

Kinetic Modeling for Biosorption of Methylene Blue onto H₃PO₄ Activated *Acacia arabica*

N. Sivarajasekar[▲], S. Srileka, S. Samson arun prasath, S. Robinson and K. Saravanan

Department of Chemical Engineering, Kongu Engineering College, Erode-638 052, Tamilnadu, India

[▲]e-mail: sivarajasekar@gmail.com

(Received June 7, 2008; Accepted August 12, 2008)

Abstract

Batch sorption experiments were carried out for the removal of methylene blue from its aqueous solution using H₃PO₄ activated *Acacia arabica* carbon (AAC). The prepared activated carbon was characterized and was found as an effective adsorbent material. The operating variables studied were initial methylene blue concentration, AAC concentration and solution pH. AAC activated carbon possesses a maximum sorption capacity for the range of initial dye concentrations studied (60~100 mg L⁻¹). The sorption kinetics were analyzed using reversible first order kinetics, second order, reversible first order, pseudo-first order, and pseudo-second order model. The sorption data tend to fit very well in pseudo-second order model for the entire sorption time. The average pseudo-second order rate constant, K₁₁ and regression coefficient value were determined to be 0.0174 mg g⁻¹ min⁻¹ and 0.9977. The biosorption process also fit well to reversible I order kinetics with a regression coefficient of 0.9878.

Key words : *Acacia*, activated carbon, Biosorption, Chemical activation, Dye

1. Introduction

Disposal of dyeing industry wastewater poses one of the major problems, because such effluents contain a number of contaminants including acid or base, dissolved solids, toxic compounds, and color. Out of these, color is the first contaminant to be recognized because it is visible to the human eye. Removal of many dyes by conventional waste treatment methods is difficult since these are stable to light and oxidizing agents and are resistant to aerobic digestion. Possible methods of color removal from textile effluents include chemical oxidation, froth flotation, adsorption, coagulation, etc. Among these, adsorption currently appears to offer the best potential for overall treatment because of its simplicity and economical viability. It can be expected to be useful for a wide range of compounds, more so than any of the other listed processes. Recognizing the high cost of activated carbon, many investigators have studied the feasibility of cheap, commercially available materials as its possible replacements. Such materials range from industrial waste products such as waste rubber tyres, blast furnace slag, and lignin to agricultural products such as wool, rice straw, coconut husk, saw dust, and peat moss.

Activated carbon from cheap and readily available sources such as coal, coke, peat [1], wood charcoal [2], heat treated sulphurised activated carbon [3], sugarcane bagasse pith [4], bioresource [5], rice husk [6], palm shell [7,8], almond shell [9] and agricultural waste materials like olive seed waste

residue [10,11], pine waste [12], pine wood [13] wood char [14] and rubber saw dust [15] have been used as a raw material.

In this present investigation *Acacia* barks were taken as precursor for activated carbon and adsorption studies were carried out. The different types of kinetics were studied and compared.

2. Experimental procedures

2.1. Materials and methods

All reagents used for analysis were of analytical grade. The stock solution of methylene blue was prepared by dissolving methylene blue in double distilled water. The pH of the solutions was adjusted using sulfuric acid and sodium hydroxide.

2.2. Phosphoric acid activation of *Acacia arabica* barks

The *Acacia arabica* tree barks were collected in the premises of Kongu engineering college and they were sun dried for thirty days. The dried barks were chopped in to small pieces. The pieces of dried barks were activated with phosphoric acid at its boiling point based on the dry weight of the sample in the ratio of 2:1. After impregnation, the mixture was transferred to a Pyrex glass plate and placed in the muffle furnace for drying at 110°C for 1.5 h. After

Table 1. Characteristics of AAC

S. No.	Activated carbon	pH	Iodine number (mg g ⁻¹)	Methylene Blue number (mg g ⁻¹)	Methyl violet number (mg g ⁻¹)	BET Surface area (m ² g ⁻¹)	Yield
1.	AAC	6.78	784.21	231	168	1701	0.596

