract

Coloring agents are widely used to color products manufactured in many industries. Among the numerous coloring removal techniques, adsorption is the preferred method and gives the best results. However, its use is still limited because of its high operating cost. Many researchers have focused on finding alternative low cost adsorbents. The aim of this work was to produce the low cost adsorbent *M. cajuputi* activated carbon (MCAC) derived from *Melaleuca Cajuputi* Powell by CO₂ activation. Batch experiments were carried out to determine the optimum conditions for methylene blue dye adsorbed on MCAC samples. Kinetic data and an adsorption equilibrium isotherm were performed on the batch experiments. The results showed that the MCAC samples had high surface areas in the range of 673-1,497 m²/g. The maximum adsorption capacity of the MCAC samples was found in the range of 40.16-73.53 mg/g. The optimum adsorption conditions of the MCAC were obtained at the contact time of 480 min, the initial MB concentration of 20 mg/L, the initial solution pH in the range of 7-8, the agitation speed of 150 rpm, and the temperature of 30°C. The fixed bed column was investigated and the Thomas model was found to fit the experimental data well with the correlation coefficients of 0.9807, while the adsorption capacity was obtained as 249.66 mg/g. This finding is a useful tool for scale-up and design purposes. It can be concluded that the MCAC can be used effectively as a low cost adsorbent for the removal of color from wastewater.

Keywords: *Melaleuca cajuputi* Powell, adsorption, CO₂ activation, color removal

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Introduction

Coloring agents are widely used to color products manufactured in many industries such as textile, paint, paper, and printing. They are harmful to human beings and hazardous to aquatic organisms. There are many methods available for the removal of color from wastewater, but several methods have been found to exhibit certain limitations (Gupta, 2009; Maryam *et al.*, 2016). Among the numerous color removal techniques, adsorption is the preferred method being one of the simplest and most effective methods with easy operational conditions for the treatment of aqueous textile effluents (Xue *et al.*, 2010; Vimonses *et al.*, 2010). Adsorption processes using activated carbon are widely used to remove pollutants from wastewater. However, commercially available activated carbon is expensive. Thus, to lower the cost, many researchers have focused on finding alternative low-cost adsorbents. Based on our preliminary results (Wirikitkhul *et al.*, 2017), *M. cajuputi* charcoal has potential properties to be a material for activated carbon production because it has a high percentage of carbon (48.57) and fixed carbon (13.17) and a low percentage of ash (0.86). And it was found that activation with CO₂ is a feasible method to produce *M. Cajuputi* activated carbon (MCAC) as an efficient adsorbent. *Melaleuca cajuputi* Powell is an important economic tree in the southern part of Thailand. It is a multipurpose tree, every part of which is usable and the local people have recognized its usefulness for a long time. It grows very well, with high growth and yield, in the disadvantageous areas where most agricultural crops and forest trees cannot grow successfully. It is considered to be one of the potential tree species for development of economic plantations (Nuyim, 2002). The conversion of this plant into activated carbon for color removal would add considerable economic value, help reduce the cost of textile wastewater treatment and, most importantly, provide a potentially inexpensive alternative to existing commercial activated carbon. In this study, *M. cajuputi* charcoal was selected as a material to produce MCAC by using CO₂ activation. Methylene

blue (MB) was used as a useful indicator to evaluate the color adsorption capacity of the MCAC in batch experiments. Adsorption batch experiments were carried out to study the effects of the initial concentration, contact time, initial solution pH, agitation speed, and temperature on MB adsorbed on the MCAC samples. Kinetic data and an adsorption equilibrium isotherm were performed in batch experiments and were analyzed using different models. Also, the fixed bed column experiment was explored, based on the results of the adsorption batch experiments, as it is widely used for color removal from wastewater and engineering design purposes.

Method

Materials

Melaleuca cajuputi Powell charcoal (*M. cajuputi* charcoal) was obtained from the southern part of Thailand. It was crushed and sieved by sieve analysis following ASTM 136-04 (ASTM, 2004) to obtain samples in the range of 1.70-2.38 mm.

Methylene blue (MB) was chosen in this study because it is one of the most commonly used substances for coloring cotton, wool and silk. Thus, this study has used MB as a model color. The stock solution of MB was prepared with a concentration of 100 mg/L. The concentration of MB was analyzed using a spectrophotometer (GENESYS 20, Sigma-Aldrich, St.Louis, MI, USA) at 600 nm.

Preparation of Adsorbents

The *M. cajuputi* charcoal sample was loaded on a ceramic boat which was placed in a horizontal tubular furnace (CTF 12/75/700/201, Carbolite Gero Ltd., Hope Valley, UK) and then heated up to the desired carbonization temperatures, i.e. 900, 950, and 1,000°C, at a heating rate of 5°C/min⁻¹ under the flow of N₂ gas. When the desired activation temperature was reached, the CO₂ gas was allowed to flow into the furnace. The activation time varied at 60, 120, 180, and 240 min. When the activation

was completed, the samples were cooled to room temperature under N_2 gas flow. In this study, the MCAC samples were named $MCAC_{\text{temperature, time}}$ which indicated the activation conditions of the temperature and time, e.g., $MCAC_{1000,240}$.

