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Adsorption of Methylene Blue from Aqueous Solutions on Carbon Coated Monolith

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Carbon coated monolith was used as adsorbent to remove methylene blue from aqueous solution. Adsorption rate and equilibrium parameters of methylene blue were investigated in a batch system. Equilibrium adsorption data were predicted by two isotherms, *i.e.* the Langmuir and the Freundlich isotherms. The best fit to the data was obtained with the Langmuir isotherm with maximum monolayer adsorption capacity of 191.307 mg/g. Kinetics of adsorption with respect to the initial concentration of dye was described by using both the pseudo-first-order and pseudo-second-order models. It was found that kinetic data fitted well with the pseudo-first-order model.

Keywords: Adsorption, Carbon coated monolith, *and* Methylene blue

INTRODUCTION

Dyes are extensively used in large quantity in many industries such as textile, leather, paper production, food technology, etc to color their products (Yener et al. 2008, Hameed et al. 2008). Untreated wastewaters directly discharged into water bodies from these industries will cause environmental damage to surface water (Crini and Badot 2008). Dyes, in generally, are synthetic in nature and have complex aromatic structures which make them carcinogenic, mutagenic, and chemically stable (Ofomaja 2008, Aksu and Tezer 2005). Methylene blue is a basic (cationic) dye identified as that which dissociates in aqueous solution to give a positively charged colored ion. This dye has harmful effects on living organisms on short periods of exposure. Several techniques are available for the treatment of industrial wastewaters. Among these methods, adsorption technique for wastewater treatment has become more popular in recent years. The most commonly used adsorbent in this process to remove dyes is activated carbon in form powder or granular (Al-Degs et al. 2001).

The use of carbon in these forms for fixed bed is associated with high pressure drops, potential channeling, and other disadvantages. The problems encountered above may be overcome by the use of carbon monoliths. Compared to the conventional fixed bed column, monolithic columns provide the advantages of low pressure drop, larger external surface area, and shorter diffusion lengths (Kapteijn et al. 1999). It can also be located in a vertical or horizontal position and in mobile system without losing shape and is easier to be scaled up due to its simple design and uniform flow distribution (Irandoust and Andersson 1998).

This study is to examine the applicability of carbon coated monolith for the adsorption of methylene blue dye from aqueous solution.

EXPERIMENTAL METHODS

Materials

The chemical compositions of the monolithic substrate used in this investigation are SiO_2 50.9 ± 1 %, Al_2O_3 35.2 ± 1 %, MgO 13.9 ± 0.5 %, and others < 1 %. The cell shape of the monolithic channels is square cross section with channel width 1.02 ± 0.02 mm equivalent to a channel density of 62 cell cm^{-2} (400 cpsi) and wall thickness 0.25 ± 0.02 mm. These ceramic monoliths were obtained from Beihai Huihuang Chemical Packing Co. Ltd, China.

The starting chemicals for the preparation of carbon coated monolith are furfuryl alcohol 99% (FA) as carbon source, poly ethylene glycol (PEG) (molecular weights: 1500 g/mol) as pore forming agent, pyrrole 99% as binder, and nitric acid 65% as catalyst (Acros Organics, Belgium).

For adsorption application, a standard dye (methylene blue) was used. The standard dye (methylene blue) was supplied in powder form by BDH Gurr-Cersistain, England and used without further treatment. The chemical formula of methylene blue is shown in Figure 1 (Wang et al. 2005, Aguedach et al. 2008, Liu and Chiou 2005).

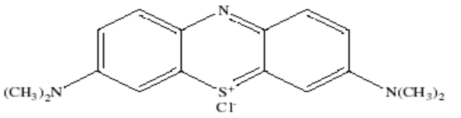

Figure1. Structural Formula of Methylene Blue (MB).

Characterization

The prepared synthesis carbon coated monoliths was characterized using scanning electron microscopy (SEM) and elemental analysis. The texture was also analyzed by using N_2 adsorption, CO_2 adsorption, and mercury porosimetry.

Scanning electron microscopy (SEM) was performed on LEO 1455 variable pressure equipped with a pioneer EDX and detector for secondary electron operated at high vacuum mode by acceleration voltage of 10 kV and working distance 10 mm.