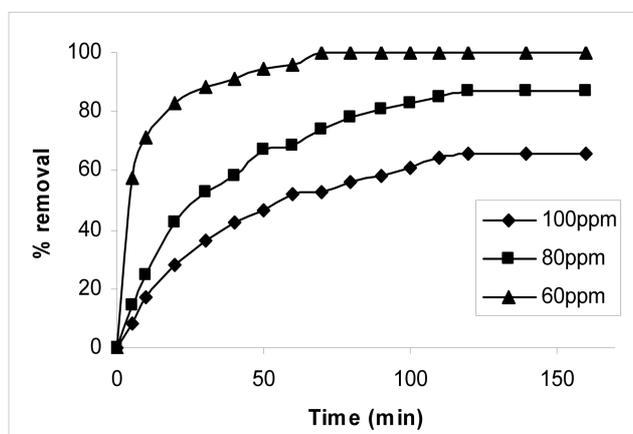
drying, the mixture was transferred to a sealed ceramic container and was activated in a muffle furnace. The temperature of carbonization was being 200°C for a period of half an hour. The activated carbon samples thus produced were then repetitively washed with distilled water to remove all the acid from the material until it attains neutral pH. After washing, the activated carbon was dried in a hot air oven at a temperature of 105±5°C. The drying was continued until a constant weight of activated carbon was reached.

2.3. Characterization of activated carbon

Activated carbon prepared from *Acacia* barks was characterized by finding out its yield, iodine number, methylene blue number, methyl violet number and BET surface area. The iodine number is a measure of the porosity of the activated carbon and it is defined as the milligrams of iodine adsorbed per gram of carbon. Methylene blue and methyl violet number indicate the decolorizing power and are defined as milligrams of methylene blue and methyl violet adsorbed per gram of carbon. These numbers were determined as per the standard procedures. The surface area was determined using N₂ adsorption method. The values obtained are given in Table 1 and 2.

Table 2. Thermo gravimetric analysis values for AAC

Composition	Percentage (%)
Ash	0.82
Carbon	65.88
Moisture	2.10
Volatile	31.20

**Fig. 1.** Effect of contact time and initial concentration on percentage adsorption.

2.4. Adsorption studies

All adsorption experiments were carried out by agitating the carbon with 100 ml of methylene blue dye solution of desired concentration and at room temperature in a mechanical shaker at a fixed agitation speed of 180 rpm. The experiments were carried out for various carbon loading, different initial methylene blue concentrations, contact time and pH.

At the end of predetermined time interval, samples were withdrawn from the shaker, centrifuged and the supernatant solution was analyzed for residual methylene blue concentration. The concentration of methylene blue was determined spectrophotometrically at a wavelength of 664 nm.

3. Result and discussion

3.1. Effect of contact time on percentage adsorption

The adsorption was carried out in a solution containing 80 mg L⁻¹ of methylene blue solution with constant carbon loading of 0.5 g per 100 ml of solution at room temperature and pH 7. (Fig. 1). The adsorption on activated carbon samples increased with contact time and attained equilibrium value at 2 h for 80 mg L⁻¹ and 100 mg L⁻¹. But 60 mg L⁻¹ reached equilibrium earlier with AAC may be the reason of lower concentration. Further increase in the contact time did not show a significant change in percentage adsorption. The equilibrium time was hence taken as 2 h.

3.2. Effect of pH on percentage adsorption

The effect of pH on adsorption of methylene blue on AAC was studied at room temperature by varying the initial pH of 80 mg L⁻¹ of methylene blue solution from 2 to 12 pH ranges for a constant carbon dosage of 0.5 g per 100 ml of solution and this is presented in Fig 2. The adsorption experiments were conducted for equilibration time previously determined. The pH of the aqueous solution is an important controlling parameter in the adsorption process [16]. The percentage removal of methylene blue was found to increase with increasing pH, showing maximum adsorption at pH 7. At pH 2, there was only little adsorption. The decrease in the methylene blue uptake at low pH is due to the fact that the H⁺ ions compete with methylene blue cation for the exchange of sites in the system, thereby partially releasing the latter. Under these conditions, adsorption is due to chemical interaction and must possess enough energy to overcome the repulsive forces between the

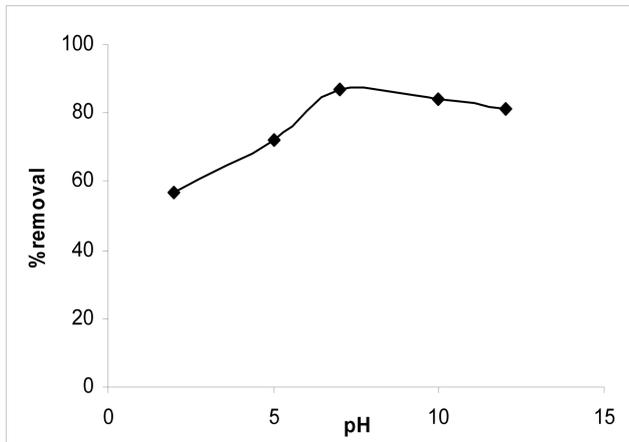


Fig. 2. Effect of pH on percentage adsorption.