The porous properties of the MCAC samples were characterized by a nitrogen adsorption isotherm with an accelerated surface area and a porosimetry system (the Brunauer-Emmett-Teller (BET), Belsorp Mini-II, MicrotracBEL Corp., Osaka, Japan). The BET surface area was calculated from the isotherms by using the BET equation. The Dubinin-Astakhov (DA) equation was used to calculate the micropore volume. The total volume was found from the amount of N_2 adsorbed at a relative pressure (P/P_0) of 0.99 and converted to N_2 volume in liquid state.

Adsorption Experiments

In order to investigate the effects of contact time, initial MB concentration, initial solution pH, agitation speed, and temperature on MB adsorption, 0.1 mg MCAC samples were added into 200 mL MB solutions. The contact time in the range of 60-660 min, the initial MB concentration in the range of 5-20 mg/L, the initial solution pH in the range of 2-12, the agitation speed in the range of 100-350 rpm, and the temperature in the range of 30-60°C were varied in order to study these factors. The concentration of MB in the supernatant solutions before and after the adsorption of MB was analyzed.

Adsorption Isotherms and Kinetics

The equilibrium isotherms of the MB adsorption on the MCAC samples were conducted through the batch experiments. Adsorption isotherms were performed by varying the mass of the MCAC (0.02-0.2 g), and then 200 mL MB solution with the initial MB concentration of 20 mg/L was added to 250 Erlenmeyer flasks which were placed in a shaker (agitation speed of 150 rpm) at an ambient temperature and pH 7-8 for 480 min. The initial and remaining concentrations of the MB solution were measured. For comparison purposes, the similar batch adsorption experiments were also

conducted for commercial activated carbon. The commercial activated carbon (AC) which was used to compare with the MCAC samples was obtained from C. Gigantic Carbon Co., Ltd., Nakhon Ratchasima, Thailand (Lot NO: 600724-097, 2017) and had iodine number 1200. The adsorption kinetics studies were carried out, and the 200 mL MB solution with the initial concentration of 20 mg/L was withdrawn at certain time intervals (10 min) until the equilibrium was reached.

Fixed-bed Adsorption Experiment

Fixed bed columns are commonly used for adsorption in flow mode. Mass transfer is favorable with the existence of a gradient concentration which is a driving force of the adsorption process. The continuous sorption process is usually characterized by the so-called breakthrough curves, i.e. a representation of the effluent pollutant concentration versus time profile in a fixed bed column (Franco *et al.*, 2018). In this study, fixed bed experiments were carried out using a plastic column of 1.3 cm internal diameter and 11.3 cm total length. The MB solution was pumped in down-flow mode through the column at a controlled flow rate using a peristaltic pump, as shown in Figure 1.

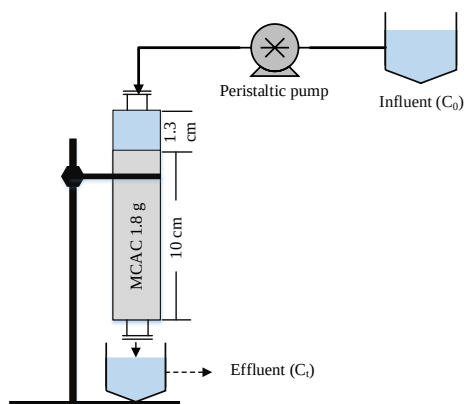


Figure 1. Schematic diagram of fixed-bed column

The $MCAC_{1000,240}$ samples were closely packed in the column of 1.8 g and 10 cm in length (calculated from the results of the isotherm experiments). The operating conditions of the fixed bed experiments including flow rate

(13.8 ml/min, 0.125 kg/m².h), pH (7-8), MB concentration (20 mg/L), and temperature of 30°C were derived based on the batch adsorption experiments and the isotherm results. The MB concentration in the effluent of the column was analyzed at a regular interval by spectrophotometer. The breakthrough curves were expressed by C_t/C_0 as a function of time to show the adsorption performance of the fixed bed column. The breakthrough time (t_b) and the exhaustible time (t_e) were measured when $C_t/C_0 = 0.05$ and $C_t/C_0 = 0.95$, respectively. The adsorption capacity of the MB was calculated by dividing the amount of the MB adsorbed in the column by the MCAC sample.

Results and Discussion

Yield and Characterization of MCAC

As for the properties, a pore structure (in terms of a surface area and a pore volume) is an important characteristic of activated carbon. Also, yield is one of the factors for the granular activated carbon production industry. Normally, a yield value over 25% is satisfactory for granular activated carbon products (Teng *et al.*, 1997; Sun and Jiang, 2010). In general, activated carbon with a high surface area, porosity, and high percent yield, allowing a large capacity of adsorption, is desirable. In this study, the results of the porosity parameters calculated from nitrogen sorption isotherms and the percent

yield are shown in Table 1. The percent yields of the samples are in the range of 11.98-58.17%. Only the yield of the MCAC_{1000.180} (24.27%) and MCAC_{1000.240} (11.98%) samples were too low to produce acceptable activated carbon. However, both samples obtained high surface areas in the range of 1,411-1,497 m²/g and the most desirable properties. As for the application of color removal in this study, the commercial activated carbon that has typically been used as water purification media has surface areas ranging from 800 to 1,200 m²/g (Jung and Kim, 2014). Therefore, 5 MCAC samples (MCAC_{950.180}, MCAC_{950.240}, MCAC_{1000.120}, MCAC_{1000.180}, and MCAC_{1000.240}) with surface areas in the range of 1,089-1,497 m²/g were selected to further investigate the effects of the factors on the adsorption, isotherm, and kinetic experiments.