Elemental analysis was performed on a LECO analyzer Tru-Spec CHN for CHNS analysis and CHNS-932 series for oxygen analysis. The products of combustion in CHNS analysis were CO_2, H_2O, N_2 and SOx. High temperature combustion was used as the means of removing the elements from material. In the combustion process, a nominal 2 mg sample was encapsulated in a tin capsule. The sample was placed in the sample loading chamber and held there until a dose of oxygen had been released. The sample was then dropped into the furnace. The sample was combusted in the heated oxygen rich environment. Calibration was performed with sulfamethazine for CHNS test and benzoic acid for oxygen test.

The texture of activated carbon coated monoliths and unsupported carbons was analyzed by using nitrogen and CO_2. Nitrogen and CO_2 adsorptions were performed on Sorptomatic 1990 series at 77 K and 273 K, respectively after outgassing samples for 24 hours at 423 K in vacuum. The pore volume and the average pore size were calculated by the BJH (Barret-Joyner-Halenda) method for mesopore.

Mercury porosimetry was performed on a Pascal 140 series in the pressure range of 1 to 400 kPa and then followed by a Pascal 440 series in the pressure range of 100 kPa to 250 MPa, after outgassing the samples at 423 K in vacuum overnight.

Adsorption Studies

The experimental work for batch studies was divided into two main parts, namely equilibrium and contact time studies.

Equilibrium Studies

The effect of solution of pH was studied by agitating 0.9 g of carbon coated monolith (FA+ PEG) and 0.4 L of dye solution of dye concentration 250 mg/L using Flocculator SW1 at 303K. The experiment was conducted at different pH from 2.5 to 11 adjusted by using 1N HCl, 0.1N HCl or 0.1 N NaOH solutions. The solution was stirred at 60 rpm for 10 days contact time which was sufficient to reach equilibrium.

The equilibrium isotherms were determined by contacting a constant mass of carbon about 0.9 g with 400 mL sorbate solution in beakers at 303 K and agitation speed 60 rpm. For each isotherm, initial concentrations were varied up to 11 sorbate solutions of consecutively increasing concentrations that ranged from 50 to 500 mg/L at initial solution pH 2.5.

After equilibration, the equilibrium concentrations, C_e (mg/L), were analyzed by UV-vis spectrophotometer. Concentrations of the solid phase sorbates, q_e (mg/g), were calculated from the material balance on the adsorption system:

$$q_e = (C_0 - C_e) \cdot V / m \qquad (1)$$

Kinetic studies

All kinetic studies were carried out in a finite batch adsorber system. It consisted of an agitated batch adsorber that was a 1 L cylindrical glass vessel of 9 cm diameter and 20 cm height containing 0.5 L liquid to give a liquid depth of 8 cm. Mixing was provided by a monolithic impeller extending vertically halfway down the solution. The agitator was driven by an Overhead Stirrer Kika Labortechnik Type Rw 20.

Kinetic studies provided kinetic data in the form of concentration decay versus time curves. In each experimental run, a weighed amount of carbon coated monolith of 1.6 g (FA+ PEG) was brought into contact with 0.5 L sorbate solution at different initial adsorbate concentrations, *i.e.* 20, 50, and 100 mg/L and at two different agitation speeds of 60 and110 rpm. At the moment of sorbate-sorbent contact, mixing was started at a pre-fixed impeller agitation speed. At regular time intervals, about 2 mL samples of solution were withdrawn by a sampling system and then placed in sample bottles. Sample withdrawal started at t = 0 throughout to 10 hours then the run was terminated. Each sample was analyzed to determine the solutes concentrations using UV-vis spectrophotometer as for the equilibrium studies.

Equilibrium adsorption isotherms

Contact time is an important variable in adsorption. Generally speaking, the adsorption capacity and the removal efficiency of dyes by activated carbon become higher on prolonging the contact time.

In general, the adsorption capacity increases with time and, at some point in time, reaches a constant value where no more dye is removed from the solution. At this point, the amount of dye being adsorbed onto material is in a state of dynamic equilibrium with the amount of dye adsorbed from adsorbent. The time required to attain this state of equilibrium is termed the equilibrium time (t_e) and the amount of dye adsorbed at t_e reflects the maximum dye adsorption capacity of the adsorbent under these conditions.