positively charged carbon surface and methylene blue cation. Increase in pH showed increase in methylene blue adsorption, in which the surface of the activated carbon finds less H^+ ions competing for the adsorption site with methylene blue cations. In this case adsorption occurs by electrostatic force of attraction between methylene blue cation and surface of the adsorbent. At still higher pH (i.e.) above pH 7, there is no appreciable change in the quantity uptake, henceforth, all experiments were carried out at a pH of 7.

3.3. Effect of initial concentration on percentage adsorption

The effects of initial concentration on percentage removal of methylene blue for AAC were presented in Fig 1. The plot represents the percentage removal of methylene blue with change in initial concentration at pH 7 maintained at room temperature for a period of 2 h, with a constant carbon loading of 0.5 g per 100 ml of solution containing different concentration of methylene blue. As the initial concentration of methylene blue was increased, the percentage removal also decreased. The decrease in the percentage removal of methylene blue was greater at lower initial methylene blue concentration and smaller for higher initial methylene blue concentration. As the concentration of the adsorbate increases the number of sites for adsorption remaining the same, because of that the availability of free sites for adsorption decreases. Further, increase in concentration did not show an appreciable change in the percentage adsorption.

3.4. Effect of carbon dosage on percentage adsorption

To determine the necessary activated carbon quantity required for the maximum removal of methylene blue cations, the effect of activated carbon dosage on percentage

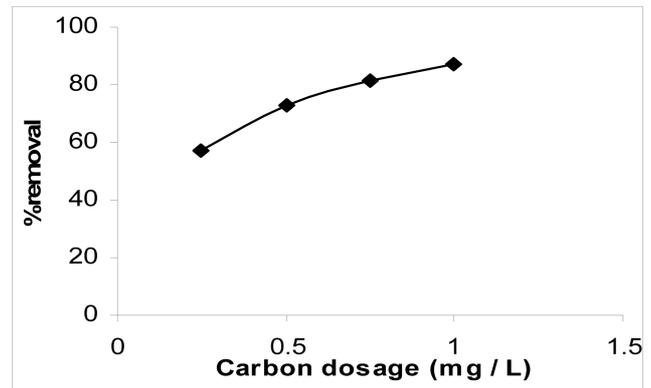


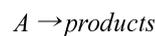
Fig. 3. Effect of carbon dosage on percentage adsorption.

removal was studied. This is shown in Fig. 3. The adsorption studies were carried out at pH 7 and room temperature for equilibration time, taking 100 ml of 80 mg L^{-1} of methylene blue solution for various activated carbon dosages. It can be easily inferred that the percent removal of methylene blue increased with increasing weight of the activated carbon. This is due to the fact that the more activated carbon, greater will be the availability of the exchangeable sites or surface offered to the adsorption of methylene blue cations. So 0.5 g L^{-1} is moderately taken for all adsorption experiments.

3.5. Kinetic Studies

3.5.1. First order model

This model is based upon the assumption that the change in dye concentration with respect to time is proportional to the power one. It is also based on the assumption as the following reaction proceeds,



Thus the rate of reaction r can be expressed as:

$$-r = -dC/dt = K_1 C \quad (1)$$

Separating and integrating Equation (1) with respect to limits $C=C_0$ at $t=0$ and $C=C$ at any time t :

$$-\int_{C_0}^C \frac{dC}{C} = K_1 \int_0^t dt \quad (2)$$

Or

$$\ln(C/C_0) = -K_1 t \quad (3)$$

Thus the rate constant K_1 can be calculated from the slope of plot between $\ln(C/C_0)$ versus time t . Fig. 4 shows the plot between $\ln(C/C_0)$ versus time t at three different dye concentrations. The calculated K_1 values and their corresponding linear regression correlation coefficient values are shown in Table 3 and 4. From Table 3, it was observed that the sorption data were not very well represented by first order kinetic model at all initial dye concentrations. The very

