ADSORPTION OF METHYLENE BLUE ONTO ACTIVATED CARBON PREPARED FROM MALAYSIAN MUKAH BALINGIAN LOW-RANK COAL BY POTASSIUM HYDROXIDE (KOH) ACTIVATION

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ABSTRACT

Being abundantly in many regions in the world, low rank coal is apparently one of the great potential precursors for activated carbon production. Potassium hydroxide (KOH) was used as an activator for coal-based activated carbon preparation from Mukah Balingian low rank Malaysian coal. This potassium hydroxide – treated activated carbon (KAC) has been used as adsorbent for the removal of cationic dye, methylene blue (MB) from aqueous solution. In this study, the adsorption of MB onto KAC was investigated in a batch arrangement. The ability of KAC to adsorb MB was evaluated at different pH values (pH 3-11), adsorbent dosage (0.02 – 0.20 g), initial dye concentration (50 to 400 mg/L), contact time (0 – 510 min). The results indicated that the optimum conditions for the adsorption system were found as follows: adsorbent dosage of 0.1 g/L with 99.20 % color removal, unadjusted of initial pH when there are similarities in the color removal percentage, while effect of initial MB concentration shows that at higher concentration resulted in lower of the color removal. The experimental data best fits the Langmuir isotherm model with maximum adsorption capacity, q_m is 256.41 mg/g. The recognition of KAC surface charge is carried out by pH_{PZC} method and shows that the $pH_{PZC} > pH$ of solution which indicates that the surface is positively charge. The characterization results of porous surface structure and functional groups (FTIR) of KAC act as an important role in the adsorption of MB onto KAC. Therefore, these findings revealed that KAC is a good low cost precursor of activated carbon for adsorption of MB from aqueous solutions.

Keywords: Activated carbon, adsorption, methylene blue, Mukah Balingian low rank coal, potassium hydroxide.

INTRODUCTION

Methylene blue (MB) is one of the synthetic dyes, which is widely used in different industrial fields. MB is used in textile, plastic, rubber and cosmetic industry due to their durability, ease of applicability and good fastness to materials [1]. However, the presence of MB even at very low concentrations in discharge effluents to the environment is worrying for both toxicological and esthetic reasons [2]. Exposure to the MB can cause several harmful effects to humans such as vomiting, increased heart rate and necrosis [1], therefore these dyes must be removed completely from effluents for environmental protection.

There are several treatments used to treat dyes from effluents such as flocculation, ion-exchange, membrane separation, and adsorption [3]. However, removal of dyes from aqueous solution by adsorption with the use of activated carbon is the most superior technique account to methodology and efficiency which due to its highly porous structure and high surface area [4] Activated carbon has been used for decades, but the high operating cost and the non-regenerability retarded the use of activated carbon as adsorbent in large-scale application [4]. Therefore, a number of non-conventional sorbents have been tried for the treatment of wastewater.

Numerous studies have been focused for producing an alternative adsorbents such as industrial solid waste [4], agricultural waste [5-7] and natural materials [8, 9]. Low-cost and greatly effective sorbents have been prepared from peat and various kinds of low rank coals-materials containing humic substances as an active constituent. The coal-based sorbents are capable to retain various kinds of pollutants, ranging from inorganic ionic species (heavy metal cations [10, 11] to low-polarity organic compound (napthlaelene [12-14], including ionic organic compounds, such as synthetic dyes [8, 15, 16]

Brown coal, lignite and sub-bituminous are low rank coals that reported to be almost half of the global coal reserve. Currently low rank coals are not extensively used primarily for electricity generation, but their use for other applications will increase in the future because they do have certain advantages over black coals. These advantages include low mining cost, high reactivity and low pollution-forming impurities such as sulfur, nitrogen, and heavy metals [17]. Some studies use low rank coals as adsorbent [9, 10, 18]. Coals in Malaysia are present in the Tertiary basins in all three geographical provinces i.e. Sarawak, Sabah and Peninsular Malaysia. As at the end of 2011, total coal resources in Malaysia stood at 1819 Mt, of which 1468 Mt or 80.7% were located in Sarawak, 334 Mt or 18.3% in Sabah, and the remaining 1% in Peninsular Malaysia. When considered the abundantly available and cheap material of low-rank coal, the utilization of Mukah Balingian low-rank Malaysian coal as an adsorbent for wastewater treatment process is an attractive proposition. The primary objective of this study is to characterize and optimize Mukah Balingian low-rank Malaysian coal as a potential low-cost high performance industrial adsorbent for aqueous process effluents.

