

Adsorptive Removal of Methylene Blue Using Activated *Prosopis Spicigera*: A Low Cost Adsorbent

V. VENKATESWARAN¹, P. KALAAMANI² and N. KARPAGAM^{2*}

¹Saraswathi Thyagaraja College, Pollachi-642001, Tamilnadu, India

²Dept. of Chemistry, NGM College, Pollachi-642001, Tamilnadu, India
nkarpagam82@gmail.com

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Abstract: Adsorption of methylene blue, a basic dye onto activated *Prosopis spicigera*, prepared from dried fruit of the member of leguminasae family by batch adsorption method has been investigated. The operating variables studied are the initial dye concentration, initial solution pH, adsorbent dosage and contact time. Equilibrium data were successfully applied to study the kinetics and mechanism of adsorption of dye onto activated carbon. The kinetics of adsorption was found to be pseudo second order with regard to intraparticle diffusion. The pseudo second order is further supported by Elovich model, which in turn augments the fact of chemisorption of dye onto the carbon. Quantitative removal of dye at higher pH of dye solution confirms the basic nature of MB and acidic nature of activated carbon. Equilibrium adsorption data were also analyzed by Langmuir and Freundlich models.

Keywords: Methylene blue, Activated carbon, Adsorption isotherm, Kinetics, Elovich, SAPS

Introduction

Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries. Color stuffs discharged from these industries pose many hazards and environmental problems. These colored compounds are not only aesthetically displeasing but they also inhibit the sunlight penetration into the stream thus affecting aquatic ecosystem. Dyes are usually composed of complex aromatic molecular structures which makes them carcinogenic and mutagenic, inert and non biodegradable when discharged into water. Furthermore, many dyes are toxic to some microorganisms and hence may cause direct destruction or inhibition of their catalytic capabilities. Hence the removal of such coloured agents from aqueous effluents is of significant environmental, technical and commercial importance. Conventional methods of removing dyes include coagulation, flocculation, oxidation or ozonation and membrane separation¹. However, these methods are not preferred because of their high cost and economic disadvantage. Chemical and electrochemical oxidations, coagulation are generally not feasible on a large scale.

In contrast, an adsorption technique is by far the most versatile and widely used method because of several advantages. The most commonly used adsorbent materials include alumina, silica, metal hydroxides, fruit wastes^{2,3} and activated carbon. As proved by many researchers, removal of dyes by activated carbon is economically favorable and technically easier as activated carbons possess high adsorption capacity, high surface area and micro porous structure^{4,5}.

Experimental

Fruits of *Prosopis Spicigera* are collected from various areas in and around Pollachi, India. Sun dried fruits were cut into small pieces and ground well. The powder (100 g) was impregnated with 40 mL of 40% H₂SO₄ for 2 hours, then carbonized and digested in an oven at 120 °C for 12 h. The carbonized material was then impregnated in 50% solution of NaHCO₃, washed with distilled water to remove the free acid until the pH of the activated carbon reached 6.6–6.8 and finally dried at 105 °C. After that the impregnated samples were again activated in a carbonization furnace at 500 °C for 60 min under nitrogen atmosphere. The clean biomass obtained was mechanically ground and finally sieved to get particles of different sizes.

Adsorbent: SAPS

Adsorbate

The adsorbate used was methylene blue (basic dye, C.I. 52015, λ_{max} abs.=665 nm. Doubly distilled water was used for solution preparation. The solution pH was adjusted using 0.1 N HCl or 0.1 N NaOH, (Merck India). A stock solution was prepared by dissolving 1 g of dye in 1000 mL of doubly distilled water⁶. The stock solution MB was diluted to the required concentration for obtaining a standard solution containing 10-40 mg/g of the dye.

Batch equilibrium studies

Entire batch mode adsorption studies were carried out with 100 mg adsorbent and 50 mL of dye solution of desired concentration at an initial pH of 2 in 100 mL conical flasks, which were agitated at 140 rpm for predetermined time of 3 hours except for time study at room temperature in a rotary shaker. The adsorbent and adsorbate were then separated⁷. All the experiments were carried out in duplicate and the mean values are presented in Table 1. Studies on the effect of adsorption dose were carried out by taking different amounts of adsorbent. All other studies were carried out using known amount of adsorbent and 50 mL of dye solution of different concentrations.

Table 1. Characteristics of carbonized *Prosopis spicigera*

Parameter	Value
pH	6.9
pH _{zpc}	5.46
Moisture content %	8.5
Porosity%	70
Specific gravity	1.48
Ash content %	3.86
Bulk Density g/cm ⁻³	0.3915
Total Nitrogen as N %	0.004
Solubility in water %	2.676

Results and Discussion

Effect of SAPS dose

The effect of SAPS dose on the removal of MB at initial concentrations of the dye solutions of 20 and 40 mg.L⁻¹ was studied (Figure 1). Increase in the percent removal with increase in carbon concentration can be attributed to increased surface area and hence availability of more adsorption sites⁸.