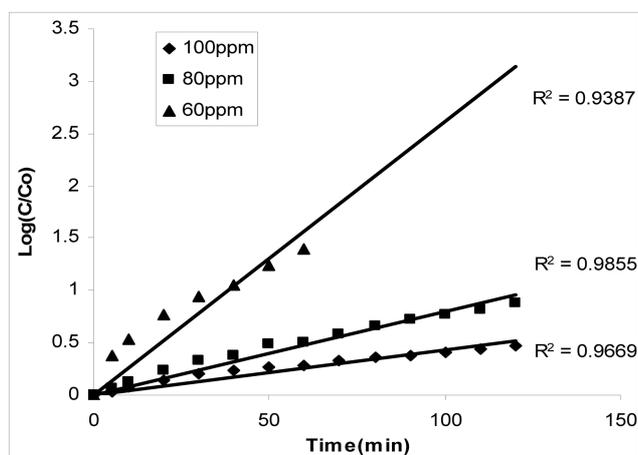
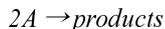


Fig. 4. First order kinetics for methylene blue adsorption onto AAC.

lower correlation coefficient (average value=0.9637) shows that this model is not an appropriate one in predicting the sorption kinetics of methylene blue onto AAC.

3.5.2. Second order model

The sorption kinetics were further analyzed using second order model. This model is based on the assumption as the following reaction proceeds:



Where, A is the dye component, which is being accumulated onto solid adsorbent. Then the rate of reaction r can be written as:

$$-r = -dC/dt = K_2 C^2 \quad (4)$$

Integrating Equation (4) with respect to limit $C=C_0$ at time $t=0$ and $C=C$ at any time t , equation simplifies to:

$$1/C = 1/C_0 + K_2 t \quad (5)$$

Table 3. Regression correlation coefficient values for all type of kinetics

Solution concentration (ppm)	I order model	II order model	Pseudo I Order model	Pseudo II Order model	Reversible I Order model
100	0.9669	0.9944	0.9501	0.9948	0.9931
80	0.9855	0.972	0.979	0.9987	0.9979
60	0.9387	0.9376	0.9068	0.9997	0.9724
Average value	0.9637	0.9680	0.9453	0.9977	0.9878

Table 4. Kinetic rate constant values for biosorption of methylene blue onto AAC

Solution concentration (ppm)	I order rate constant K_1 (min^{-1})	II order rate constant K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	Pseudo I Order rate constant K_I (min^{-1})	Pseudo II Order rate constant K_{II} ($\text{g mg}^{-1} \text{min}^{-1}$)	Reversible I Order rate constant K^*
100	0.0037	0.0002	0.0052	0.0173	0.0244
80	0.0071	0.0007	0.0058	0.0168	0.0518
60	0.0207	0.0061	0.0094	0.0182	0.0651
Average value	0.0105	0.0023	0.0068	0.0174	0.0471

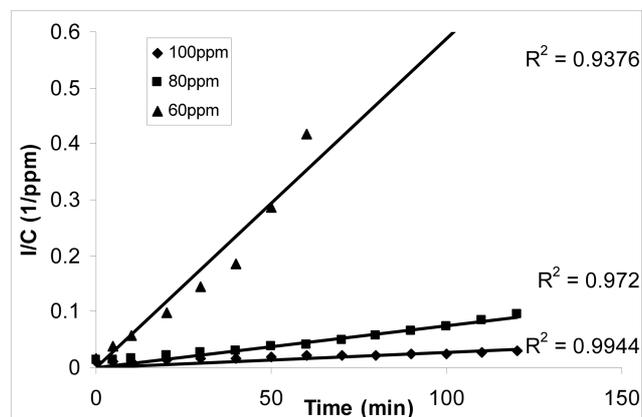


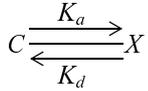
Fig. 5. Second order kinetics for methylene blue adsorption onto AAC.

The second order rate constant K_2 can be calculated from the slope of plot between $1/C$ versus time t (Fig. 5). The determined second order rate constants K_2 and their corresponding linear regression correlation coefficient values are shown in Table 3 and 4. From the table it was observed that the kinetic data fit second order with average regression coefficient of 0.9680. Though the higher regression values show the applicability of this model, these values were found to be lower than the reversible first order kinetic model and pseudo second order model, regression values at all dye concentrations confirming that the dye sorption process tends to follow pseudo second order rate kinetics.