Figure 2 shows that the increases in the activation temperature and time have a notable positive effect on the development of the surface area and the total volume of the porous structure (V_T). These results indicated that the activation temperature had a significant effect on the development of the porous structure (Bonelli *et al.*, 2007; Ding *et al.*, 2014; Kacan, 2016). Pore size distribution is a very important property of absorbents because the differences in the pore sizes affect the adsorption capacity for molecules of different sizes and shapes, and this is also one of the criteria by which carbon adsorbents are selected for a particular

Table 1. Percent yield and parameters of porous structure of MCAC samples

Activation conditions		Yield (%)	S_{BET} (m ² /g)	V_T (cm ³ /g)	D_{ap} (nm)
Temp (°C)	Time (min)				
900	60	58.17	673	0.299	1.775
	120	51.96	804	0.364	1.807
	180	45.46	950	0.453	1.907
	240	40.42	993	0.497	2.003
950	60	57.69	660	0.301	1.827
	120	45.05	963	0.459	1.905
	180	35.28	1,258	0.622	1.977
	240	26.33	1,417	0.734	2.072
1,000	60	52.10	753	0.362	1.921
	120	39.01	1,089	0.538	1.976
	180	24.27	1,411	0.749	2.123
	240	11.98	1,497	0.807	2.155

application (Xiao *et al.*, 2012). From the data presented in Table 1, the pore size distribution of the MCAC samples illustrates that the mean pore diameter (D_{ap}) is in the range of 1.775-2.155 nm which is very near 2.0 nm. These measurements indicated a great development of micropores based on the classification adopted by the International Union of Pure and Applied Chemistry (IUPAC): micropores (<2 nm), mesopores (2-50 nm) and macropores (>50 nm). Besides, it was found that the increase in the activation temperature and time changed the mean pore diameter from micropores to mesopores, although it showed that there was a high value of the BET surface area. This was supported by previous studies (Ismadji and Bhatia, 2001; Demiral *et al.*, 2011; Ani *et al.*, 2015) showing that, at a low temperature, the pore structure mainly consisted of microscopic pores; however, with the increase in the carbonization temperature, the creation of mesopores increased and the total pore volume of the activated carbon also increased.

Effects of Factors on MB Adsorption onto MCAC

Effect of Contact Time

The contact time between adsorbate and adsorbent is one of the most important parameters that affects the performance of an adsorption process. The effect of the contact time on the performance of the MCAC samples in adsorbing MB was individually investigated, and the results are shown in Figure 3. It was observed that the adsorption

speed of the MB was rapid in the first 480 min. After that, the equilibrium was gradually reached within 660 min. The results suggested that the adsorption took place rapidly at the initial stage on the external surface of the adsorbent followed by a slower internal diffusion process which might be the rate determining step (Allen and Koumanova, 2005; Gialamoudis *et al.*, 2010). In addition, the fast adsorption at the initial stage might be due to the fact that a large number of surface sites were available for adsorption but, after a lapse of time, the remaining surface sites were difficult to be occupied. This was because of the repulsion between the solute molecules of the solid and bulk phase; thus, it took a long time to reach the equilibrium (Idris *et al.*, 2011). Therefore, further experiments were carried out keeping the contact time as 480 min.

Effect of Initial Concentration

The effect of the initial concentration of MB on the MCAC adsorption was investigated and the results are shown in Figure 4 as the amount of MB adsorbed per gram of MCAC (q_e) versus the initial concentration. Since the amount of MB adsorbed was a function of the concentration at equilibrium, increasing the initial MB concentration caused an increase in the amount of MB adsorbed in all MCAC samples as expected, which suggested the filling of available adsorption sites on the MCAC surface. The initial MB concentration provided an important driving force to overcome the mass transfer resistance of the

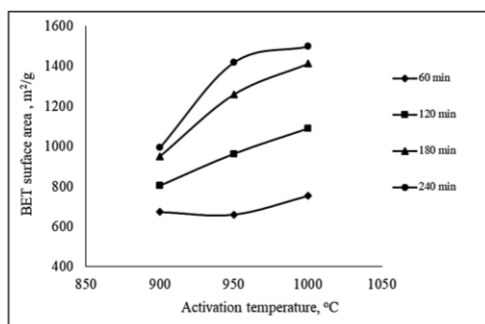


Figure 2. The relation between activation temperature (°C) and surface area (m²/g)

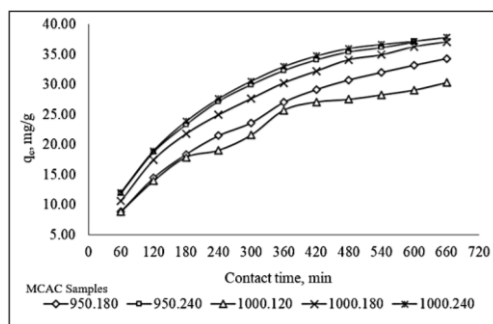


Figure 3. Effect of contact time on the adsorption of MB on MCAC samples

MB between the aqueous and solid phases (Kuppusamy *et al.*, 2016). Therefore, the following studies were performed with the initial MB concentration of 20 mg/L.

