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Adsorption of Methylene Blue Dye onto Activated Carbon Prepared from Pongamia Pinnata Seed,

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***Abstract*-The present study explored the adsorption of Methylene blue (MB) dye from aqueous solution onto activated carbon prepared from the shell of Pongamia Pinnata seed. Batch experimental studies were carried out by Pongamia Pinnata Seed Shell Carbon (PPSSC) to determine the influence of various adsorption parameters like adsorbent dose (m), initial pH (*pHo*), contact time (*t*) and initial concentration (C_o) on the removal of MB. The optimum conditions were found to be: *m* = 4 g/l, *pHo* = 7.2 and *t*= 90 min. The kinetic study shows that, the second-order kinetic model represented the adsorption kinetics of MB onto PPSSC.**

Keywords - Adsorption; Methylene blue; Pongamia Pinnata Seed Shell Carbon; Adsorption kinetics.

I. INTRODUCTION

Contamination of water bodies by methylene blue and similar dyes is a major environmental issue, as most of these dyes are toxic, mutagenic and carcinogenic [1]. Release of dye based effluents into the ecosystem is a source of aesthetic pollution, also cause perturbation to aquatic life [2]. Textile industry is the largest consumer of dye stuff consuming more than 80% of the total production [3]. Different physicochemical methods have been developed to remove synthetic dyes from waters and wastewaters to decrease their impact on the environment. Physicochemical process like electro-kinetic coagulation, ion-exchange, membrane filtration, electrochemical oxidation and photo-catalytic degradation process have found to be successful in treating these wastewaters [4, 5, 6, 7, 8], however they have certain drawbacks. Treatment process like coagulation produces huge sludge leading to high disposal expenditure, while ion-exchange process is expensive. Membrane separation process is effective, but due to membrane fouling problem and high investment its application is restricted. And as dyes are difficult to decompose biologically, due to wide range in pH, conventional biological methods are ineffective in their treatment.

Adsorption has been emerged out as an alternate effective treatment process in the purification of dye based wastewaters, especially when the adsorbent is readily available and is inexpensive i.e. low cost adsorbent. Adsorption process has gained attention because of its simplicity, ease of handling, sludge free operation and regeneration capacity. Also, it is economically feasible giving a high quality product [9]. Activated carbon (AC) is the most commonly used adsorbent with a great success. However, commercially available AC is expensive and their use requires elaborate regeneration and reactivation procedure. The gradual loss of AC during regeneration can be materially affecting the economic viability of the process. This has led many investigators to search for cheaper sources to prepare ACs or cheaper substitutes like fly ash, bagasse, rice husk and coir pith carbon [10, 11], saw dust [12], wollastonite [13], Jatrophacurcus seed shell, Delomixregia seed shell and Ipomeacarnia stem are the materials which have been already studied for the removal of colour and organic matters [14]. Various researchers have utilized adsorption technique for the removal of toxic MB dye from waters and wastewaters [15, 16, 17, 18, 19].

Pongamia pinnata seeds with shell, commonly known as *Karanja* seeds, are readily available as an agricultural waste. These seeds contain 30 to 40% of oil [20], while the seed shell can be effectively used for the preparation of AC. The PPSSC has good adsorptive properties and has been used for removal of dyes [20].

This study is an attempt to explore the possibility of using PPSSC for the removal of MB dye from aqueous solutions by performing batch studies. The effect of parameters such as dose (*m*), initial pH (pH_0), contact time (*t*) and initial concentration (C_0) on the adsorption efficiency of MB on PPSSC has been investigated.