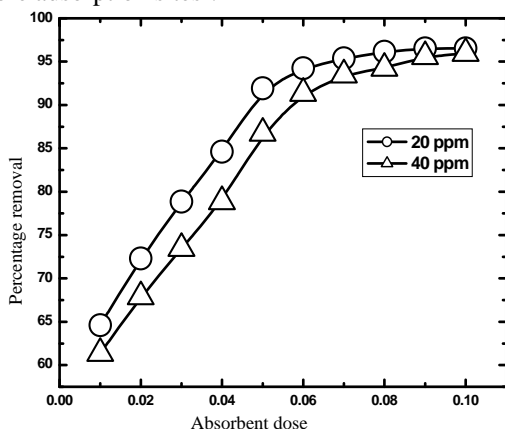


Figure 1. Effect of adsorbent dose

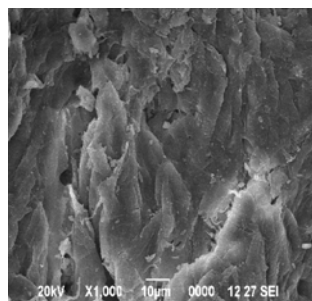


Figure 2. SEM image of SAPS

Characterization of adsorbent

Figure 2 shows the SEM micrograph of the adsorbent. The image clearly shows the heterogeneous morphology.

Effect of contact time

In order to innovate more effective modeling of the adsorption process, kinetics of the process was monitored⁹. Adsorption experiments were carried out at different concentrations (10-40 mg.L⁻¹) for different contact time with a fixed adsorbent dose. It was observed that percent adsorption increased with increase in initial dye concentration and attains equilibrium in 80 min (Figure 3).

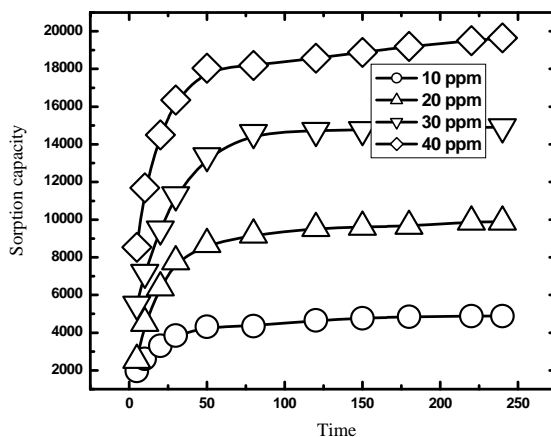


Figure 3. Effect of contact time

Effect of initial pH

Figure 4 shows the effect of pH on the removal of dye with increase in pH of dye solution from 2 – 10. The dye uptake was found to increase with increase in pH. When the pH of dye solution is greater than pH_{zpc} of adsorbent, the surface of SAPS becomes negatively charged, adsorption of dyes decrease leading to a decrease in removal of dye with increase in pH¹¹.

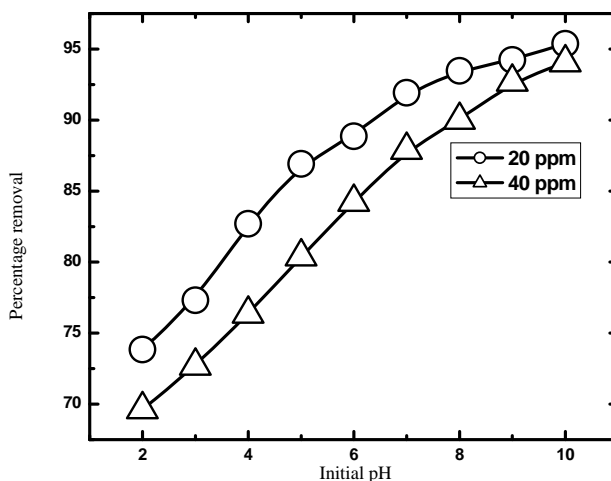


Figure 4. Effect of initial pH

Adsorption isotherm

Langmuir model

Langmuir isotherm is represented by the following equation

$$C_e / q_e = 1 / bq_o + C_e / q_o$$

Where C_e is the equilibrium concentration of the dye solution (mg.L^{-1}) at equilibrium, q_e is the amount of dye adsorbed at equilibrium (mg.g^{-1}) and Q_0 and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The linear plot of C_e/q_e vs. C_e in Figure 5 shows that the adsorption obeys Langmuir isotherm model with $R^2 > 0.95$, confirming the monolayer coverage of dye on the adsorbent.