METHODOLOGY

Materials

Methylene blue (MB) dye that being used as adsorbate was purchased from R & M Chemicals (chemical formula: $C_{16}H_{18}CIN_3S_3H_2O$, molecular weight: 373.9 g/mol, solubility in water: 40 g/L, purity 82%). Potassium hydroxide with an assay of 99.99% was obtained from HmbG Chemicals. Other chemicals such as sodium hydroxide (NaOH), hydrochloric acid (HCI), iodine, sodium sulfate, sodium chloride and potassium bromide were analytical grade quality. The sorbent low rank coal originated from Mukah Balingian, Sarawak, Malaysia Coal Basin.

Preparation of activated carbon

The coal was crushed and washed repeatedly with hot boiling distilled water to remove any contaminants like adhering dirt and dried at 110˚C for 24 h by using a drying oven, Memmert, model UFB-400. The dried sample was then grinded and sieved to powdered form with a particle size less than 75µm. The coal activated carbon (KAC) was produce by thoroughly mixing KOH with a coal/ KOH impregnation ratio of 1:3 (wt. %) (predetermined as an optimum mixing ratio) and then stored in an oven for 24 h at 110℃. The mixing sample was then undergoing carbonization process in a furnace under purified nitrogen gas (99.99%) atmosphere with 0. 4 L/ min N_2 flowrate, 30℃/ min of heating rate and the temperature was maintained at 700℃ for 1 hour. The sample was then allowed to cooled to room temperature and finally the products were washed repeatedly with 3M HCI and hot boiling distilled water until the pH value of the filtrate turn into pH 7 (neutral). Then, the product was dried in oven for 24 hours at 110℃. After that, the activated products were ground and sieved to acquire particle size (< 75µm) and finally the obtained KAC was stored in desiccators until required. Figure 1 illustrated the expected porosity on the surface of the produced activated carbon.
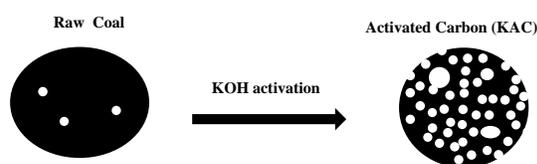

Figure 1 Porosity illustration of sample before and after chemical treatment

Characterization of adsorbent

The physicochemical properties of KAC were determined by using bulk density, ash content, moisture content, iodine number and $pH_{PZC \ (point \ of \ zero \ charge).}$. The method for examined the point of zero charge, pH_{PZC} is described elsewhere (Mei, 2016). In this study, 100 mL of 0.01 M NaCI solutions were placed in various Erlenmeyer flasks. The pH of the solutions was adjusted from 3 to 12 by the addition of 0.1 M HCI and NaOH solutions. 0.1 g adsorbent was added to each of the flask and shake overnight. The final pH was recorded. The pH_{zpc} point is confirmed when $pH_{final} - pH_{initial} = 0$. The iodine number was determined according to procedure from standard test method of iodine number determination [19].

The surface functional groups presence in KAC was investigated by using Fourier-transform infrared (FT-IR) spectrometer (Model Perkin Elmer). Muffle furnace was used to study the proximate analysis of the KAC, while the elemental analysis was evaluated by using CHN analyzer (Perkin-Elmer, Series II, 2400).