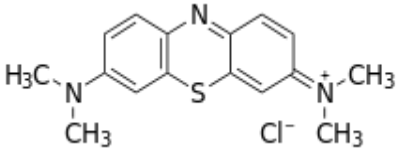

Fig.1. Molecular structure of Methylene Blue

II. MATERIALS AND METHODS

A. *Adsorbent Preparation*

The *Karanja* (Pongamia Pinnata) seed shell was collected from Pauni, District Bhandara, Maharashtra, India. The seed shell waste was sundried, crushed to desirable size to obtain fine powder and then chemically activated with Orthophosphoricacid (H_3PO_4) in the weight

to volume ratio of 1:1 (w/v in g/ml) for 24 hours [16]. This mixture was then charred at 450°C for 1 hour to complete the carbonization and activation process. The resulting carbon was washed multiple times with Double Distilled Water (DDW) till a neutral pH of the slurry was reached. The carbon was then dried at 105°C in a hot air oven for 12 hours [15]. The dried material was grounded well to fine powder and sieved in the size range of 150 – 300 µm and stored in air tight container.

B. Adsorbate Preparation

The adsorbate MB dye (C.I. No. 52015, Chemical formula = $C_{16}H_{18}N_3CIS$, M.W. =319.85 and λ_{max}= 663-667nm) was supplied by Merck Specialities Pvt. Ltd., India. The dye was of analytical reagent grade cationic dye in the form of dark green powder. The structure of MB is illustrated in Fig. 1. Stock solution (1000 mg/l) of dye was prepared by dissolving 1 g of MB dye in 1000 ml of DDW. Solutions of required concentrations were prepared by successive dilutions of stock solution with DDW.

C. Analytical Measurements

A double beam UV-VIS Spectrophotometer (Shimadzu, UV-2450) was used to determine the concentration of dye samples by finding out the absorbance at the characteristic wavelength. The wavelength corresponding to maximum absorbance (λ_{max}) as determined from this plot was 664nm. This wavelength was used for preparing the standard graph of concentration of MB dye versus absorbance. The samples with higher concentration of MB (> 0.600 absorbance) were diluted with DDW for the accurate determination of the MB concentration with the help of linear portion of the calibration curve. All the readings were taken in duplicate and the mean values are presented.

D. Batch Adsorption Studies

Batch adsorption studies were conducted to determine the effect of important parameters like m, pH_0, t and C_o on the adsorptive removal of MB. For each experimental run, 50ml of MB solution of known concentration, pH_o and a known adsorbent dose were taken in 250ml stoppered conical flask. This mixture was agitated at 150 rpm at 30°C in a temperature controlled Orbital Shaker. At preset time intervals the solutions were taken out and filtered with Whatmann No.1 filter paper. The supernatant liquid thus obtained was analyzed for the residual dye concentration.

For determining the optimum dose of absorbent, 50ml of known concentration of MB dye solution was agitated with different doses of PPSSC till equilibrium was achieved. To study the effect of pH_0 on the removal of MB, adsorption experiments were carried out at pH_0 range of 2 – 12. The pH_0 was maintained by adding required amount of diluted 0.1N HCl and 0.1N NaOH solutions. The adsorptive kinetics was studied by analyzing adsorptive uptake of the dye from aqueous solution at different time intervals. This was done repeatedly at different concentrations of dye solution.

III. Results and Discussion

A. Effect of adsorbent dose (m)

The effect of m on removal of MB by PPSSC at C_0= 50mg/l is shown in Fig.2. It was observed that the dye removal increases up to certain limit with increase in adsorbent dose, and then it remains almost constant. Optimum m was found to be 4 g/l. An increase in percent removal of dye with the increase in adsorbent dose can be attributed to increased carbon surface area, and the availability of more adsorption sites [21, 22]. Hence the entire studies are carried out with adsorbent dose of 0.2 mg/50ml i.e. 4 g/l of adsorbate solution.

