Sorption Studies of Methylene Blue Dye in Aqueous Solution by Optimised Carbon Prepared from Guava Seeds (*Psidium guajava L.*)

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The aim of this investigation was to determine the adsorption behavior and kinetics of methylene blue in aqueous solution on activated carbons prepared from guava seeds by way of the two stage activation method in self-generated atmosphere using a muffle furnace. The yield and ash contents of the activated carbons obtained decreased with the increase of activation temperature and time. FT-IR spectra indicated high surface functional groups present in the carbons. The optimised activated carbon, AK6, had a sorption kinetics that complied with the pseudo-second order kinetics and was fitted well to Langmuir isotherm model. The highest adsorption capacity was obtained when the samples (AK6) were subjected to activation temperature of 500 °C for 45 minutes giving iodine number of 198.12 mg g^{-1} and the percentage of methylene blue removal efficiency of 84.75 %.
Keywords: adsorption kinetic, methylene blue, activated carbons, guava seeds, Langmuir adsorption isotherm.

INTRODUCTION

Activated carbons can be prepared from a large number of sources, such as palm shells [1 – 2], wood [3 – 4], coconut shells, coals, carbon fibers and pitch. Activated carbon adsorbs molecules from both liquid and gaseous phases were found to depend on the specific surface area, pore size distribution, surface functional groups (also denoted as surface complexes). Applications of activated carbons include drinking water purification, waste-water treatment, sweetener discolouration, food and chemical processing, solvent recovery, gasoline emission control, cigarette filters and industrial emission gas treatment.

Activated carbon is generally considered non-toxic and will not have any detrimental chemical interactions with any other chemicals. Activated carbon is a mild reducing agent and a catalyst [4 – 6], but will not react strongly with any organically allowed substances. Thus, it is used medically to adsorb a wide variety of toxins. If trace quantities of the activated carbon is left behind, it is basically nothing but carbon, and ash (metallic elements). Heavy metals content of activated carbon may be of interest when it comes in direct contact with food. Large doses of activated carbon are routinely given in human poisoning cases. The human dose for poisoning is 1g activated carbon per kg. body weight [7 – 8]. In Malaysia, the state of Perak particularly Bidor, is the largest area for guava *Psidium guajava L* plantation. Guava is an important tropical fruit in Malaysia and claims superiority over other fruits by virtue of its commercial and nutritional values.

In the last decade, guava in Malaysia has grown in importance from a neglected fruit to one grown largely for processing. In the processing line, the fruit is either canned or converted into juice or puree, or used for producing jam and guava paste. Guava seeds are agricultural by-products that are currently of no economic value. The seeds are considered waste product during guava juice processing (seeds represent about 5 % of the fresh fruit) [9]. The seeds have high amount of lignocellulosic materials which make it suitable for the preparation of activated carbons [10].

The aim of this investigation was to determine the adsorption behavior and kinetics of methylene blue in aqueous solution on activated carbons prepared from guava seeds by way of the two stage activation method in self-generated atmosphere using a muffle furnace.

EXPERIMENTAL

The seeds (from the species *Psidium guajava L.*) were collected from a wet market in Sabah (Malaysia). The seeds were washed and dried in an oven at 110 °C for 24 hours. Carbonization by pyrolysis was carried out in a muffle furnace (Carbolite, RHF 1500). The sample was placed on a pyrex petri dish, and placed in the hot zone of the furnace. The samples were heated at 200 °C for 15 minutes. The carbonized samples were taken out of the furnace and stored in a desiccator until the furnace reached the set activation temperature (400 °C – 600 °C) before being put back in for activation. After activation at the required temperature, the activated samples were repetitively washed with 0.1 M phosphorus acid to reduce the ash and mineral content of the samples. The washing was carried out in a water bath shaker at 70 °C for 4 hours. Finally, the carbon was neutralized with 0.1 M sodium hydroxide. The end product was characterized for percentage of yield, moisture and ash content, pH value, iodine number and methylene blue adsorption capacity from aqueous solution. The yield is defined as the ratio of the mass of activated carbon obtained to the initial mass of the guava seed, both based on dry weight [11]. The ash and moisture contents, pH value, iodine number and methylene blue adsorption capacity were evaluated by using SIRIM

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standard method [12]. Iodine number is commonly used in the industry, as a rough estimate of the surface area of the activated carbon [11]. The removal efficiency of methylene blue by the activated carbons at specific time and concentration was calculated according to equation (1) [13]. In order to study the adsorption kinetics and adsorption isotherm for the optimized sample prepared, different mixing times with a specific initial concentration of methylene blue were used as parameters. The adsorption behaviour of the samples was studied by evaluating the removal efficiency, R_E, of methylene blue, calculated as

$$R_E = \frac{(C_0 - C)}{C_0} \times 100 , \tag{1}$$

where C_0 is the initial concentration of aqueous solution of methylene blue placed in a flask and shaken at 70 °C for 4 hours with a 0.2 g samples, and C is the solution concentration after adsorption, R_E is expressed in term of percentage. The surface functional group of prepared activated carbon was determined by using Fourier Transform Infrared Spectrometer (FT-IR) [14 – 15].

