The Malaysian Journal of Analytical Sciences, Vol 11, No 11 (2007): 400 - 406

ADSORPTION OF METHYLENE BLUE ONTO TREATED ACTIVATED CARBON

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Abstract

The potential feasibility of treated and untreated activated carbon for removal of methylene blue from aqueous solution was investigated. The effects of various experimental parameters such as contact time, solution pH and adsorbent dosage were investigated. The extent of methylene blue removal increased with the increased in contact time, solution pH and amount of adsorbent used. Adsorption data was better fitted to the Langmuir isotherm. The results in this study indicated that the treated activated carbon was an attractive candidate for removing organic dye of methylene blue which shows great reduction of colour while reducing the time contact to achieve equilibrium.

Keywords: adsorption; treated activated carbon; colour removal; adsorption isotherm

Introduction

Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries [1]. Colour stuff discharged from these industries poses certain hazards and environmental problems. These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem [2]. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade [3]. Furthermore, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities [4].

There are various conventional methods of removing dyes including coagulation and flocculation [5], oxidation or ozonation [6] and membrane separation [7]. However, these methods are not widely used due to their high cost and economic disadvantage. Chemical and electrochemical oxidations, coagulation are generally not feasible on large scale industries. In contrast, an adsorption technique is by far the most versatile and widely used. The most common adsorbent materials are: alumina silica [8], metal hydroxides [9] and activated carbon [10]. As proved by many researchers [11, 12], removal of dyes by activated carbon is economically favorable and technically easier.

This paper aims to compare the efficiencies of two activated carbons for removing of methylene blue dye from aqueous solutions using treated and untreated activated carbons. The activated carbon (AC) used in this study is a commercial product, prepared by activation with an acidic agent. The other is treated activated carbon (TAC) which was prepared in our laboratory by activation of the commercial activated carbon (AC) with potassium hydroxide (KOH). It has been shown that KOH-activated carbon is essentially microporous with high surface area [13].

Materials and methods

Materials

Coconut shell activated carbon bought from a local manufacture was used in this study. The samples were washed several times and dried in an oven at 120°C overnight and was ground into fine powder form before being used. Methylene blue supplied by Merck was used as received. The cationic dye having molecular formula of $C_{16}H_{18}N_3SCl$ with molecular weight of 320 and CI number of 52015 was chosen as adsorbate.

Preparation of dye solution

Methylene blue in commercial purity was used without further purification. The dye stock solution was prepared by dissolving accurately weighed dye in distilled water to a concentration of 500 mg/l. The experimental solution was obtained by diluting the dye stock solution in accurate proportions to different initial concentrations.

Preparation of treated activated carbon (TAC)

A commercial activated carbon produced form coconut shell was used in this study as a precursor for the preparation of treated activated carbon. The chemicals used were potassium hydroxide (KOH) and sulphuric acid (H_2SO_4). The granular coconut shell activated carbon of about 0.1 to 1 cm in size was dried in an oven at about 80 °C for a week. About 10 g of activated carbon was impregnated with 100 ml of freshly prepared concentrated solution of KOH (5%-60%). The impregnation was carried out at 70°C in an oil bath until the remaining solution was evaporated. The sample was then dried at 120 °C overnight in an oven. The impregnated activated carbon was then carbonized in a horizontal furnace. The furnace temperature was set at 500 °C under nitrogen gas flow for 3 hours followed by carbon dioxide gas for 1 hour. The resulting treated activated carbon was then cooled to room temperature and then washed with 0.5 M H_2SO_4 to remove remaining KOH. Surface area of treated activated carbon was analyzed using a Micromeritics ASAP 2000, surface area analyzer.

Adsorption experiments

Adsorption of methylene blue (MB) on activated carbon was carried out using a bath experiments method in a rotary shaker at 150 rpm. The effect of contact time, solution pH and adsorbent dosage were investigated. The adsorption process was carried out with two different initial concentrations at 50 ppm and 100 ppm MB. The effect of contact time was used to determine equilibrium time for the adsorption. For the effect of contact time study, 25 ml of MB solution was added into a conical flask containing 0.25 g activated carbon and shaken constantly. Samples solutions were withdrawn at predetermined time intervals for the colour removal analysis. In the pH study, the pH of MB solution was adjusted in the range of 1.5-12 by adding 0.5 M sulphuric acid or 0.5 M sodium hydroxide. About 0.25 g adsorbent was then added to the solution and shaken at predetermined time. In the experiment to investigate the effect of adsorbent dosage on MB adsorption, various amounts of adsorbent in the range of 0.05 g to 0.3 g were added to 50 ppm and 100 ppm MB without pH adjustment and shaken until equilibrium. After shaking the flasks for predetermined time intervals, all samples were withdrawn from the conical flasks and the MB solutions were separated from the adsorbent by filtration then followed by centrifugation. Dye concentrations in the supernatant solutions were estimated by measuring absorbance at maximum wavelengths of dye with Lambda 20 UV-visible spectrophotometer and computing from the calibration curves. The isotherms study was carried out by varying the dosage of the adsorbent with the same concentration of MB solution. Each solution (25 ml) was treated with (0.05-0.4) g of adsorbent. All experiments were conducted in duplicate and the controls (with no adsorbent) were simultaneously carried out to ensure that adsorption was by activated carbon and not by the container.