B. Effect of initial pH (pHo)

Dependence of dye adsorption on varying pH_0 of dye from 2-12 is shown in Fig.3. The study was carried out with MB solution of C_0=50 mg/l having natural pH_0 of 7.2. Dye adsorption efficiency is affected by pH_0 variation [23]. The adsorption of MB increased with an increase in pH_0. It can be inferred that dye removal is maximum and constant for pH_0 greater than or equal to 4.0. This can be explained by considering the electrostatic attraction that exists between the negatively charged surface of adsorbent and MB, a cationic dye. Lower adsorption at acidic pH_0 was probably due to presence of excess H^+ions competing with the dye cations for adsorption sites. At alkaline pH_0, the number of positively charged sites decrease and the number of negatively charged sites increase, this favors the removal of cationic dye. Similar results were observed for the adsorption of MB onto

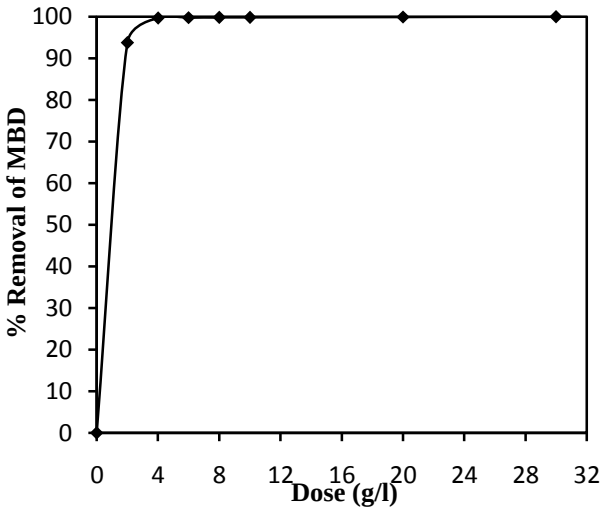

Fig.2. Effect of adsorbent dose on the adsorption of MB by PPSSC (T = 300C, t = 60 min, C_0 = 50 mg/l)

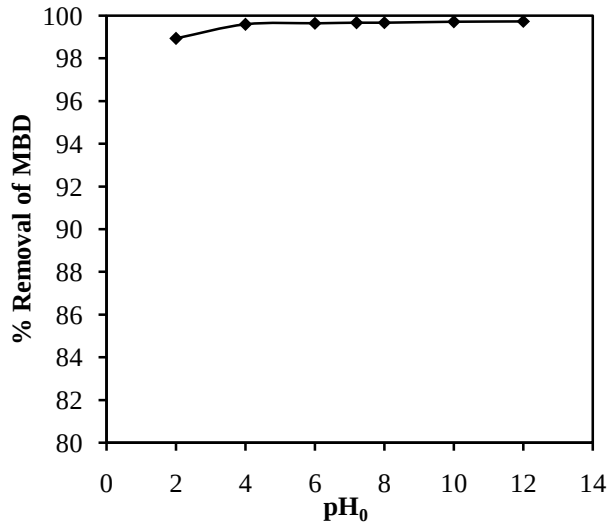

Fig.3. Effect of initial pH on the adsorption of MB by PPSSC (T = 30^{0}C, t = 60 min, C_0 = 50 mg/l, m = 4 g/l)

Fe(III)/Cr(III) hydroxide [24], malachite green onto agro-industry waste [25], methylene blue onto various carbons [26].

C. Effect of contact time (t) and initial dye concentration (C_o)

The effect of contact time on the removal of MB by PPSSC at C_0= 50, 100 and 200 mg/l is shown in Fig.4. The

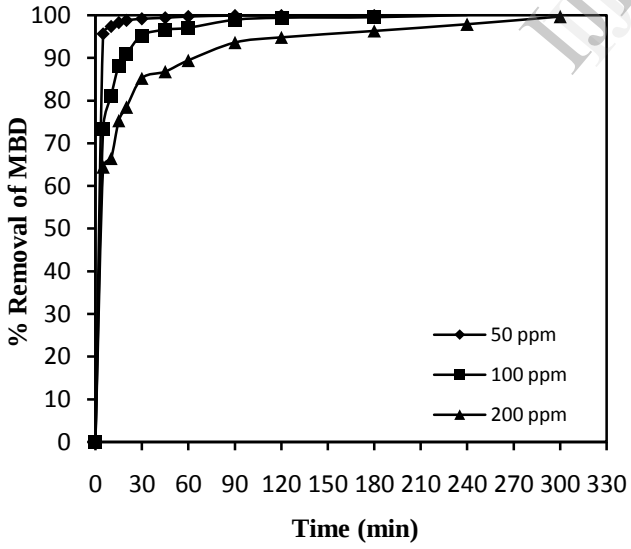

Fig.4. Effect of contact time on the adsorption of MB by PPSSC (T = 30^{0}C, m = 4 g/l)