Batch adsorption experiments

The effects of experimental parameters, such as adsorbent dosage (0.02 – 0.2 g /L), pH (3-11), and MB initial concentration (50 – 400 mg/ L) on dye adsorption by KAC were studied in batch adsorption experiments as illustrated in Figure 2. The pH of the dye solutions was adjusted by addition of 0.1 M HCI and 0.1 M NaOH (pH meter, Metrohm, Model 827 pH Lab, Switzerland). All adsorption study was carried out in 250 mL Erlenmeyer flasks containing 100 mL of MB solution (with desired concentration and pH) for pH and concentration study. Parameters of adsorbent dosage and pH solutions were agitated in a rotary shaker at 125 rpm for 1 hour at room temperature. While, effect of initial MB concentration experiments was agitated in an isothermal water bath shaker (Memmert, water bath, model WNB7-45, Germany) at 30˚C and fixed shaking speed of 120 strokes/min until equilibrium was obtained. The solutions were then filtered by using 0.45 µm Nylon syringe filter and HACH DR 2800 Direct Reading Spectrophotometer was used to monitor the concentration of MB at a wavelength of 661 nm.
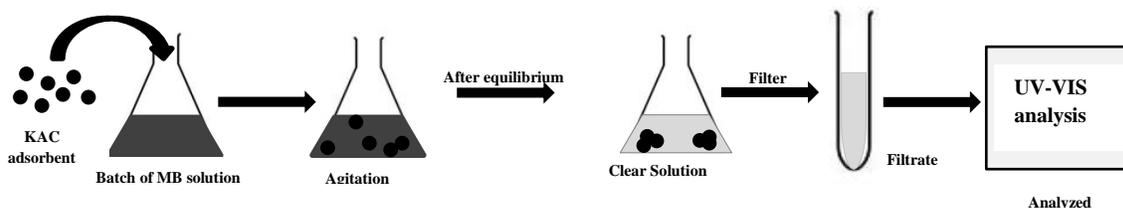

Figure 2 Illustration of adsorption experiments

RESULTS AND DISCUSSION
Characterization of KAC
Physical properties of KAC
    The results of physical characterization of KAC are tabulated in Table 1. The results show that KAC has a low bulk density, ash content and moisture content.

Table 1 Physiochemical characteristic of the KAC powder

Typical properties	Bulk density (g/ mL)	Iodine number (mg/ g)	Proximate analysis (wt. % dry basis)			Ultimate analysis (wt. %)				
			Ash content	Fixed carbon (yield)	Volatile Matter	C	H	N	S	O (by difference)
	0.45	937	6.41	49.14	44.45	58.91	2.20	1.40	0	37.49

FTIR spectral analysis
    The FTIR spectra of the KAC before and after MB adsorption are presented in Figure 3. FTIR analysis of KAC before adsorption in Figure 3 (a) shows bands at 3156 cm^{-1} corresponding to the stretching mode of free O-H groups, hydrogen-bonded O-H and chemisorbed water, while bands at 1,778, 1,563, 1,483 and 860 cm^{-1} are the characteristic of stretching vibrations alkane, carboxylate, alkene groups and secondary cyclic alcohol respectively. After MB adsorption is shows in Figure 3 (b) reveals that new peaks appeared. New band appear at 2,280 cm^{-1} refer to the aliphatic C-H stretching such in a methyl, methoxyl group and methylene blue groups of side chains.
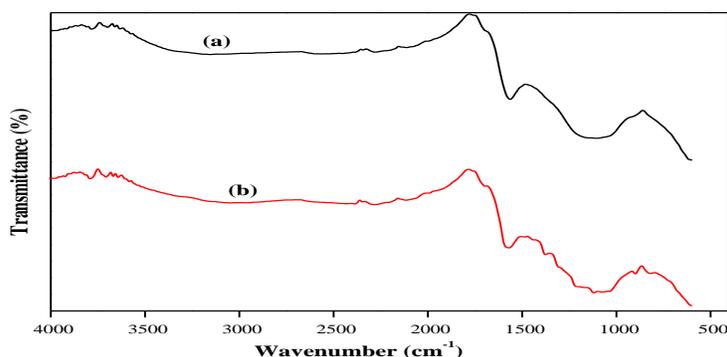

Figure 3 FT-IR spectra of KAC (a) before MB adsorption and (b) after MB adsorption

pH$_{PZC}$ of the KAC
    The charge of KAC surface was identified by point of zero charge (pH$_{PZC}$) analysis and shown in Figure 4. The pH$_{PZC}$ of KAC was 5.0. KAC surface becomes positively charged when pH MB solution below than pH$_{PZC}$ value, indicate that the concentration of H$^+$ was high and resulted in small dye uptake due to competition of H$^+$ with MB$^+$ for empty adsorption sites. While, above pH$_{PZC}$ the KAC surface become negatively charged and gives a strong electrostatic force of attraction between the adsorption sites of MB$^-$. Thus, higher adsorption happened at pH higher than pH$_{PZC.}$
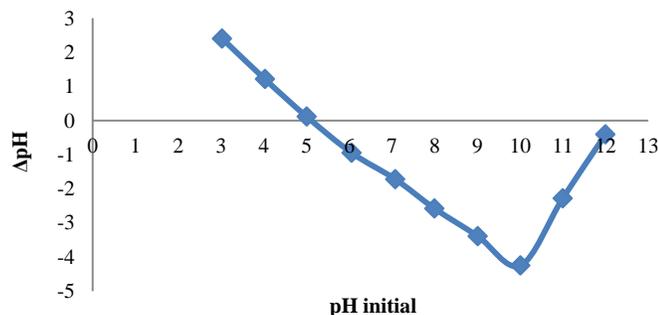

Figure 4 pH$_{PZC}$ KAC suspensions.