Boki et al. (1981) and Tanada et al. (1983) reported an equilibrium time of 8 day for methylene blue (MB) adsorption onto activated carbon. They observed that the process was initially to adsorb MB in the micropores. Chiou and Li (2003) noted that the maximum accumulation occurred within 5 days for reactive dye on cross-linked chitosan.

In order to successfully represent the dynamic adsorptive behavior of any substances from the fluid to the solid phase, it is important to have a satisfactory description of the equilibrium state between the two phases composing the adsorption system. The Langmuir and Freundlich isotherms are the two most well-known isotherms which have been used to describe the equilibrium of adsorption systems.

The Langmuir isotherm has commonly quoted form, *i.e*. Eqs.(2) as follows:

$$q_e = \frac{K_L \cdot C_e}{(1 + a_L \cdot C_e)} \qquad (2)$$

where K_L (L/g) and a_L (L/mg) are the Langmuir constants. $K_L/a_L = Q_o$ (mg/g) represents the monolayer capacity of adsorbent.

Freundlich Isotherm

The Freundlich adsorption equation is a special case for heterogeneous surface energies in which the energy term, a_L, in the Langmuir equation varies as a function of surface coverage, q_e, strictly due to variations in heat of adsorption (Weber 1972, Faust and Aly 1998, Al-Duri and McKay 1988). The Freundlich isotherm may be derived by assuming a heterogeneous surface with adsorption on each class of sites that obey the Langmuir model (Noll et al. 1992). This isotherm is another form of the Langmuir approach for adsorption on an "amorphous" surface. Freundlich proposed the equation:

$$q_e = K_F (C_e)^{1/n} \qquad (3)$$

where K_F and $1/n$ are empirical constants dependent of the nature of sorbent and sorbate and the temperature. Both of these values (K_F and $1/n$) are important in selecting an adsorbent as a separating medium, in which K_F (mg/g) is the over-all adsorption capacity (q_e at C_e = 1 mg/L or log C_e = 0) and $1/n$ is the heterogeneity factor. The heterogeneity factor $1/n$ indicates the strength of bond energy between sorbate and sorbent.

Adsorption kinetics

In present research, the kinetics of adsorption of MB on the activated carbon coated monolith was studied. Two types of kinetic models, pseudo-first-order (Lagergren equation) and pseudo-second-order model (Ho equation) (Ho et al. 2000), were employed to fit experimental data.

Lagergren equation

The pseudo-first-order model can be described as follow:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (4)$$

where q_t (mg/g) is the solid phase concentration at time *t* (min), k_1 (min^{-1}) is the pseudo- first-order rate constant. The equation (4) represents initial value problems and has analytical solution when combined with the initial condition *t* =0, q_t =0.

The solution for equation (4) is as follows:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad (5)$$

Ho equation

The pseudo-second-order model can be written as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (6)$$

where k_2 (g m/g.min) is the pseudo- second-order rate constant.

The solution for equation (6) at the initial condition *t* =0, q_t =0 is given as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

If the adsorption follows the pseudo-first-order rate equation, a plot of $\ln(q_e - q_t)$ against time *t* should be straight line. Similarly, $\frac{t}{q_t}$ should change linearly with time *t* if the adsorption obeys the pseudo-second-order rate equation.

RESULT AND DISCUSSION

Scanning electron microscopy (SEM)

The coating thickness of ~ 38 µm was investigated by taking SEM pictures of a channel of the coated monolith (Fig. 2a). Part of the monolith was visible and part was well coverage with carbon. The carbon was presented within the monolith covering the walls of its macro-pores as a thin layer on the external surface (Fig. 2b), whist the corners of the monolith channels were filled with more carbon.

Elemental analysis

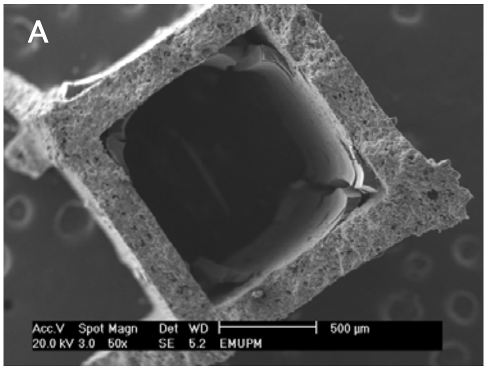

Figure 2. SEM Photographs of Coated Monolith: A) Channel of Monolith Coated B) Coverage along Channel Wall of Coated Monolith.