contact time curve shows rapid adsorption of MB in first 15 min., thereafter it decreases gradually and the adsorption attains equilibrium in 90 min. (optimum contact time). Further increase in contact time showed that the MB removal increases slightly over those obtained for optimum contact time.

It is also evident from Fig.4, that percent adsorption decreased with increase in initial dye concentration, but the actual amount of MB absorbed per unit mass of carbon increases with increase in initial dye concentration. It means that the adsorption is highly dependent on initial concentration of dye. It is because of that at lower concentration, the ratio of initial number of MB dye molecules to the available surface area is low, and subsequently the fractional adsorption becomes independent of initial concentration. Moreover at higher concentration, the available sites of adsorption become fewer and hence the percentage removal of MB dye is dependent upon initial concentration [21, 22]. Fig.4 revels that the curves are single, smooth and continuous leading to saturation, indicating the possible monolayer coverage of MB dye on the surface of PPSSC.

D. Adsorption Kinetic study

Pseudo-first order and Pseudo-second order models

The pseudo-first order equation is given as:

$$\frac{dq_t}{dt} = k_f (q_e - q_t) \quad (1)$$

where,

q_t = amount of adsorbate absorbed per unit weight of adsorbent at any time t (mg/g)

q_e = the adsorption capacity at equilibrium (mg/g)

k_f = pseudo-first order rate constant (min^{-1}), and

t = contact time (min.)

the integration of equation (1) with initial conditions, C_0= 0 at t = 0, leads to following equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303} t \quad (2)$$

The value of q_t at C_0 = 50, 100 and 200 mg/l were determined from the plot of *log* (q_e-q_t) versus t (not shown here). The values of k_f thus obtained (refer Table 1) for C_0=50, 100 and 200mg/l are comparable to k_f values for MB adsorption on Babul seed carbon [18]. These values of q_e indicate that the adsorption rate increases with increase in Co.

Pseudo-second order model

The pseudo-second order model is represented as [27]:

$$\frac{dq_t}{dt} = k_s (q_e - q_t)^2 \quad (3)$$

where, k_s = pseudo-second order rate constant (g/mg.min)

the integration of equation (3) with initial conditions, q_t=0 at t=0, the following equation is obtained,

$$\frac{t}{q_t} = \frac{1}{k_s q_e^{\,2}} + \frac{1}{q_e} t \quad \text{or} \quad \frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \qquad (4)$$

$$q_t = \frac{t\, k_s\, q_e^{\,2}}{1 + t\, k_s\, q_e} \qquad (5)$$

The initial sorption rate h (mg/g.min), at t → 0 is defined as, $h = k_s q_e^{\,2}$ (6)

The q_e is obtained from the slope of the plot of t/q_t against t (Fig. 5), at C_0=50, 100 and 200mg/l, and the h value is obtained from the intercept. The best fit values of q_e and k_s along the correlation coefficients for the pseudo-first order and pseudo-second order models are shown in Table 1. The calculated correlation coefficients R^2 are closer to unity for pseudo-second-order kinetics in comparison with pseudo-first-order. kinetics. Hence, the sorption can be approximated more appropriately by the pseudo-second-order kinetic model for adsorption of MB on PPSSC.