RESULTS AND DISCUSSION

The effect of activation conditions on the percentage of yield, pH value, moisture and ash contents are shown in Table 1. The results show that the yield decreases with increasing temperature. The carbon yield also decreases as the pyrolysis time was increased. The pyrolysed samples at about 400 °C and above consisted of black carbonaceous material which is carbon [9]. Low activation temperature cause incomplete burn off and resulting higher yield are obtained. The activated carbon prepared from guava seed is basic due to the final washing with NaOH. Overall, the samples prepared had a pH range of 8.00 to 8.30. The average moisture content of the activated samples was in the range of 2 % – 3 %. The moisture content detected was from the contact with the moisture in the atmosphere after activation. The ash content decreased with increasing pyrolysis time and temperature up to 600 °C. The ash content of the activated carbons was less than 3 %. Therefore, the pyrolyzed guava seeds were favorable for the preparation of activated carbons. The adsorptive capacities of the samples were analyzed by liquid

adsorption techniques known as iodine number and methylene blue removal efficiency as shown in Figure 1. We found that the removal efficiency trend of the methylene blue coincided with the iodine number, indicating that pore enlargement occurred and gave rise to higher adsorption capacity. The adsorptions increased as the activation time was increased until 60 minutes and decreased afterwards. Whilst there was an increased in adsorption as the activation temperature increased from 400 °C to 500 °C, adsorption decreased as the activation temperature was increased above 500 °C. The results indicated that the control of activation temperature and time is very important to produce optimized activated carbon. Activation at 500 °C for 45 minutes, produced carbons with the highest iodine number and the highest methylene blue removal efficiency that is 198.12 mg g^{-1} and 84.75 % respectively. The iodine number is comparable with the physically activated carbons prepared from milo grain (about 190 mg g^{-1}) [16].

Due to the high removal efficiency of sample AK6, adsorption studies such as adsorption isotherms and kinetics were done using sample AK6 in methylene blue aqueous solution.

Figure 2 shows the removal efficiency of sample AK6 versus shaking time. The adsorption pattern of methylene blue by sample AK6 can be described into two regions. The first corresponds to a fast removal rate, followed by the second slow removal until equilibrium was achieved. The equilibrium time for the adsorption of methylene blue on the activated sample AK6 is 40 minutes. The kinetics and dynamics of adsorption of methylene blue on activated carbon can be studied by applying the Lagergren first order and pseudo-second order rate equations that have been most widely used for the adsorption of an adsorbate from an aqueous solution, which are expressed by the equations

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} , \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_{ad} q_e^2} + \frac{1}{q_e} t , \tag{3}$$

where q_e and q_t are the amount of dye adsorbed per unit mass of the adsorbent (in mg g^{-1}) at equilibrium time and time t, respectively, and k_{ad} is the rate constant [17].

Table 1. The effect of activation time and temperature on the percentage of yield, pH value, moisture and ash content of the activated carbons

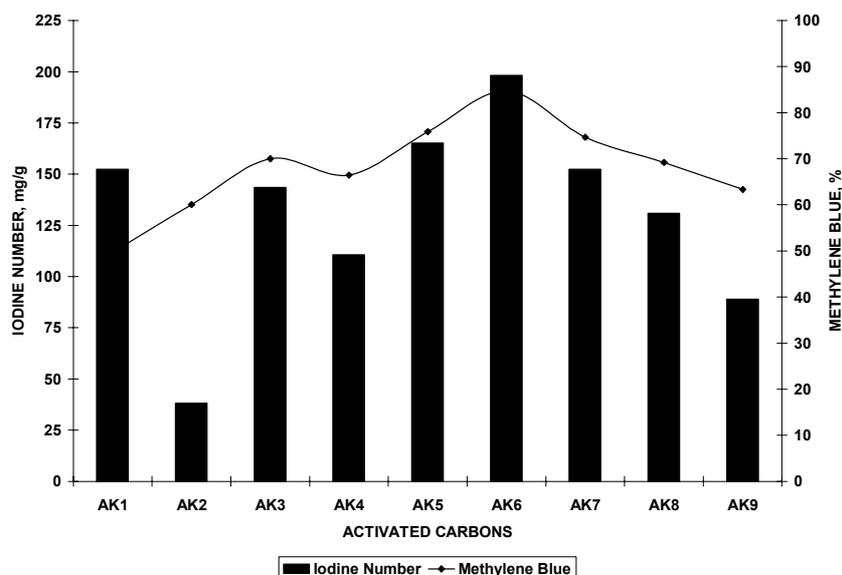| Sample | Activation condition | | pH | Yield, % | Moisture content, % | Ash content, % |
	Temperature, °C	Time, min				
AK1	400	30	8.27	51.80	2.90	4.70
AK2	400	45	8.20	40.63	2.77	3.28
AK3	400	60	8.21	23.27	2.56	1.76
AK4	400	90	8.02	16.05	2.71	0.86
AK5	500	30	8.18	39.50	2.70	2.85
AK6	500	45	8.10	30.99	2.87	1.50
AK7	500	60	8.25	17.75	2.50	0.77
AK8	500	90	8.08	12.24	2.24	0.40
AK9	600	45	8.21	4.09	2.10	0.20