The elemental compositions of the polymers and the resulting carbon were determined by using elemental analysis. Table 1 shows the elemental compositions of mixture of polymers before and after carbonization at 973 K and PEG concentration at 40% vol. The polymer composition changes with respect to the raw materials. After carbonization, the carbon content was increased, whist oxygen and hydrogen were decreased, and the nitrogen content remained almost the same.

N_2 and CO_2 adsorption isotherms

Measurements of N_2 adsorption isotherms at 77 K are shown in Figure 3. The sample FA at temperature carbonization 973 K exhibits adsorption isotherm Type I behavior defined by the International Union of Pure and

Table 1. Elemental Composition of Polymers Before and After Carbonization

Carbon type	Elemental composition of furfuryl alcohol (FA) based carbon coated monolith							
	C (wt %)		H (wt %)		N (wt %)		O (wt %)	
	before carbonized	after carbonized	before carbonized	After carbonized	before carbonized	after carbonized	before carbonized	after carbonized
FA +PEG	58.01	74.41	5.16	1.24	3.72	3.67	30.39	8.65
FA	66.09	87.22	4.61	1.97	0.34	0.22	27.14	6.37

Table 2. Pore Structure Parameters of Furfuryl Alcohol Based Activated Carbon Measured by Nitrogen Adsorption at 77 K.

Sample	S_{BET} (m^2/ g_{carbon})	Total pore volume (cm^3/ g_{carbon})	Meso-pore area (m^2/ g_{carbon})	Meso-pore volume (cm^3/ g_{carbon})
FA	362.71	0.20	31.67	0.0388
FA + PEG_{unsup}	431.00	0.38	186.55	0.2313
FA + PEG_{sup}	21.31	0.002	-	-

Table 3. CO_2 Physisorption at 273 K and Mercury Porosimetry.

Sample	S_{BET} (m^2/g_{carbon})	Micro-pore volume (cm^3/g_{carbon})	Hg intrusion Total pore volume (cm^3/g_{carbon})
FA	227.82	0.1546	0.0362
FA + PEG	428.54	0.2697	0.1281

Table 4: Values of Estimated Langmuir and Freundlich Isotherms Constants

Langmuir isotherm		Freundlich isotherm	
$Q_o = K_L/a_L$	K_L	K_F	n
191.307	19.3763	42.4507	3.0771

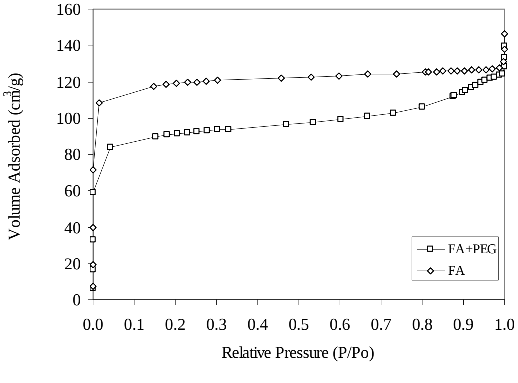

Figure 3. Adsorption Isotherms of N_2 at 77 K on Carbon.

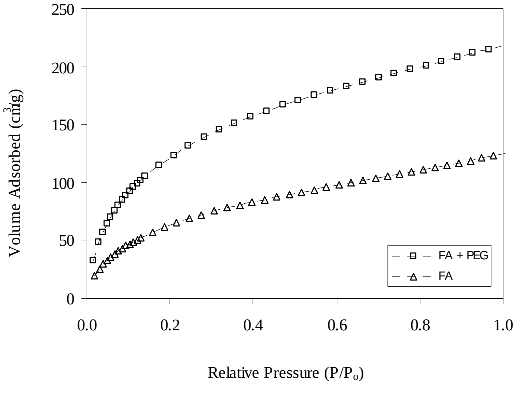

Figure 4. Adsorption isotherms of CO_2 at 273 K on carbon.