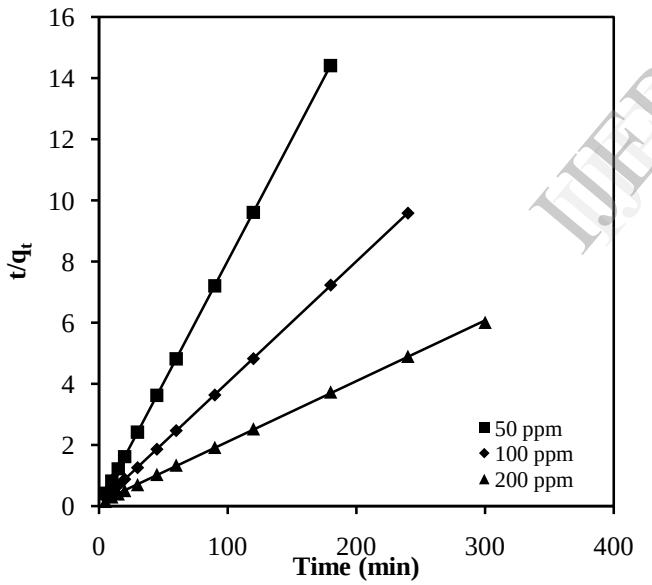

Fig.5 Pseudo-second-order kinetic model for the removal of MB by PPSSC (T = 30°C, m = 4 g/l)

Weber – Morris intra-particle diffusion equation

The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in an intra particle diffusion plot. The overall adsorption process may be controlled by one or more than one steps, e.g. film or external diffusion, pore diffusion,surface diffusion and adsorption on the pore surface, or a combination of more than one step. Weber and Morris, has explored the possibility of intra – particle diffusion by using intra-particle diffusion model. [28].

$$q_t = k_{id}\, t^{0.5} + C \qquad (7)$$

where, k_{id} = intra-particle diffusion rate constant (mg/g $min^{1/2}$) and C (mg/g) is a constant. If the Weber-Morris plot of q_t vs. $t^{0.5}$ gives linear relationship for the experimental data, then the sorption process is found to be controlled by intra-particle diffusion only. But, if the data exhibit multi-linear plots, then two or more than two steps influence the sorption process.

The Weber Morris plot (not shown here) shows only one linear portion depicting mesopore diffusion. The intercepts of on the y-axis gives the value of C, which provides the measure of the boundary layer thickness. Larger the intercept, the boundary layer effect will also be large. The amount of adsorbate and the driving force for MB adsorption is a rate –limiting step, and therefore MB gets absorbed in mesopores only.

Table 1. (Kinetic Parameters)

1) Pseudo-first-order model			
C_0 (mg/l)	k_f (min^{-1})	q_e (mg/g)	R^2
50	0.013	0.17	0.708
100	0.021	3.481	0.946
200	0.016	16.173	0.904
2) Pseudo-second-order model			
C_0 (mg/l)	k_s (g/mg min)	q_e (mg/g)	R^2
50	0.305	12.516	1
100	0.019	25.253	1
200	0.003	50.251	0.999
3) Weber – Morris intra particle diffusion model			
C_0 (mg/l)	k_{id} (mg/g $min^{1/2}$)	C	R^2
50	0.0247	12.167	0.561
100	0.3324	20.569	0.6062
200	1.09	33.738	0.818

IV. CONCLUSION

The experimental study reveals that the PPSSC is an effective adsorbent for the removal of MB from aqueous solution. For lower Co, the percentage removal of MB was higher. The optimum dose of the PPSSC was found to be 4 g/l. The percentage removal increased towards alkaline nature of the adsorbate, and for $pH_0 \geq 4.0$, it showed almost maximum and constant dye removal, hence natural pH_0 7.2 is considered as optimum value. The equilibrium between the adsorbate in the solution and on the adsorbent surface was practically achieved in 90 minutes. Adsorption kinetics was found to follow second-order kinetics based on the correlation coefficients. The result obtained through this work concludes that, the Pongamia Pinnata Seed Shell Carbon can be employed as an effective low cost adsorbent for the removal of Methylene blue dye from aqueous solution.

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