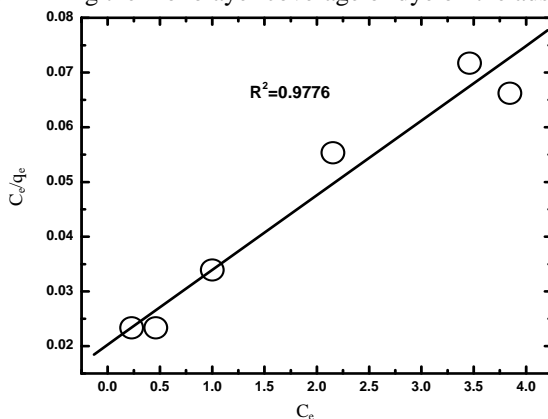


Figure 5. Langmuir adsorption isotherm

The adsorption capacity, Q_0 was found to be 73.26 mg.g^{-1} for MB onto SAPS, respectively. For comparison the adsorption capacity, Q_0 of other non-conventional materials are shown in Table 2. The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor R_L .

$$r = 1/[1 + bC_o]$$

Where C_o is the initial dye concentration (mg.L^{-1})¹² and R_L values indicate the shape of the isotherm. The R_L values (Table 2) were found to be between 0 and 1 confirming the favourable uptake of the dye on the adsorbent.

Table 2. Langmuir parameters

C_0	A	B	Q_0	b	R_L	R^2
20					0.0690	
40					0.0357	
60					0.0241	
80					0.0182	
100					0.0146	
120	0.0202	0.0136	73.2600	0.6737	0.0122	0.9776

Freundlich model

The Freundlich isotherm, in its logarithmic form can be represented as

$$\log q_e = \log K_f + 1/n \log C_e$$

Where K_f ($\text{mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$) and $1/n$ (g/L) are Freundlich constants related to adsorption capacity and adsorption intensity of the sorbent respectively. Linear plots of $\log q_e$ versus $\log C_e$ (Figure 6) show that the adsorption of dye follows the Freundlich isotherm. The value of n evaluated as 1.7729, indicate that the process was favourable. The values of K_f was found to be 26.3554 ($\text{mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$).

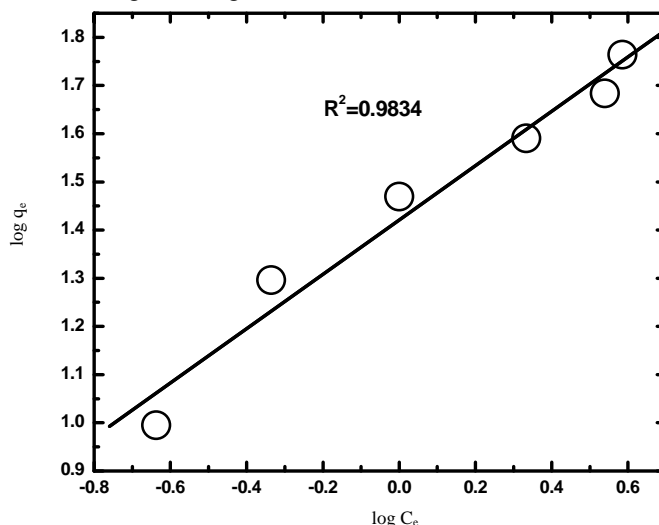


Figure 6. Freundlich adsorption isotherm

Adsorption kinetics

In order to examine the controlling mechanism of adsorption process such as chemical reaction, diffusion control and mass transfer, several kinetic models have been considered. The experimental data does not fit with Pseudo first order kinetic model.

Pseudo second order equation

The pseudo second order equation is represented in its integrated form as

$$t / q_t = 1 / K_2 q_e^2 + 1 / q_e t$$

Where k_2 is the second order rate constant. A plot of t/q_t vs. t is shown in Figure 7. The linearity of the plots and data in Table 3 clearly indicate that the adsorption process followed Pseudo second order kinetics.