3.5.3. Reversible first order kinetic model

The sorption of methylene blue from liquid phase to solid may be considered to follow a reversible first order reversible reaction model. This model is derived on the assumption that the rate of the forward reaction (adsorption) and reverse rate (desorption) constants are the same and are equal to the equilibrium reaction constant. Thus, the net rate

of reaction can be expressed in terms of the forward rate constants K_a and the equilibrium constant K . Thus, a simple first order reaction kinetic model can be used to correlate the rates of reaction, which can be expressed as:



Where, C (mg L⁻¹) and X (mg L⁻¹) represent the concentration of solute in liquid and in solid phases, respectively. If this model holds true then the change in dye concentration with respect to time (min) can be expressed as:

$$-dC/dt = K_a C - K_d X \quad (6)$$

If X_0 and C_0 represent the initial solute concentration in the solid phase and liquid phase, then the expression for X can be obtained by a simple mass balance equation given by:

$$X = X_0 + C_0 - C \quad (7)$$

Substituting Equation (7) in Equation (6), the rate expression becomes:

$$-dC/dt = (K_a + K_d)C - K_d(C_0 + X_0) \quad (8)$$

At equilibrium the forward reaction and reverse reaction rate are equal, and then the Equation (6) becomes:

$$K_a C_e = K_d X_e \quad (9)$$

or

$$K = K_a/K_d = X_e/C_e \quad (10)$$

Where C_e (mg L⁻¹) and X_e (mg L⁻¹) represents the concentration of methylene blue in liquid and solid phase at equilibrium respectively and K is the equilibrium constant. Rearranging Equation (10), the reaction rate expression is given by:

$$-dC/dt = K_a \left\{ \left(1 + \frac{K_d}{K_a} \right) C - \frac{K_d}{K_a} (C_0 + X_0) \right\} \quad (11)$$

or

$$-dC/dt = K_a \left\{ \left(1 + \frac{1}{K} \right) C - \frac{1}{K} (C_0 + X_0) \right\} \quad (12)$$

Substituting Equation (10) in Equation (12), the rate equation simplifies to:

$$-dC/dt = K_a \left\{ \left(\frac{K+1}{K} \right) C - \frac{1}{K} (C_0 + X_0) \right\} \quad (13)$$

Combining Equations (7) and (10), the expression for equilibrium constant, K can be obtained:

$$K = \frac{X_0 + C_0 - C_e}{C_e} \quad (14)$$

or

$$(K+1)C_e = X_0 + C_0 \quad (15)$$

Substituting Equation (15) in Equation (13), rate equation can be obtained as:

$$-dC/dt = K_a \left\{ \left(\frac{K+1}{K} \right) C - \frac{K+1}{K} C_e \right\} \quad (16)$$

or

$$-dC/dt = K_a \frac{K+1}{K} (C - C_e) \quad (17)$$

Replacing the term, $K_a(K+1)/K$ in Equation (17) with K^* , Equation (17) simplifies to:

$$-dC/dt = K^* (C - C_e) \quad (18)$$

or

$$\frac{-dC}{C - C_e} = K^* dt \quad (19)$$

Integrating Equation (19) with respect to limits $C=C_0$ and $C=C$ at $t=0$ and $t=t$, respectively, the final rate expression is obtained:

$$-\ln \frac{C - C_e}{C_0 - C_e} = K^* t \quad (20)$$

Thus, the rate constants K^* can be obtained from the slope of plot between $-\ln \{(C - C_e)/(C_0 - C_e)\}$ versus time t . Based on the calculated K^* values, the forward rate constant K_a and reverse rate constant K_d can be obtained from Equations (21) and (22), respectively:

$$K_a = K^* K / (K + 1) \quad (21)$$

$$K_d = K_a / K \quad (22)$$

Where the equilibrium rate constant K can be obtained using Equation (10). Fig 6 shows the reversible first order kinetic plot for the sorption of methylene blue onto AAC. The calculated K^* values and their corresponding linear regression correlation coefficient values were shown in Table