Effect of Initial Solution pH

The effect of each individual initial solution pH 2-12 on the equilibrium adsorption capacity of MB is represented in Figure 5. It was apparent that the amount of the adsorbed MB on the MCAC samples was not significantly different between pH 4-10 and the q_e was in the range of 29.12-36.86 mg/g. This might be associated with the functional groups on the adsorbent surface which could be protonated even at pH extremes (Luo *et al.*, 2011). The high resistance to a wide range of pH with maximum adsorption capacity thus gave the MCAC the potential to be used in many industrial applications. Therefore, the following studies were performed at pH 7-8.

Effect of Agitation Speed

The effect of the agitation speed on the MB adsorption of the MCAC samples was investigated and the results are shown in Figure 6 as the amount of MB adsorbed per gram of MCAC (q_e) versus the agitation speed. The q_e increased with an increase of the agitation speed. It was observed that the q_e of all MCAC samples was not significantly different between the agitation speeds of 150-300 rpm and the q_e was in the range of 22.05-38.76 mg/g. Beyond that, the q_e gradually decreased. The effect of the agitation speed is one of the important factors which plays a key role to control the solid-liquid mass transfer mechanism while affecting the external boundary film as well as the distribution of the solute in the bulk solution (Priyadarshini *et al.*, 2018). Therefore, further experiments were carried out keeping the agitation speed at 150 rpm.

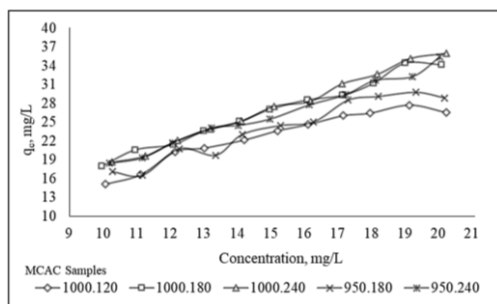


Figure 4. Effect of initial MB concentration on the adsorption of MB on MCAC samples

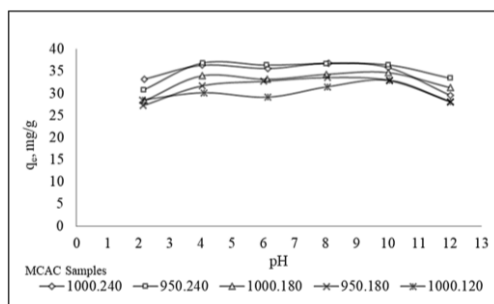


Figure 5. Effect of initial solution pH on the adsorption of MB on MCAC samples

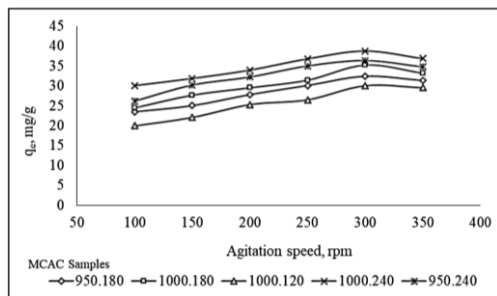


Figure 6. Effect of agitation speed on the adsorption of MB on MCAC samples

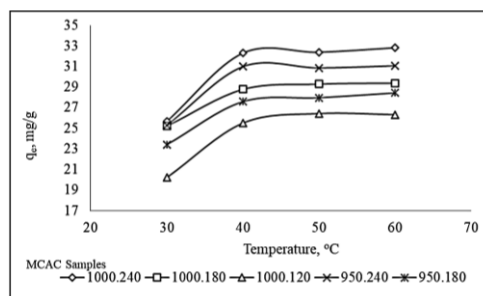


Figure 7. Effect of temperature on the adsorption of MB on MCAC samples

Effect of Temperature

Variation of adsorption of MB on the MCAC with the temperature is shown in Figure 7. The amount of the adsorbed MB increased with increasing the temperature, indicating an endothermic process. This might be due to increasing mobility of the dye molecules and an increase in the number of active sites for the adsorption with the increasing temperature (Yagub *et al.*, 2014). This was comparable with the results obtained during various studies reported in the literature (Dural *et al.*, 2011; Karacetin *et al.*, 2014). Therefore, further experiments were carried out keeping the temperature at 30°C.

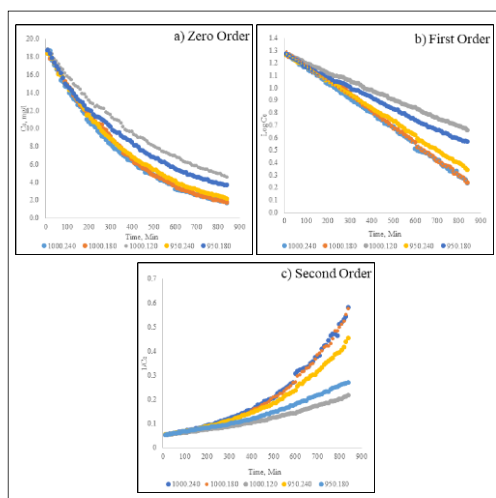


Figure 8. The kinetic models for MB adsorption on MCAC samples a) zero order kinetic; b) first order kinetic c) second order kinetic

Adsorption Isotherms and Kinetics

Adsorption Kinetic Study

Adsorption kinetics is a critical tool in the investigation of the adsorption mechanism. Therefore, to utilize the commonly used kinetic models, zero order, first order, and second order were used to describe the adsorption process. The best fitted model was considered based on the correlation coefficient (R^2). The constants obtained from the 3 kinetic models are shown in Figure 8 and Table 2. It was apparent that the coefficients of the first order (0.9977-0.9991) were higher and closer to unity. Hence, it was concluded that the MB adsorption on the MCAC was described by the first order model. The kinetics of the MB adsorption onto the MCAC adsorbents were prerequisite for choosing the best operating conditions for the full-scale batch process to treat color from wastewater.