Results and discussion

Surface area analysis of TAC and AC

Surface area analysis of the washed and dried samples was performed using a Micromeritics ASAP 2000 by nitrogen gas adsorption at 77K. Prior to the measurements, the samples were outgassed at 320 °C under nitrogen flow for 3 hours. BET, Langmuir, micropore and the percentage of micropore to the total surface area of the resulting treated activated carbon prepared form coconut shell with various concentrations of KOH are given in Table 1. The results showed that BET and Langmuir surface area decreased when the concentration of 5% and 10% KOH solutions were introduced. However, the BET and Langmuir surface area increased at the concentrations of 15 % to 30 % KOH were introduced and reached an optimum point at the concentration of 30 % KOH and decreased at the concentration of 40 % and 60 % KOH. The values of BET and Langmuir surface area at optimum point were 1389 and 1836 m^2/g, respectively.

The micropore area of the resulting treated activated carbon increased as the percentage of KOH solution introduced increased and reaches a maximum at the concentration of 30 % KOH with a value of 1051 m^2/g. However, the percentage of micropore to the total surface area of treated activated carbon decreased with the increased in the concentration of KOH introduced. This showed that the KOH impregnation solution plays an important role in conversion of micropore to others pores if a right concentration and conditions is introduced.

The results show that the treatment with concentration of 30% KOH produced treated activated carbon with high surface area (1389 m^2/g) as compared with untreated activated carbon (950 m^2/g). This treated activated carbon (30%) was subsequently used as adsorbent materials in the present study.

Table 1: BET, Langmuir, micropore and the percentage of micropore of the resulting treated activated carbon with various concentration of KOH.

Sample	BET (m^2/g)	Langmuir (m^2/g)	Micropore (m^2/g)	Micropore %
0%	1089	1447	865	60
5%	1034	-	337	33
10%	980	1330	427	32
15%	1132	1534	717	47
20%	1132	1536	611	40
25%	1113	1483	911	61
30%	1389	1836	1051	57
40%	1160	1573	686	44
60%	962	1303	506	39

Effect of contact time

A series of experiments has been performed to optimize the adsorption time at initial concentrations of 50 ppm and 100 ppm by KOH treated activated carbon (30%-ACKOH) and untreated activated carbon (AC). The effect of contact time on the adsorption of methylene blue dye on both adsorbents is presented in Figure 1. The extent of dye removal by activated carbon increased with the increased of contact time. The removal of dye by adsorption using activated carbon was found to be rapid at the initial period of contact time and then become slower with the increase of contact time. This is due the strong attractive forces between the dye molecules and the adsorbent. As shown in the Figure 1, the capacity uptake of methylene blue at equilibrium on both adsorbents at 50 and 100 ppm are fairly similar with the capacity uptake of 80-90 %.

In general, the results indicate that AC and 30%-ACKOH were capable to be used in colour removal of methylene blue from the aqueous solution. The results showed that the contact time required to achieve equilibrium was about 120 minutes for adsorption using ACKOH and the time needed for AC to achieve equilibrium was longer than that of 30%-ACKOH, which was 180 minutes. This may be due to higher surface area of 30%-ACKOH as a result of reactivation treatment compared to the AC. The results strongly indicate that the activated carbons used in this study are effective in removing methylene blue, especially for 30%-ACKOH in which a great reduction of colour and contact time to achieve equilibrium was observed.