Table 5. Comparison of The Pseudo-First and Second-Order Adsorption Rate Constants and Values of Calculated and Experimental Q_e for Different Initial Dye Concentrations.

Parameter Initial concentration at pH of 2.5	$q_{e, exp}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		k_1 (min^{-1})	$q_{e, cal}$ (mg/g)	R^2	k_2 (g/mg.min) $x10^{-4}$	$q_{e, cal}$ (mg/g)	R^2
20 mg/L	5.066	0.0066	4.711	0.988	23.9	5.510	0.924
50 mg/L	11.796	0.004	11.023	0.984	5.64	13.175	0.944
100 mg/L	30.417	0.0015	28.620	0.974	1.26	20.747	0.827

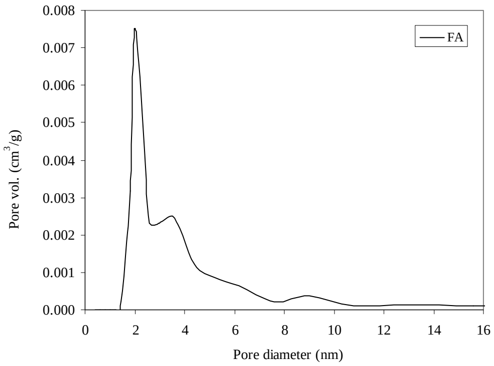

Figure 5. Pore Size Distribution of The Samples Studied by N_2 Adsorption at 77 K.

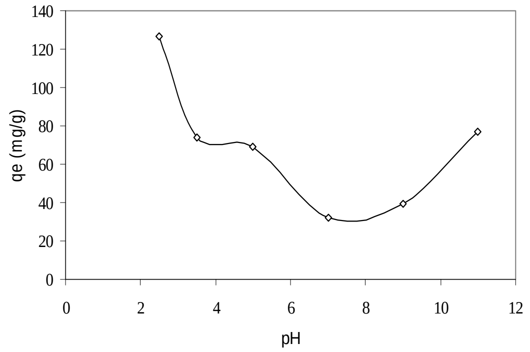

Figure 6. The Effect of pH on Adsorption Capacity of Methylene Blue onto Carbon Coated Monolith.

Applied Chemistry (IUPAC) for characteristic of a microporous material (Wang et al. 2005, Aguedach et al. 2008). Adsorption equilibrium for sample FA establishes at a very low relative pressure. Isotherm of FA+PEG at 40 vol.% and carbonization temperature 973 K is of Type IV (Onal 2006, Basar 2006). After micro-pore volume filling, the adsorption amount for sample FA+PEG keeps increasing with increasing relative pressure, therefore sample FA+PEG can be expected to be meso-porous. The isotherms performed for CO_2 at 273 K and sub-atmospheric pressures, from 2 x 10^{-3} to 0.1 MPa are presented in Figure 4. The CO_2 isotherms are of Type I, characteristic of a microporous material (Lozano-Castello 2004).

Table 2 contains meso-pore volume calculated from N_2 adsorption data applying the BJH equation for two different samples. The results for CO_2 adsorption at 273 K are compiled in Table 3. From their characterization, it indicates the presence of narrow micro-porosity, which can not be characterized by N_2 adsorption at 77 K. Thus, if only N_2 adsorption at 77 K is employed, even though the samples do respond to N_2 adsorption, potentially important information about narrow micro-porosity is being missed.

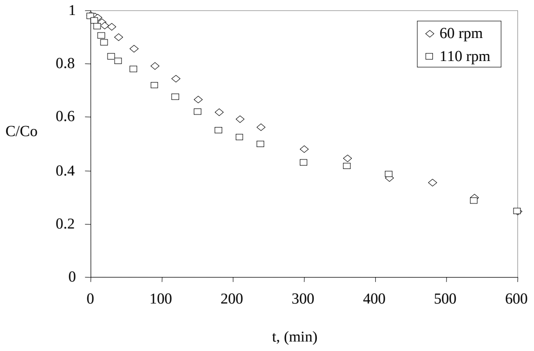

Figure 7. Effect of Agitation Speed on The Adsorption of MB by Carbon Coated Monolith at Initial Concentration of 50 ppm, pH of 2.5, and Ambient Temperature.