Batch adsorption studies

Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of MB dye was study at 100 mg/L of initial MB solution. The range of KAC adsorbent i.e. from 0.02 to 0.2 g was added to 100 mL to the MB solution. Other aspects were kept constant at contact time of 1 hour, shaking speed 125 rpm, 303 K and an unadjusted pH at 5.70. The results displayed in Figure 5 shows that when adsorbent dosage increases, the removal (%) of MB also increases due to an increases of adsorbent surface area and adsorption sites [2] .From the observation, the maximum MB removal was obtained using 0.1 g of KAC and after that remained almost constant. Therefore, in this study 0.1 g/100 mL was chosen as an optimum KAC dosage for all adsorption studies
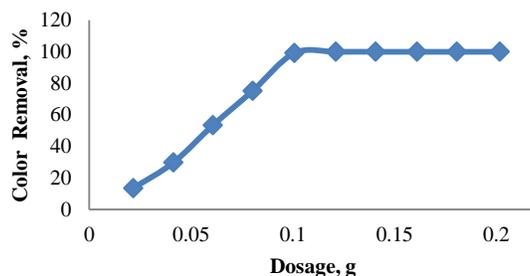

Figure 5 Effect of KAC dosage on MB removal (%) at $[MB]_0 = 100$ mg/L, V = 100 mL, unadjusted pH 5.70, T = 303 K, shaking speed = 125 rpm and contact time = 1 hours.

Effect of pH

The effect of initial pH on removable of MB dye was performed with pH range from 3 - 11 as shown in Figure 6. The percent of MB removal by KAC was not influenced by pH value where the removal percentage slightly similar for each pH. This happens due to buffering effect of the adsorption. Similar observation has been stated in the removal of methylene blue by *Cocos nucifera* [20]. Hence, the unadjusted pH value (pH 5.70) of MB solution was used for the whole investigation.
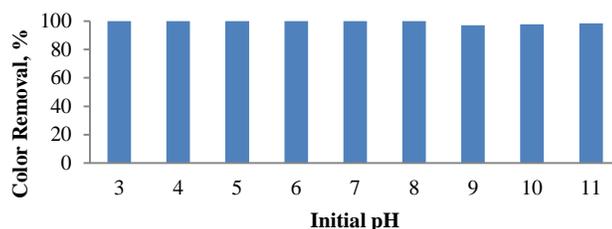

Figure 6 Effect of pH on MB removal (%) using 0.1 g of KAC, [MB] = 100 mg/L, V = 100 mL, T = 303 K, shaking speed= 125 rpm and contact time = 1 hours.

Effect of initial dye concentration and contact time

Figure 7 shows the results of initial dye concentration effect on adsorption capacity of MB onto KAC ranged from 50 to 400 mg/ L. This study recorded that when the initial MB concentration increased from 50 to 400 mg/, the adsorption capacity of KAC adsorbent increased from 17.40 to 260.73 mg/g. At higher initial dye concentration, the strong collision rate between KAC surface and MB occurred. Thus, extra quantities of MB cations were transferred to the KAC surface. Higher dye concentration required longer contact time to reach equilibrium due to the ability of MB to pass through deeper inside the interior surface of the KAC and be adsorbed at active pore sites.
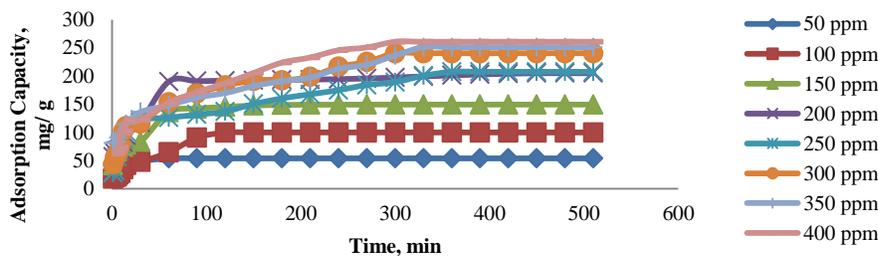