Fig. 1. The effect of the activation conditions on the iodine number and the percentage of methylene blue removal efficiency of the activated carbons (notations of samples are given in Table 1)
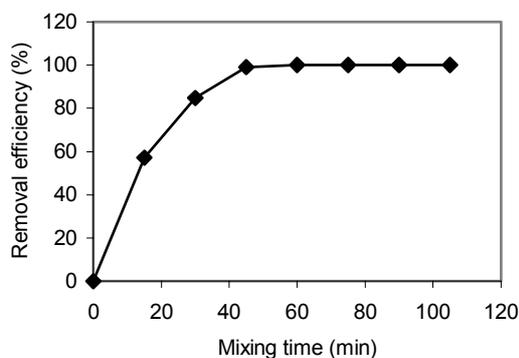

Fig. 2. Removal efficiency of methylene blue versus time for sample AK6 (temp. = 70 °C)

Figure 3 and Figure 4 show the Lagergren first order and pseudo-second order plots, respectively. As shown, the pseudo-second order plot gives a straight line with correlation coefficient, $R^2 = 0.9915$ and $k_{ad} = 0.0282$, indicating that the applicability of the pseudo-second order equation was the best result as compared to the Lagergren first order plot with $R^2 = 0.9368$ and $k_{ad} = 0.1253$ only.
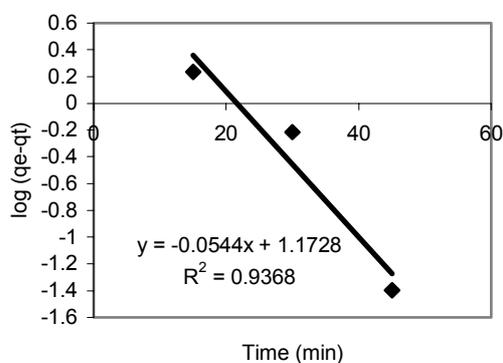

Fig. 3. Lagergren first order rate plot for methylene blue adsorption by activated carbon AK6
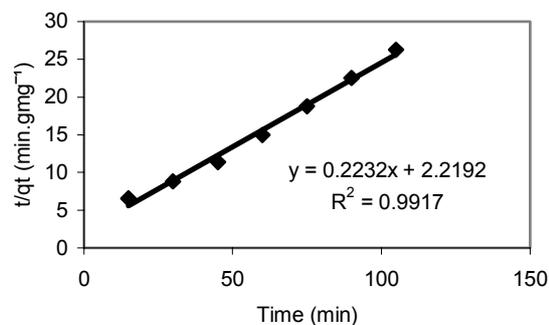

Fig. 4. Pseudo-second order rate plot for methylene blue adsorption by activated carbon AK6

The adsorption data were applied to the linear Langmuir equation (Figure 5):

$$\frac{C_e}{X_e} = \frac{1}{X_m K} + \frac{1}{X_m} C_e \tag{4}$$

and the Freundlich equation (Figure 6):

$$\log X_e = \log K_F + \frac{1}{n} \log C_e , \tag{5}$$

where C_e is the amount of adsorbate in the solution at equilibrium, X_e is the amount of adsorbate adsorbed, X_m is the amount of adsorbated adsorbed to form monolayer coverage, and K, n and K_F are the equation constants [9]. We found that the adsorption data fitted best to the Langmuir model as indicated by its relatively linear correlation coefficients, $R^2 = 0.8352$. Figure 4 and Figure 5 represent comparison of the experimental data of activated carbons with Langmuir and Freundlich equations.