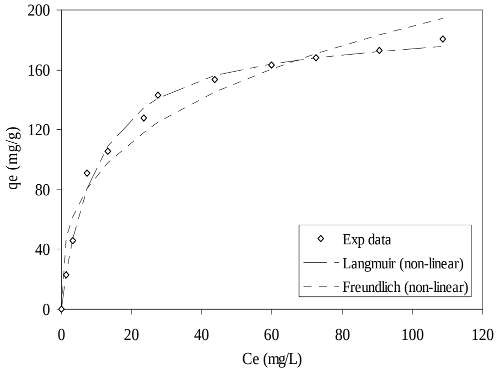

Figure 8. Equilibrium Adsorption Isotherm of MB on Activated Carbon Coated Monolith at pH of 2.5.

Pore size distribution

A sample of porous solid may be characterized by its pore size distributions (PSDs). Each pore size will contribute to the total adsorption isotherms in proportion to the fraction of total area or pore volume of the sample that it presents. Sample FA posses a reasonable amount of micro-pores with a small fraction of meso-pores, whilst sample FA+PEG is meso-porous and a small fraction of micro-porous. These PSDs are illustrated in Figure 5.

Effect of pH

The solution pH of adsorption medium being conducted was an important controlling parameter which dictated the uptake and release of solutes bound by sorption (Inbaraj et al. 2008, Mittal et al. 2008, Dogan and Alkan 2003). The magnitude of electrostatic charges imparted by the ionized dye molecules and functional groups on surface of adsorbent was primarily controlled by pH of medium (Dogan and Alkan 2003).

Figure 6 illustrates the effect of pH on the adsorption of methylene blue by using carbon coated monolith at ambient temperature by varying the initial pH of a 250 mg/L solution for fixed adsorbent mass of 0.9 g. The adsorption capacity increased significantly with decreasing the solution pH. At solution pH of 2.5, the amount of dye adsorbed was 126.8 mg/g. Higher adsorption of the dye at low pH might be due to increased protonation by neutralization of the negative charge at the surface of adsorbent (Mittal et al. 2008). For pH values higher than 7.0, the amount of dye removal also increased, in this case, maybe in alkaline solutions, methylene blue might be stepwise demethylated to other common dyes (Batzias and Sidiras 2007). This indicated that the adsorption capacity of carbon coated monolith was pH dependent.

Effect of Agitation Speed

Agitation is an important parameter in adsorption phenomena influencing the distribution of the solute in the bulk solution and the formation of the external boundary film. Generally, the rate of dye adsorption is influenced by the degree of agitation and the uptake increases with agitation rate. The degree of agitation reduces the boundary layer resistance and increases the mobility of the system. In this work, it is reported that agitation speed gives a small effect on the adsorption of

MB by carbon coated monolith as shown in Figure 7. This phenomenon may be caused by chemical affinity forms between positive and negative charges of sorbate-sorbent in the system. As a result of this chemical affinity, the external boundary film surrounding the adsorbent weakens (Uzun 2006).

Adsorption Isotherm

Equilibrium adsorption data were collected at pH 2.5, agitation speed 60 rpm, and ambient temperature. The isotherms, in general, are fitted to experimental data. The adsorption is generally favorable. Adsorption isotherms of MB show that the data fitted better in Langmuir isotherm equation (see Fig. 8). The values of the constants in the isotherms (Q_o, K_L, a_L, K_F, and n) are shown in Table 4.

Kinetics of Adsorption

The slopes and intercepts of plots of equations (5, 7) were employed to calculate the pseudo-first- and -second-order rate constants (k_1 and k_2) and q_e. The calculated results were listed in Table 5. A comparison of results with the correlation coefficients (R^2) was also presented in Table 5. The correlation coefficients for pseudo second-order kinetic model were rather low.

The straight lines in plots of ln (q_e - q_t) versus t showed a good agreement of experimental data with pseudo-first-order model for different initial concentrations (see Figure 9, 10, and Table 5).