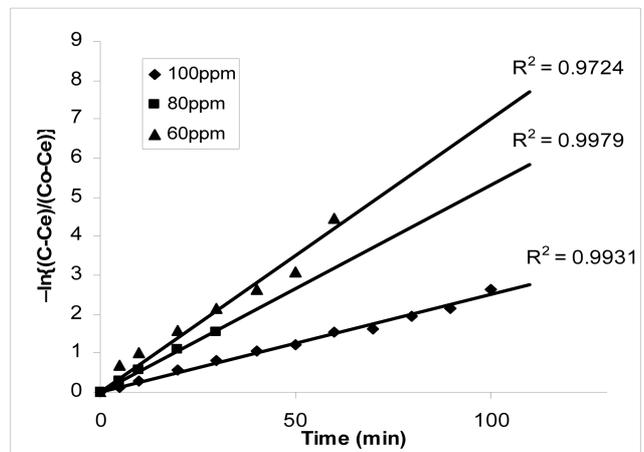


Fig. 6. Reversible first order kinetics for methylene blue adsorption onto AAC.

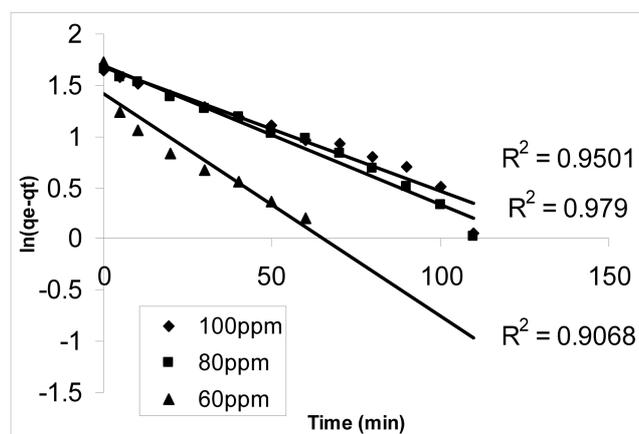


Fig. 7. Pseudo first order kinetics for methylene blue adsorption onto AAC.

3 and 4. The linear regression correlation coefficient values were found to fall in the range of 0.9724–0.9979 with an average value of 0.9878. This higher regression value confirms the applicability of this model but not an appropriate one than pseudo II order model.

3.5.4. Pseudo-first order model

The possibility of sorption data following Lagergren pseudo-first order kinetics is given by:

$$dq_t/dt = K_I(q_e - q_t) \quad (23)$$

Integrating Equation (23) with respect to integration conditions $q_t = q_t$ to $q_t = q_0$ at $t = 0$ to $t = t$, the kinetic rate expression becomes:

$$\ln(q_e - q_t) = \ln q_e - K_I t \quad (24)$$

The first order rate constant K_I can be obtained from the slope of plot between $\log(q_e - q_t)$ versus time t . Fig. 7 shows the Lagergren pseudo-first order kinetic plot for the sorption of methylene blue onto AAC. The first order rate constant K_I values were calculated from the slope of Fig. 7. The calculated K_I values and their corresponding linear regression correlation coefficient values are shown in Table 3 and 4. The linear regression correlation coefficient values found in the range of 0.9068–0.9501 with an average value of 0.9453, which shows that this model can not be applied to predict the sorption kinetics.

3.5.5. Pseudo-second order model

A pseudo-second order model proposed by Ho and McKay [17] can be used to explain the sorption kinetics. This model is based on the assumption that the biosorption follows second order chemisorption. The pseudo-second order model can be expressed as:

$$dq_t/dt = K_{II}(q_e - q_t)^2 \quad (25)$$

Separating the variables in Equation (25) gives:

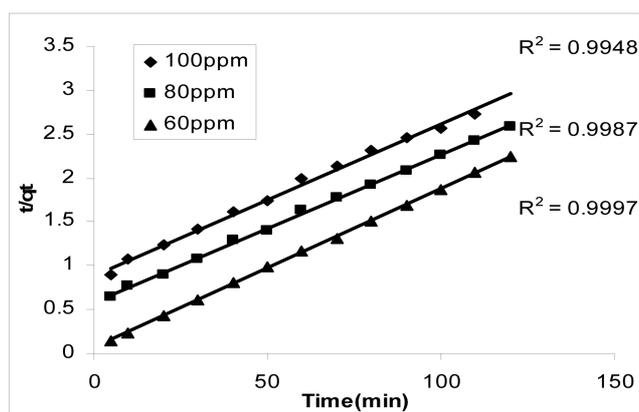


Fig. 8. Pseudo second order kinetics for methylene blue adsorption onto AAC.

$$dq/(q_e - q)^2 = K_{II} dt \quad (26)$$

Integrating Equation (26) for the boundary conditions $q_t = 0$ to $q_t = q_0$ at $t = 0$ to $t = t$, Equation (26) simplifies to:

$$t/q_t = 1/(K_{II}q_e^2) + t/q_e \quad (27)$$

Where t is the contact time (min), q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amount of dye adsorbed at equilibrium and at any time, t . A plot between t/q_t versus t gives the value of the constants K_{II} (g mg min^{-1}) and also q_e (mg g^{-1}) can be calculated.