Adsorption Isotherm Study

Langmuir and Freundlich isotherms are widely recognized and have been successfully applied to define many adsorption equilibria and evaluate adsorption equilibrium of MB from aqueous solutions. Therefore, MB adsorption data were analyzed by Langmuir and Freundlich Equations 1 and 2, respectively:

$$\frac{C_e}{q} = \frac{C_e}{q_m} + \frac{1}{Kq_m} \quad (1)$$

$$\log q = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

where K and q_m are Langmuir constants ($L \cdot mg^{-1}$) and maximum monolayer adsorption capacity ($mg \cdot g^{-1}$), respectively, and Freundlich coefficients

Table 2. Kinetic parameters for MB adsorption on MCAC samples

Temperature (°C)	Time (min)	Zero Order		First Order		Second Order	
		K	R ²	K	R ²	K	R ²
950	180	0.0168	0.9464	0.0008	0.9985	0.0003	0.9654
950	240	0.0185	0.9336	0.0011	0.9994	0.0004	0.9287
1,000	120	0.0164	0.9629	0.0007	0.9991	0.0002	0.9712
1,000	180	0.0195	0.9387	0.0013	0.9977	0.0006	0.9027
1,000	240	0.0189	0.9200	0.0012	0.9989	0.0006	0.9118

n and K_f are related to the adsorption intensity and adsorption capacity, respectively. As for the previous finding of optimum conditions in this study, the experiment was carried out to investigate the adsorption isotherm with the initial MB concentration of 20 mg/L, the contact time of 480 min, the agitation speed of 150 rpm, the initial solution pH in the range of 7-8, and the temperature of 30°C in order to understand the mechanism of adsorption. The constants obtained from the Langmuir and Freundlich isotherm equations are shown in Figure 9 and Table 3. The best equilibrium model was determined based on the linear square regression correlation coefficient, R^2 . By comparing these 2 isotherm models, it can be seen that the data fitted better to the Langmuir model with a high correlation coefficient value in the range of 0.9739-0.9983, whereas the R^2

of Freundlich was in the range of 0.8623-0.9984.

The best fit Langmuir isotherm expressions confirmed the monolayer coverage process of MB onto the MACA samples. This might be attributed to the monolayer distribution of the dye as well as the existence of homogeneous active sites on the surface of the adsorbents (Qada *et al.*, 2006; Li *et al.*, 2017). This finding was supported by the results of the adsorption-desorption isotherm of N_2 from the BET analysis and the pore size distribution for the adsorbent as presented in Figure 10. According to the IUPAC classification, the isotherms are a typical type I. Type I isotherms are given by microporous solids having relatively small external surfaces. They are concave to the P/P_0 axis and the amount adsorbed approaches a limiting value. This limiting uptake is governed

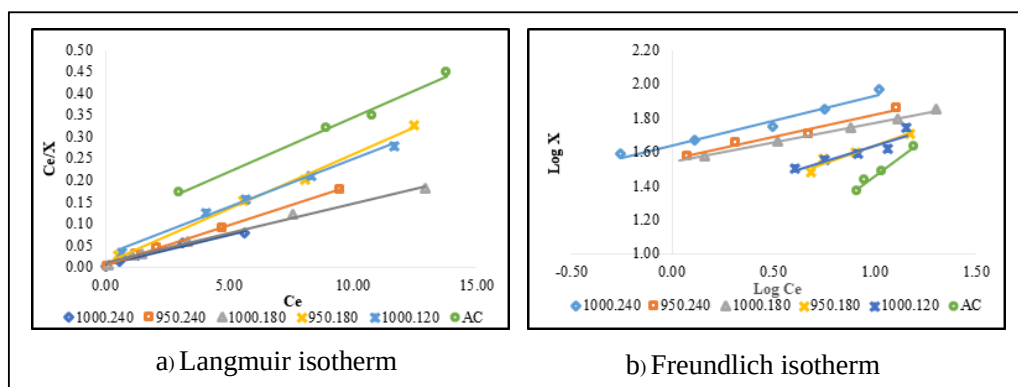


Figure 9. a) Langmuir and b) Freundlich isotherm plot for adsorption on MCAC samples under optimum adsorption conditions

Table 3. Parameter values of MCAC samples and AC sample calculated using Langmuir and Freundlich adsorption models

Activation condition		SBET (m ² /g)	Freundlich constants			Langmuir constants		
Temp (°C)	Time (min)		K_f (mg g ⁻¹)	n	r^2	q_{max} (mg g ⁻¹)	K_L (L mg ⁻¹)	r^2
950	180	1,258	16.70	2.40	0.9462	40.16	2.15	0.9968
950	240	1,417	36.12	3.82	0.9761	54.35	3.02	0.9983
1000	120	1,089	3.69	2.71	0.8623	45.45	0.78	0.9936
1000	180	1,411	34.96	4.31	0.9984	73.53	1.21	0.9932
1000	240	1,497	44.04	34.36	0.9692	73.53	2.13	0.9739
AC	-	1,200*	3.79	1.13	0.9777	40.00	0.26	0.9901

by the accessible micropore volume rather than the internal surface area. A steep uptake at a very low P/P_0 is due to enhanced adsorbent-adsorptive interactions in narrow micropores (micropores of molecular dimensions), resulting in micropore filling at a very low P/P_0 . It was assumed that any given receptor site could be empty or occupied by 1 part of the molecule in accordance with the monolayer model.