Effect of Initial Concentration

The adsorption for carbon coated monolith was investigated at different initial concentrations in range of 20, 50, and 100 mg/L at a fixed pH. Generally, the amount of MB adsorbed increased with time, initially quite sharply, but became slower after 90 min, depending on the initial dye concentration. The plot of dye concentration C_t against time was shown in Figure 11. From Figure 11, it was indicated that the rate of adsorption of MB on carbon coated monolith decreased with increase in the initial concentration of the adsorbate. This phenomenon was because of the limitation of adsorbent dose where the ratio of solid/liquid was small. In other words, the residual concentration of dye molecules would be higher for higher initial dye concentration.

Table 5 listed the results of rate constant studies for different initial dye concentrations by the pseudo-first-order and -second-order models. The correlation R^2 for the pseudo-first-order adsorption model had high values. These suggested that the pseudo-first-order adsorption mechanism was predominant. For the pseudo-first-order model, the rate constant decreased with an increasing of initial dye concentration. An increase in initial dye concentration resulted in significant increasing the q_e.

CONCLUSIONS

The equilibrium adsorption for MB is practically achieved in 10 days at carbon coated monolith dose of 0.9 g, pH of 2.5, and ambient temperature. The results followed Langmuir and Freundlich isotherm equations. Of these two equations, the Langmuir fits better with constants K_L/a_L =191.307 mg/g and K_L = 19.376 dm^3/g, respectively.

The pH of aqueous solutions and the initial dye concentrations significantly affect the adsorption capacity of MB on carbon coated monolith. Increase in pH decreased the equilibrium adsorption capacity. Rate of adsorption increases with decrease in initial dye concentration.

The pseudo-first-order kinetic model agrees well with the dynamical behavior for the adsorption of MB on carbon coated monolith under different initial dye concentrations. On the contrary, the pseudo-second-order kinetic model fit the experimental data poorly for the range under study.

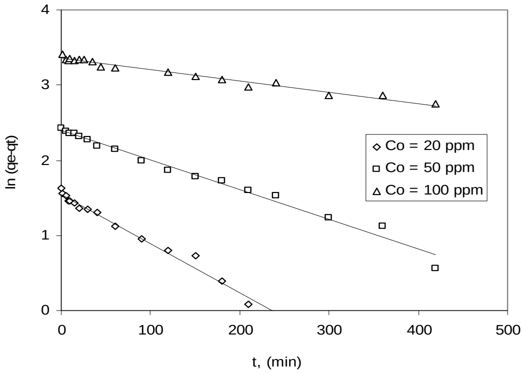

Figure 9.The Fitting of Pseudo First Order Kinetic Model for The Sorption of MB on Activated Carbon Coated Monolith at Speed of Agitation 110 Rpm and pH 2.5.

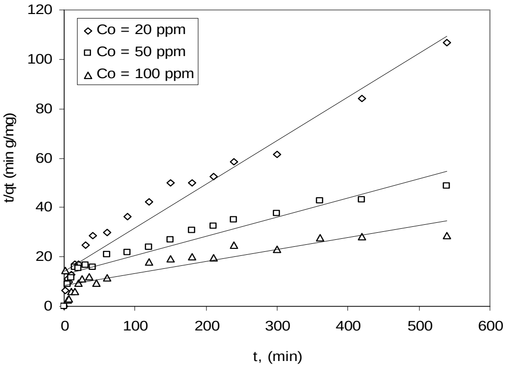

Figure 10. The Fitting of Pseudo Second Order Kinetic Model for The Sorption of MB on Activated Carbon Coated Monolith at Speed of Agitation 110 rpm and pH 2.5.

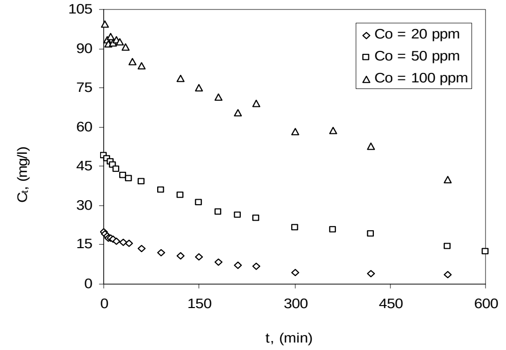

Figure 11. Effect of Initial Dye Concentrations on The Rate of Adsorption of MB on Carbon Coated Monolith at Ambient Temperature; pH = 2.5; Adsorbent Dose = 1.6 g; Agitation Speed = 110 rpm.

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