Figure 7 Effect of pH contact time and initial concentration on the adsorption of MB by KAC, KAC mass = 0.2 g, V = 200 mL, T = 303 K and shaking speed= 120 rpm

Adsorption Isotherms

Adsorption isotherms give a valuable definition about the interaction of adsorbates and adsorbents, where the equilibrium allocation of adsorbate molecules occurs between the solid and liquid phases. From the equilibrium data, the linear Freundlich and Langmuir isotherm models were evaluated. Langmuir isotherm [21] defines the monolayer adsorption process for homogenous adsorption sites which can be expressed in Eq. (1):

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

where C_e and is the equilibrium concentration (mg/L) and q_e is the amount adsorbed species per specified amount of adsorbent (mg/g), K_L is the Langmuir equilibrium constant, and q_m is the amount of adsorbate required to form an adsorbed monolayer. Hence, a plot of C_e/q_e vs C_e should be a straight line with a slope $1/q_m$ and an intercept as shown in Figure 8 (a).

Freundlich isotherm estimated the multilayer adsorption process on heterogeneous adsorption surface sites, which can be established in Eq. (2):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{2}$$

where C_e is the equilibrium concentration of dye in solution (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), K_F and n are Freundlich constants where n indicates the relative favorability of the adsorption process. The affinity constant, K_F (mg/g (l/ mg)$^{1/n}$, defined as the adsorption capacity of the adsorbent which can also be relate as the adsorption or distribution coefficient, and represents the quantity of dye adsorbed onto activated carbon for a unit equilibrium concentration. The plot of $\ln q_e$ vs. $\ln C_e$ give a straight line with slope of $1/n$, whereas; K_F was calculated from the intercept value as illustrate in Figure 8 (b).
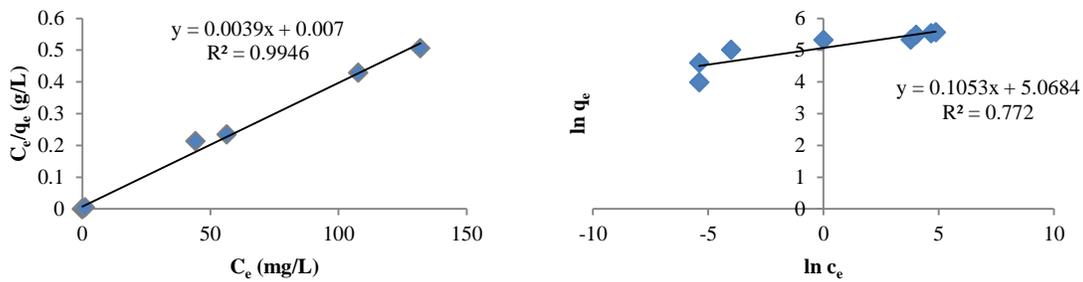

Figure 8 (a) Langmuir isotherm plots for the adsorption of MB onto KAC (b) Freundlich isotherm plot for the adsorption of MB onto KAC

For the adsorption of the methylene blue dye over KAC, the equilibrium data from Figure 7 were correlated with the Langmuir's and Freundlich's isotherm. The parameters of these models were calculated and tabulated in Table 2. From observation, the adsorption process best fitted to the Langmuir isotherm model with greater correlation coefficient (r^2) compared to Freundlich isotherm model.

Table 2 Isotherm parameters for removal of MB by KAC

	Langmuir isotherm			Freundlich isotherm		
	q_m (mg/ g)	K_L (L/ mg)	R^2	K_F (mg/ g (L/mg)$^{1/n}$)	$1/n$	R^2
KAC	256.41	0.557	0.995	158.92	0.105	0.772

CONCLUSION

The present work definitely shows that AC prepared from Malaysian low rank coal with activation using KOH supply an economic adsorbent for the removal of a basic cationic dye (methylene blue) from aqueous solutions. The maximum adsorption capacity reached 256.41 mg/g. The adsorption results at equilibrium are defined by the Langmuir model with high correlation coefficient ($R^2 = 0.995$) and high sorption capacity compare to Freudlich isotherm ($R^2 = 0.772$). This means that at the maximum adsorption, exclusively just a monolayer is developed on surface of the adsorbent. The rest of adsorbate molecules do not deposit on other but only on the free surface of the KAC adsorbent. The adsorption was achieved at neutral pH, imitating an electrostatic interaction between MB and KAC.

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