The properties of the adsorbents (surface area, pore size, and spacing) and the properties of the adsorbed materials (molecular size, boiling point, molecular mass, and polarity) could affect the quality of adsorption (Qada *et al.*, 2006). As shown in Figure 11, for the simulated figure of MB adsorbed on the MCAC, it was possible that the MB could access both micropore and mesopore volumes of the MCAC surface area because the MB had a molecular diameter of 0.8 nm (Raposo *et al.*, 2009) that was less than the mean pore diameter of the MCAC (1.775-2.155 nm). Besides, it was shown that the adsorption had been conducted by using an H-type which was activated at high temperatures and could adsorb H^+ and the MB was a cationic dye. The results of the MB adsorption of the MCAC samples increased as the solution pH

increased. These were supported by the high MB adsorbed on the MCAC samples.

As shown in Table 4, the comparison of the maximum adsorption capacity (q_m) of the MCAC with the commercial activated carbon (AC) that was obtained in this study clearly indicates that the superiority of the MCAC samples (40.16-73.53 mg/g) over the AC sample (40.0 mg/g) is almost 2 times higher and also the same result when compared with the other reported adsorbents. Hence, it can be concluded that the MCAC is an efficient adsorbent and a good candidate for dye removal from wastewater.

Fixed-bed Adsorption Experiment

Breakthrough curves of the MCAC column are shown in Figure 12 and were determined for the breakthrough time and the exhaustible time which were 20 min and 139 h, respectively. The MB adsorbed in the column was calculated from the area over the breakthrough curve and had the value of 1.24 mg/g. Hence, this finding was an applicable guide to scale up the application of the fixed bed column for color removal from wastewater. The evaluation method for scale-up fixed bed adsorption process parameters was derived based on the Thomas model to help improve the color removal from

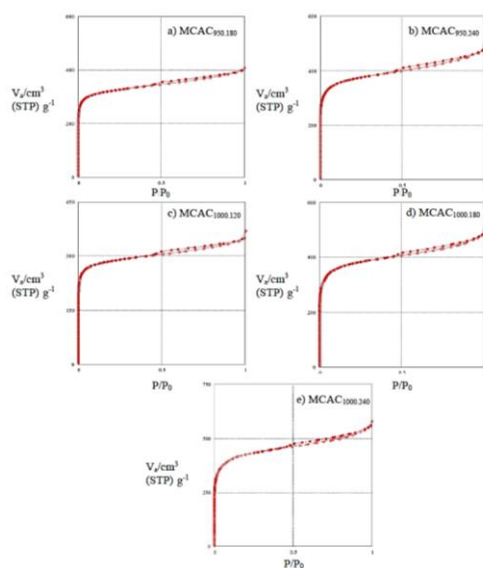


Figure 10. Type I isotherm linear plot from Nitrogen adsorption analysis

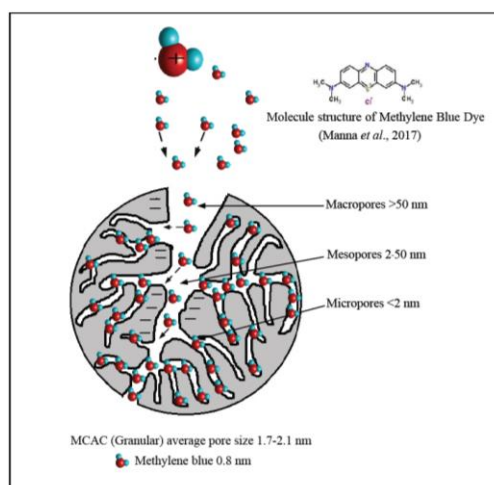


Figure 11. The simulated figure of MB adsorbed on MCAC

wastewater by the MCAC adsorbent. The Thomas model parameters (K_1 and q_e) for the MB adsorption by the MCAC were obtained by using linear regression (Equation 3) analysis based on the experimental data. The linear plots of $\ln(C_0/C_t - 1)$ against time are shown in Figure 13. As shown in Figure 13, the Thomas model fitted well with the experimental data ($R^2 = 0.9807$), and the model prediction was in good agreement with the experimental data. The values of K_1 and q_e were 2.75×10^{-5} and 249.66 mg/g, respectively. The results of the fixed bed experiments were a useful tool for scale-up and design purposes to treat color from wastewater. In addition, these findings showed that the MCAC was a good adsorbent which was widely accepted for use while the Thomas column model made the *M. cajuputi* charcoal an attractive, good, and novel adsorbent for both economic and environmental perspectives.