The surface chemistry of activated carbons was determined by the type, quantity and bonding of oxygen-containing functional groups such as hydroxyl and carboxyl groups [18]. From the FT-IR spectra shown in Figure 7, all the activated carbons had almost the same functional groups due to the same precursor; guava seeds.
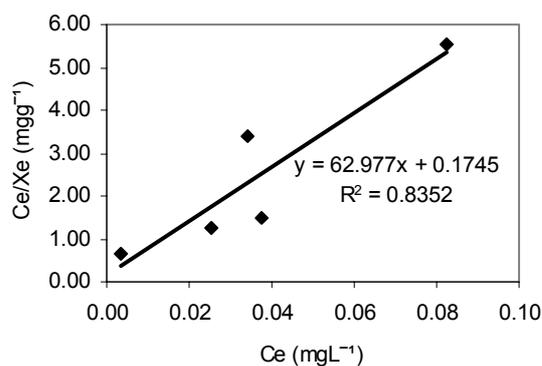
Fig. 5. Fitting methylene blue adsorption data to Langmuir model for sample AK6
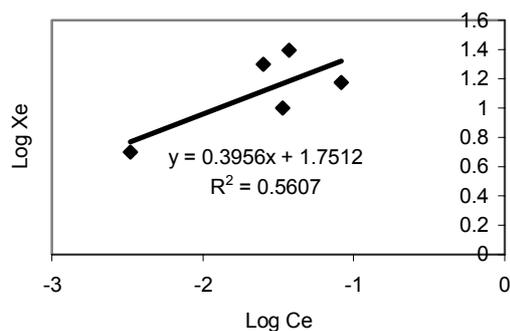

Fig. 6. Fitting methylene blue adsorption data to Freundlich model for sample AK6
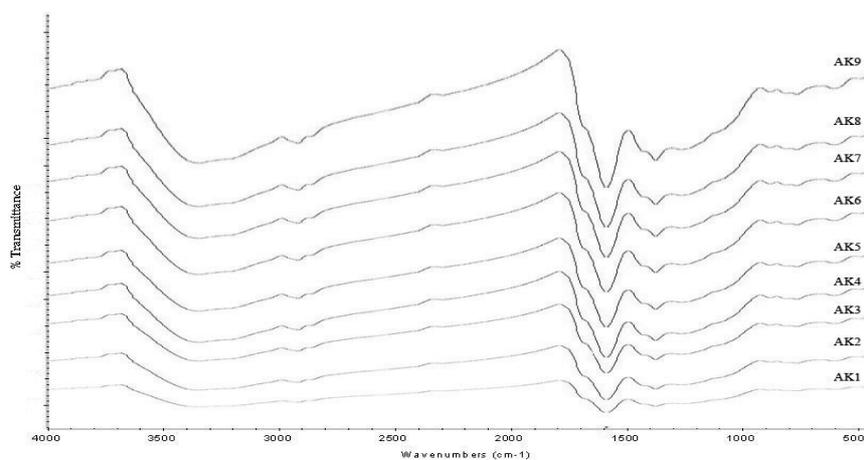

Fig. 7. FT-IR spectra of the activated carbons prepared from guava seed

The only difference was the activation process (time and temperature). The FT-IR spectrum of activated samples shows medium broad overlapping bands in the range between $3500\ cm^{-1}$ and $3300\ cm^{-1}$ and may be attributed to N–H stretching alkyl or aryl amine which may be present in the amino acid of guava seeds' protein. Two strong bands observed in the range between $2962\ cm^{-1}$ and $2853\ cm^{-1}$ are assigned to asymmetric C–H and symmetric C–H bands, respectively, present in alkyl groups such as methyl and methylene groups. Stretching absorption band around $1700\ cm^{-1}$ is assigned to carbonyl C=O present in esters, aldehydes, ketones groups and acetyl derivatives. The strong band at around $1600\ cm^{-1}$ may be ascribed C=C. The region of $1400\ cm^{-1}$ – $1300\ cm^{-1}$ may be ascribed C–H bending present in alkyl groups such as methyl. The region of $1300\ cm^{-1}$ – $1000\ cm^{-1}$ is a superposition of number of broad overlapping bands. The assignment in this region is a complex nature, so they cannot be described in terms of the simple motion of specific functional groups or chemical bonds.

CONCLUSION

Production of activated carbons derived from guava seeds with two step activation process had been demonstrated to be feasible. Due to the activated carbon produced with carbonization and followed by physical activation in open system (without gas control), only low

temperature is needed to complete the decomposition of organic constituents. Generally, lower yield of activated guava seed produce as the pyrolysis temperature and time increase. Activated carbon produce from guava seed was basic due to the washing process. The average moisture content of the activated carbon produced was in the range of 2 % – 3 %. The ash content decreased as the pyrolysis time and temperature of activation increased. Both the iodine number and removal efficiency of methylene blue increased as the activation temperature and time were increased, but decreased after 500 °C or 60 minutes, due to the pores being blocked by pyrolysis by-product. The methylene blue adsorption kinetic of guava seed activated carbon was of pseudo-second order with the Langmuir adsorption isotherm. Infra-red spectra indicated that the vast and varied surface functional groups were present. These fuctional groups were generally not affected by the activation temperature and time. Besides being an adsorbent for aqueous based impurities, these activated carbons have a potential to be used in the pharmaceutical or medical industries as no chemicals were involved in the activation process.

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