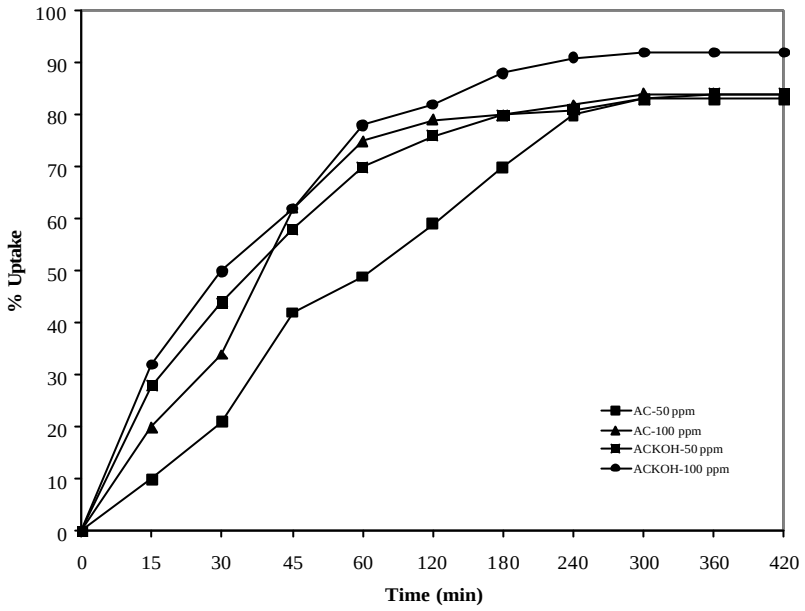

Figure 1: Effect of contact time on the adsorption of methylene blue using treated and untreated activated carbons at 50 ppm and 100 ppm. Conditions: adsorbent dose = 0.25 g / 25 ml; initial pH of MB solution = 4.5 and temperature = 28°C.

Effect of pH on adsorption

The pH of an aqueous medium is an important factor that may affect the uptake of the adsorbate. The chemical characteristics of both adsorbate and adsorbent vary with pH. Studies were carried out to see the effect of pH in the range of 1.5-12. The pH of the solution was maintained by adding sulphuric acid or sodium hydroxide. The effect of pH on the uptake of methylene blue at 50 and 100 ppm using AC and 30%-ACKOH is shown in Figure 2.

As shown in the Figure 2, the removal of methylene blue increased with the increased of pH of methylene blue aqueous solution. Lower adsorption of methylene blue at low pH is probably due to the presence of H^+ ions competing with the cations groups on the dye for adsorption sites. As surface charge density decrease with an increase in the solution pH, the electrostatic repulsion between the positively charged methylene blue and the surface of the activated carbon is lowered, this may result in an increase in the rate of adsorption. The methylene blue uptake using 30%-ACKOH is always higher than AC. Again, this indicates that 30%-ACKOH is a better adsorbent than AC. The higher surface area of 30%-ACKOH as a result of reactivation possibly contributed to this factor. Similar trends were reported in the literature for the adsorption of basic dyes, methylene blue onto jute fiber carbon [12].

Effect of adsorbent dosage on adsorption

In order to investigate the effect of adsorbent mass on the adsorption of methylene blue dyes, a series of adsorption experiment was carried out with different adsorbent dosages at initial dye concentration of 50 and 100 ppm. Figure 3 shows the effect of adsorbent dosage on the removal of methylene blue using AC and 30%-ACKOH. The results follow the expected pattern, in which the percentage sorption increased with the increased in adsorbent dosage.