$$\frac{C}{C_0} = \frac{1}{1 + e^{\left[\frac{k_1}{Q} (q_0 M - C_0 V)\right]}} \quad (3)$$

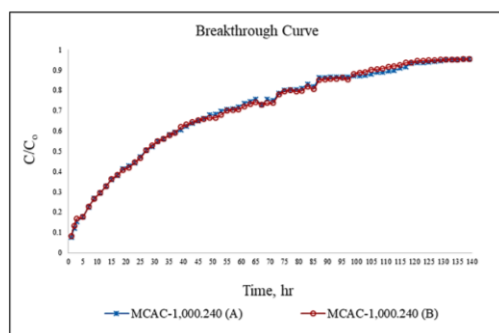


Figure 12. Breakthrough curve for MB adsorption on MCAC sample

where C = effluent solute concentration, C_0 = influent solute concentration, k_1 = rate constant, q_0 = maximum solid-phase concentration of the sorbed-solute (g/g), Q = flow rate (L/h), M = mass of adsorbent (g), and V = throughout volume (L).

Conclusions

The properties of the MCAC increased with an increase of the activation temperature from 900-1,000°C and the activation time of 60-240 min by the CO_2 activation method. The results showed the MCAC samples had high surface areas in the range of 673-1497 m²/g. The MB adsorption onto the MCAC batch studies revealed that the Langmuir equation was suitable for describing the isotherm behavior with the maximum adsorption capacity (40.16-73.53 mg/g). Besides, the MB adsorption of the MCAC kinetics best fitted the first order rate equation. The adsorption capacity depended on the contact time, the initial concentration, the pH solution, the agitation speed, and the

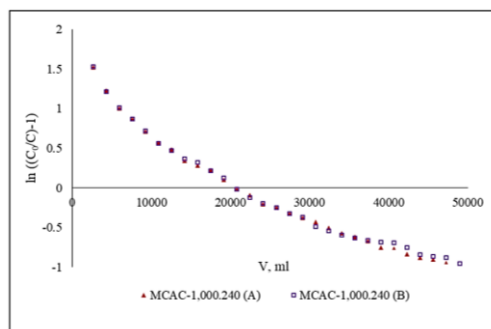


Figure 13. Fitting curves of Thomas model under operating conditions

Table 4. Methylene blue adsorption capacities of various adsorbents given in the literature

Adsorbent	q_m (mg g ⁻¹)	Reference
MCAC	40.0-73.53	This study
AC	40.0	This study
Rice husk	40.6	Vadivelan <i>et al.</i> , 2005
Saw dust	21.9-37.0	Ghaedi <i>et al.</i> , 2015
Rice husk	32.5-67.6	Leng <i>et al.</i> , 2015
Rice straw biomass	22.9-24.9	Goswami, 2017

temperature. The optimum adsorption conditions of the MCAC were obtained at the contact time of 480 min, the initial MB concentration of 20 mg/L, the initial solution pH in the range of 7-8, the agitation speed of 150 rpm, and the temperature of 30°C. The fixed bed column was investigated and the Thomas model was found to fit the experimental data well with the correlation coefficients 0.9807, while the adsorption capacity was obtained as 249.66 mg/g. This finding is a useful tool for scale-up and design purposes. It can be concluded that the MCAC can be used effectively as a low cost adsorbent for the removal of color from wastewater, and hence is an advantageous, practical, and cost effective method.