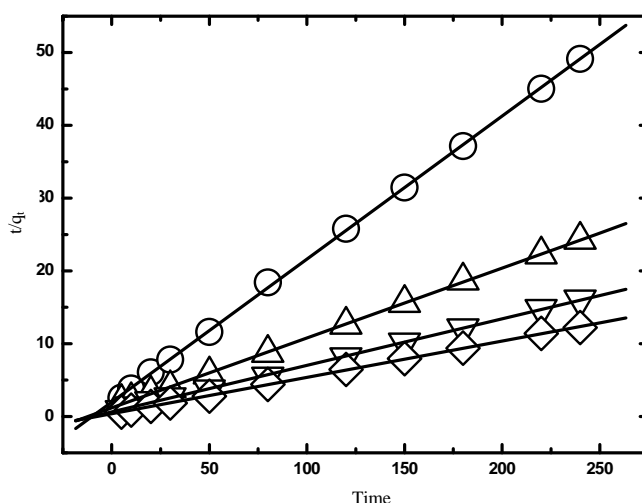


Figure 7. Pseudo second order kinetics

Table 3. Consolidated table for kinetics of adsorption

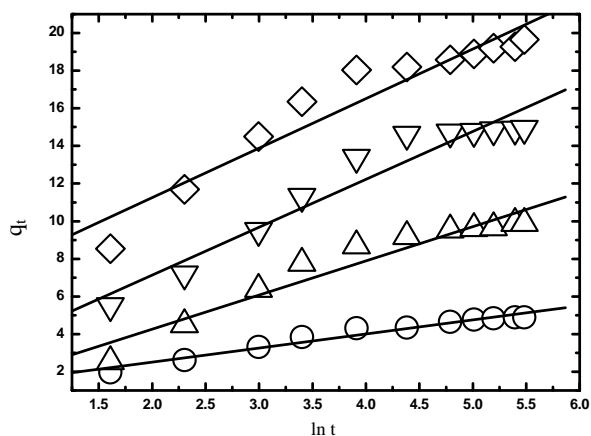
Conc. Mg/L	q_e exp, mg/g	Pseudo second order		
		q_e cal mg/g	$K_2 \times 10^{-3}$, L mole ⁻¹ min ⁻¹	R^2
10	4.846	5.0869	0.0197	0.9998
20	9.538	10.4079	0.0079	0.9998
30	14.615	15.6470	0.0064	0.9996
40	19.269	19.9960	0.0069	0.9998

Elovich model

The adsorption data were analyzed using the Elovich equation which is generally expressed in its integrated form as¹³

$$Q_t = [1/b] \ln[ab] + [1/b] \ln t$$

Where a is the initial adsorption rate (mg.g⁻¹min) and the parameter b is related to the extent of surface coverage and activation energy for chemisorption (g.mg⁻¹). A plot of q_t vs. $\ln t$ is shown in Figure 8 and data in Table 4. The linear plots obtained and lowering of b values with increase in dye concentration clearly reveal that Elovich model was applicable to the adsorption process under study.

**Figure 8.** Elovich model**Table 4.** Elovich model

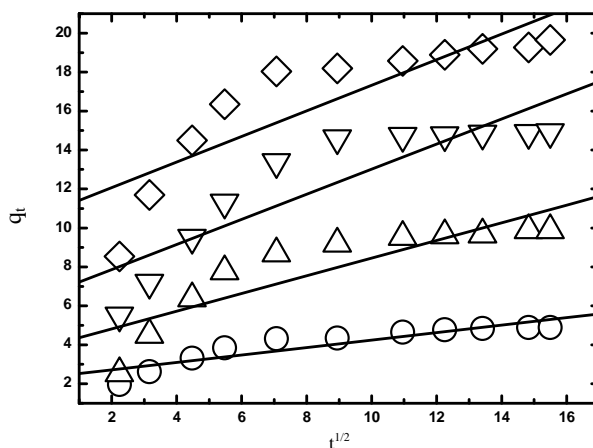
Conc.of MB mg/L	a	b	R ²
10	2.8967	1.3361	0.9804
20	2.5671	0.5508	0.9632
30	5.6700	0.3798	0.9677
40	25.5541	0.3773	0.9585

Intraparticle diffusion model

Intraparticle diffusion was characterized using the relationship between specific sorption (q_t) and square root of time ($t^{1/2}$) as

$$Q_t = K_{id}t_{1/2} + C$$

Where K_{id} is the intraparticle diffusion rate constant and C is the intercept. A plot between amount of dye adsorbed per unit mass of adsorbent q_t and $t^{1/2}$ was shown in Figure 9 and data given in Table 5.

**Figure 9.** Intraparticle model

The linear portion of the plot for wide range of contact time between adsorbent and adsorbate does not pass through the origin suggesting that pore diffusion is the only controlling step and not the film diffusion¹⁴. This deviation may be due to the variation of mass transfer in the initial and final stages of adsorption.

Table 5. Intraparticle diffusion

Conc. Mg/L	K min ⁻¹	R ²
10	0.1915	0.9081
20	0.4541	0.8719
30	0.6442	0.8861
40	0.6633	0.8698

Conclusion

The present investigations showed that SAPS can be used as an effective low cost adsorbent for the removal of MB from aqueous solution. The adsorption was dependent on the solution pH, carbon dosage and initial dye concentration. Equilibrium data agree well with Langmuir and Freundlich isotherm models¹⁵. The adsorption kinetics followed the Pseudo second-order model which was supported by chemisorptive Elovich kinetic model.

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