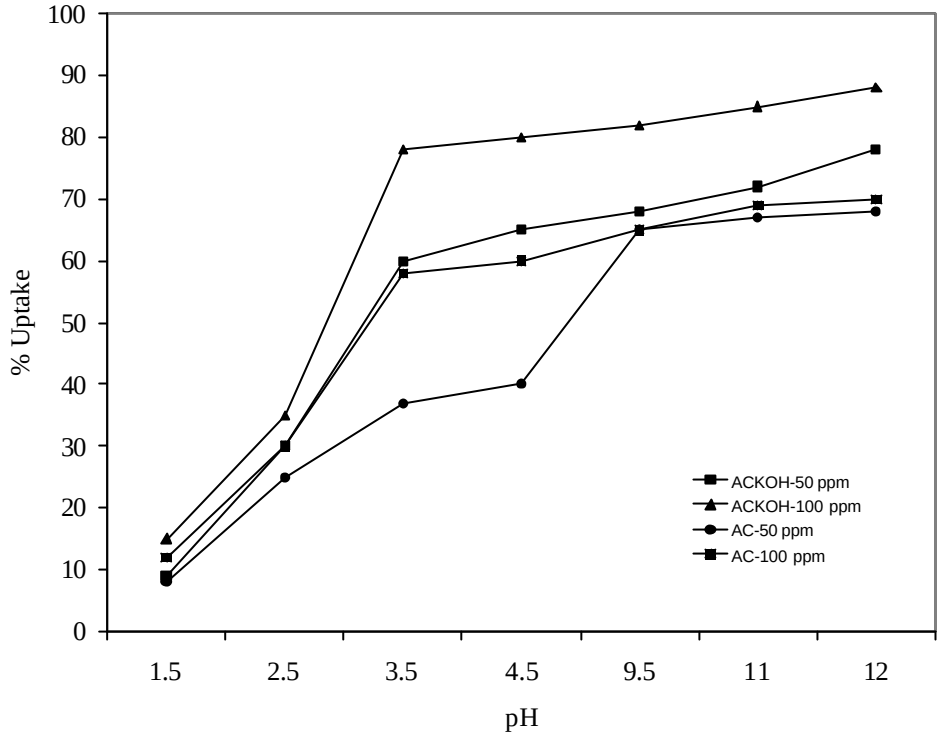

Figure 2: Effect of methylene blue pH on the adsorption of methylene blue using treated and untreated activated carbons at 50 ppm and 100 ppm. Conditions: adsorbent dose = 0.25 g / 25 ml; contact time = 180 minutes and temperature = 28°C.

As shown in the Figure 3, for both solutions, the percentage uptake of methylene blue increased very fast at low dosage up to a point, after which the increase in the dosage did not increase the uptake of methylene blue significantly. The saturation occurred at 0.3 g for both AC and 30%-ACKOH. These might be due to a larger external surface area available for the adsorption of methylene blue. It can also be seen that the methylene blue uptake by 30%-ACKOH was higher at low dosage of adsorbent in contrast to AC. For example, at 0.05 g dosage, the methylene blue uptake by ACKOH was about 10 % higher than AC, indicating that ACKOH is a better adsorbent than AC at low dosage. The higher surface area of 30%-ACKOH as a result of reactivation than AC contributed to this factor.

Adsorption isotherms

In general, the adsorption isotherm describes how adsorbates interact with adsorbents and therefore it is critical in optimizing the use of adsorbents. Langmuir isotherm can be used as a model to describe the adsorption isotherm. The Langmuir equation is given as

$$C_e / q_e = 1/Q_o * b \quad + \quad C_e / Q_o \qquad (1)$$

where C_e is the concentration of adsorbate solution at equilibrium ($mgdm^{-3}$), q_e is the amounts of adsorbate adsorbed per mass of adsorbent (mg/g), b is the equilibrium constant related to the sorption energy between the adsorbate and adsorbent (dm^3mg^{-1}) and Q_o is limiting amount of adsorbate that can be taken up per mass of adsorbent. The calculated Langmuir constants are given in Table 2. As shown in the Table, the resulting Q_o value for 30%-ACKOH is 45.9 mg/g compared to 41.8 for AC. The results indicated that 30%-ACKOH shows slightly higher adsorption capacity of methylene blue than AC. The plot of C_e/q_e against C_e in Figure 4 gave straight lines for all the concentrations, implies that the adsorption for both adsorbents well fitted to Langmuir isotherm. From the results in Table 2, it could be concluded that the adsorption isotherm of methylene blue using AC and 30%-ACKOH give a good fit to the Langmuir model.