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References

- Allen, S.J. and Koumanova, B. (2005). Decolourisation of water/wastewater using adsorption. *J. Univ. Chem. Technol. Metall.*, 40:175-192.
- Ani, F.N., Junoh, M.M., and Muis, Z.A. (2015). Granular-activated carbon from Mukah coal using carbon dioxide activation. *J. Teknologi*, 75:123-127.
- ASTM. (2004). C136-04: Standard test method for sieve analysis of fine and coarse aggregates. ASTM International, West Conshohocken, PA, USA.
- Bonelli, P. R., Bounomo, E. L., and Cukierman, A. L. (2007). Pyrolysis of sugarcane bagasse co-pyrolysis with an Argentinean subbituminous coal. *Energ. Source Part A*, 29(8):731-740.
- Demiral, H., Demiral, I., and Karabacakoglu, B. (2011). Production of activated carbon from olive bagasse by physical activation. *Chem. Eng. Res. Des.*, 89: 206-213.
- Ding, W., Dong, X., Ime, I. M., and Gao, B. I. Q. (2014). Pyrolytic temperature impact lead sorption mechanisms by bagasse biochars. *Chemosphere*, 105:68-74.
- Dural, M. U., Cavas, L., and Papageorgiou, S. (2011). Methylene blue adsorption on activated carbon prepared from *Posidonia oceanica* (L.) dead leaves: kinetics and equilibrium studies. *Chem. Eng. J.*, 168:77-85.
- Franco, M. A. E. D., Carvalho, C. B. D., and Bonetto, M. M. (2018). Diclofenac removal from water by adsorption using activated carbon in batch mode and fixed-bed column: Isotherms, thermodynamic study and breakthrough curves modelling. *J. Clean. Prod.*, 181:145-154.
- Gialamoudis, D., Mitrakas, M., and Liakopoulou-Kyriakides, M. (2010). Equilibrium, thermodynamic and kinetic studies on biosorption of Mn (II) from aqueous solution by *Pseudomonas* sp., *Staphylococcus xylosum* and *Blakeslea trispora* cells. *J. Hazard. Mater.*, 182:672-680.
- Gupta, V. (2009). Application of low-cost adsorbents for dye removal-a review. *J. Environ. Manage.*, 90: 2,313-2,342.
- Idris, M. N., Ahmad, Z. A., and Ahmad, M. A. (2011). Adsorption equilibrium of malachite green dye onto rubber seed coat based activated carbon. *Int. J. Basic Appl. Sci.*, 11:305-311.
- Ismadji, S. and Bhatia, S. K. (2001). A modified pore filling isotherm for liquid phase adsorption in activated carbon. *Langmuir*, 17:1,488-1,498.
- Jung, S. H. and Kim, J. S. (2014). Production of biochars by intermediate pyrolysis and activated carbons from oak by three activated methods using CO₂. *J. Anal. Appl. Pyrol.*, 107:116-122.
- Kacan, E. (2016). Optimum BET surface area for activated carbon produced from textile sewage sludges and its application as dye removal. *Environ. Manage.*, 166:116-123.
- Karacetin, G., Sivrikaya, S., and Mustafa, I. M. (2014). Adsorption of methylene blue from aqueous solutions by activated carbon prepared from hazelnut husk using zinc chloride. *J. Anal. Appl. Pyrol.*, 110:270-276.
- Kuppusamy, S., Thavamani, P., and Megharaj, M. (2016). Potential of *Melaleuca diosmifolia* as a novel, non-conventional and low-cost coagulating adsorbent for removing both cationic and anionic dyes. *J. Ind. Eng. Chem.*, 37:198-207.
- Li, Z., Jia, Z., Ni, T. and Li, S. (2017). Adsorption of methylene blue on natural cotton based flexible carbon fiber aerogels activated by novel air-limited carbonization method. *J. Mol. Liq.*, 242: 747-756.
- Luo, P., Zhang, J. S., Zhang, B., Wang, J., Zhao, Y., and Liu, J. (2011). Preparation and characterization of silane coupling agent modified halloysite for Cr (VI) removal. *Ind. Eng. Chem. Res.*, 50:10,246-10,252.
- Manna, S., Roy, D., Saha, P., Gopakumar, D., and Thomas, S. (2017). Rapid methylene blue adsorption using modified lignocellulosic materials. *Process Saf. Environ.*, 107:346-356.
- Maryam, K. M., Cheikhou, K., and Ndeye, O. D. (2016). Electrocoagulation process applied on pollutants treatment experimental optimization and fundamental investigation of the crystal violet dye removal. *J. Environ. Chem. Eng.*, 4:4,001-4,011.
- Nuyim, T. (2002). Potentiality of *Melaleuca cajuputi* Powell cultivation to develop for economic plantation purposes. Royal Forestry Department, Ministry of Agriculture, Bangkok, Thailand, 10p.

- Priyadarshini, B., Rath, P. P., Behera, S. S., Panda, S. R., Sahoo, T. R., and Parhi, P. K. (2018). Kinetics, thermodynamics and isotherm studies on adsorption of Eriochrome Black- T from aqueous solution using rutile TiO₂. *Mater. Sci. Eng.*, 310:012051
- Qada, E. N. E., Allen, S. J., and Walker, G. M. (2006). Adsorption of methylene blue onto activated carbon produced from steam activated bituminous coal: a study of equilibrium adsorption isotherm. *Chem. Eng. J.*, 124:103-110.
- Raposo, F., Rubia, M. A., and Borja, R. (2009). Methylene blue number as useful indicator to evaluate the adsorptive capacity of granular activated carbon in batch mode: Influence of adsorbate/adsorbent mass ratio and particle size. *J. Hazard. Mater.*, 165:291-299.
- Sun, K. and Jiang, J. C. (2010). Preparation and characterization of activated carbon from rubber-seed shell by physical activation with steam. *Biomass Bioenerg.*, 34(4):539-544.
- Teng, H. S., Ho, J. A., and Hsu, Y. F. (1997). Preparation of activated carbons from bituminous coal with CO₂. *Carbon*, 35:275-283.
- Vimonses, V., Jin, B., Chow, C. W. K., and Saint, C. (2010). Development of a pilot fluidized bed reactor system with a formulated clay-lime mixture for continuous removal of chemical pollutants from wastewater. *Chem. Eng. J.*, 158(3):535-541.
- Wirikitkhul, P., Junpirom, S., and Yimrattanabovorn, J. (2017). Adsorption of methylene blue dye from aqueous solution by activated carbon prepared from *Melaleuca Cajuputi* Powell charcoal using heating activation. *Proceedings of the 9th Eastern European Young Water Professionals Conference*; May 24-27, 2017; Budapest, Hungary, p. 698-704.
- Xiao, H., Peng, H., and Deeng, S. (2012). Preparation of activated carbon from edible fungi residue by microwave assisted K₂CO₃ activation—application in reactive black 5 adsorption from aqueous solution. *Bioresource Technol.*, 111:127-133.
- Xue, A., Zhou, S., and Zhou, Y. (2010). Adsorption of reactive dyes from aqueous solution by silylated palygorskite. *Appl. Clay Sci.*, 48:638-640.
- Yagub, M. T., Sen, T. K., Afroze, S. and Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption: a review. *Adv. Colloid Interfac.*, 209:172-184.