Fig. 8 shows the pseudo-second order plot for methylene blue onto AAC. The pseudo-second order rate constant K_{II} , the calculated q_e value and the corresponding linear regression correlation coefficient values are given in Table 3 and 4. At all initial dye concentrations, the linear regression correlation coefficient values were higher and ranged from 0.9948 to 0.9997. The higher regression values confirm that the sorption data were well represented by pseudo-second order kinetics and the supports the assumption behind the model that the sorption is due to chemisorption. The possible reaction mechanism can be generalized as Ho and McKay [17]



Average regression value of 0.9977 was which even better than that of Reversible first order regression values. This observation made clear that the sorption data tend to follow pseudo-second order kinetic model.

4. Conclusion

The *Acacia* barks can be used as a precursor for activated carbon which could possibly be used for textile waste water treatment. From the adsorption studies the optimum contact time, carbon dosage, and pH at room temperature for methylene blue adsorption were 2 h, 0.5 g L^{-1} , and 7 respectively. The modeling studies clearly predicted that the

pseudo II order kinetics was followed with higher regression coefficient of 0.9977. But the reversible I order kinetics also to be considered because of its higher regression coefficient of 0.9878. From the regression coefficient values, adsorption rate kinetics of methylene blue onto AAC followed in the following order: pseudo II order > reversible I order > II order > I order > pseudo I order.

References

- [1] Srinivasan N. "Evaluation of rice husk carbon for the removal of trace inorganics from water", Ph. D. Dissertation, Indian Inst. Technol. Chennai, 1986.
- [2] Nath, S. K.; Jena, A.; Mishra, S. P. *Trans Indian. Inst. Met.* **1997**, *50*, 235.
- [3] Gomez, V. S.; Macias, A. G.; Espinosa, A. M.; Valenzeula, C. *C. Water Research* **1998**, *32*, 1.
- [4] Anoop Krishnan, K.; Anirudhan, T. S. *Industrial Engineering Chemistry & Research* **2002**, *41*, 5085.
- [5] Basso, M. C.; Cerella, E. C.; Cukierman, A. L. *Ind. Eng. Chem. Res.* **2002**, *41*, 180.
- [6] Ajmal, M.; Rao, R. A. K.; Anwar, S.; Ahmad, J.; Ahmad, R. *Bioresource Tech.* **2003**, *86*, 147.
- [7] Daud, W. M. A. W.; Ali, W.S.W.; Sulaiman, M. Z. *J. Chem. Technol. Biotechnol.* **2003**, *78*, 1.
- [8] Tan, J.S.; Ani, F. N. *Carbon* **2003**, *14*, 840.
- [9] Toles, C. A.; Marshall, W.E.; Wartelle, L. H.; McAloon, A. *Bioresour. Technol.* **2000**, *75*, 197.
- [10] Al-Khalid, T. T.; Haimour, N. M. ; Sayed, S. A. ; Akash, B. A. *Fuel Process. Technol.* **1998**, *57*, 55.
- [11] Rodriguez-Reinoso, F.; Molina-Sabio, M.; Gonzalez, M. T. *Carbon* **1995**, *33*, 15.
- [12] Garca-Garc'a, A.; Gregorio, A.; Franco, C.; Pinto, F.; Boavida, D.; Gulyurtlu, I. *Bioresour. Technol.* **2003**, *88*, 27.
- [13] Tseng, R. L.; Wu, F. C.; Juang, R. S. *Carbon* **2003**, *41*, 487.
- [14] Tennant, M. F.; Mazyck, D. W. *Carbon* **2003**, *41*, 2195.
- [15] Sivarajasekar, N. *Carbon letters* **2007**, *8*, 199.
- [16] Elliot, H. A.; Huang, C. P. *Water Research* **1981**, *15*, 849.
- [17] Ho, Y. S.; McKay, G. *Can. J. Chem. Eng.* **1998**, *76*, 822.