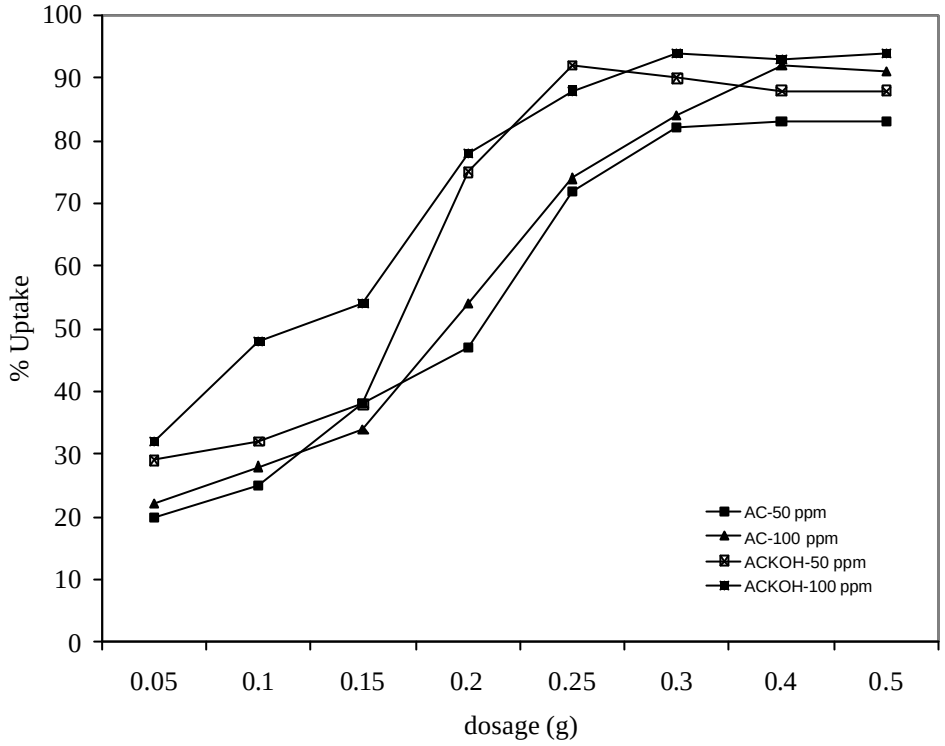

Figure 3: Effect of adsorbent dosage on the adsorption of methylene blue using treated and untreated activated carbons at 50 ppm and 100 ppm. Conditions: initial pH of MB solution = 4.5; contact time = 180 minutes and temperature = 28°C.

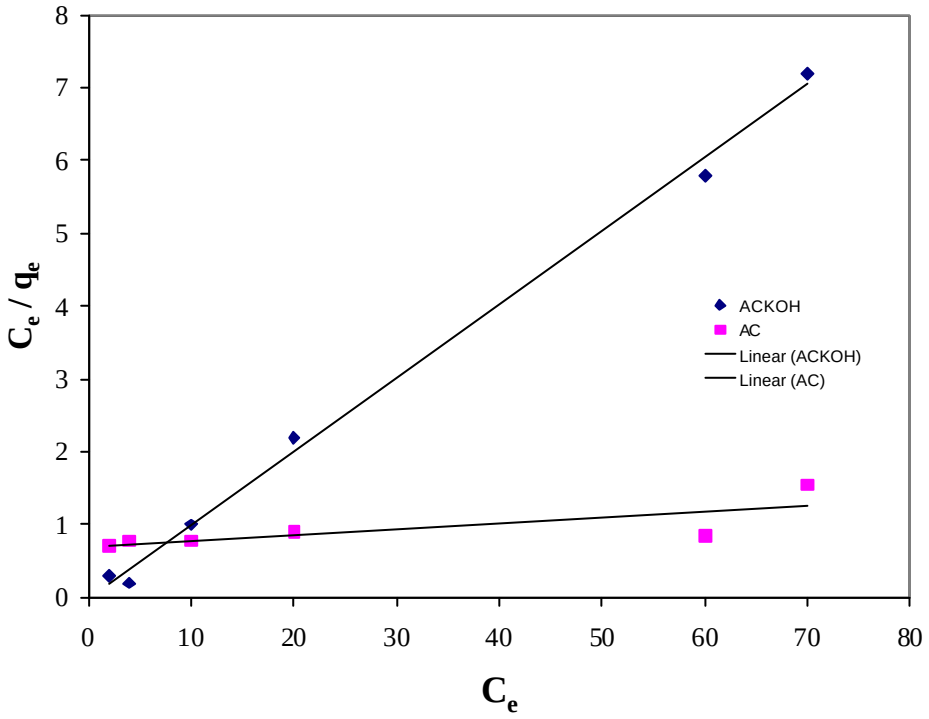

Figure 4: Langmuir adsorption isotherms for adsorption of methylene blue using treated (30%-ACKOH) and untreated (AC) activated carbons

Table 2: Parameters of Langmuir adsorption isotherm for methylene blue on 30%-ACKOH and AC

Adsorbent	Concentration (ppm)	b ($dm^3\ mg^{-1}$)	Q_o (mg/g)	regression (r^2)
30%-ACKOH	100	1.7	45.9	0.98
	50	3.7	45.8	0.95
AC	100	1.6	41.8	0.98
	50	3.1	17.8	0.98

Conclusion

The adsorption of methylene blue onto KOH treated activated carbon (30%-ACKOH) and untreated activated carbon (AC) has been studied. Adsorption test were carried out as a function of contact time, solution pH and adsorbent dosage. The adsorption experiments indicated that both adsorbents were effective in removing methylene blue from aqueous solution. The percentage of removal increased with the increased of contact time and achieves equilibrium at about 120 minutes for adsorption using 30%-ACKOH while 180 minutes when AC was used. This may be due to higher surface area of 30%-ACKOH as a result of reactivation treatment compared to the AC. The dye adsorption was also influenced by the pH of the solution and dosage of adsorbent. The removal of methylene blue increases with the increase of pH of methylene blue solution and dosage of the adsorbent used. The adsorption data was well described by Langmuir isotherm. The present study concludes that activated carbons are effective in removing methylene blue, especially the KOH treated (30%-ACKOH) in which great reduction of colour and contact time was observed.

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