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Journal of Advanced Scientific Research

Available online through http://www.sciensage.info

ISSN
0976-9595
Research Article

ADSORPTION DYNAMICS OF METHYLENE BLUE DYE ONTO SURFACE MODIFIED ACTIVATED CARBON PREPARED FROM *PTEROCARPUS MARSUPIUM* BARKS

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ABSTRACT

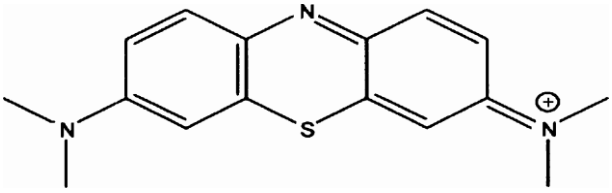
Pterocarpus Marsupium barks have been utilised to prepare activated carbon with the aid of orthogonal array experimental techniques with the parameters inclusive of microwave radiation energy, radiation time, concentration of H_3PO_4 acid and impregnation time. Radiation energy 850W, radiation time 15 min, 50% of H_3PO_4acid, impregnation time 24 hours were found to be the optimum conditions. Thus prepared carbon was designated as PBC (*Pterocarpus Marsupium* Bark Carbon). Surface of the PBC was modified with Hydrochloric acid solution and also separately with Potassium hydroxide solution. Influences of initial dye concentration on adsorption kinetics were studied. Kinetic models such as Pseudo first order, Pseudo second order and Intra Particle diffusion had been used to describe the mechanism of this adsorption process.

Keywords:

1. INTRODUCTION

Discharged wastewater through a few industries causes tremendous environmental problems. Natural water in our bodies such as ponds, lakes, rivers and their watershed would be subjected to critical environmental issue, if untreated effluent is discharged into them as such. Researchers have investigated the use of activated charcoal as an adsorbent for the elimination of dyes from the effluent water let out from big as well as tiny printing and dyeing units [1]. Adsorption method is mostly used as an effective approach for isolating organic and inorganic pollutants from water and waste water which involves carbon adsorption [2]. Activated carbon is the popular adsorbent for the elimination of many natural contaminants. The use of activated carbon for the adsorption method, however, activated carbon is expensive when produced from coal and hence limits its application. Therefore, less expensive activated carbon has to be produced from waste substances. Numerous investigations were stated the production of activated carbons from agricultural wastes [3]. A number of studies have been carried out using activated carbon prepared from agricultural wastes for the removal of dyes from aqueous solution [4, 5].

Many researchers used Methylene blue dye as a model adsorbate for adsorption of organic substance because of its known strong adsorbing ability on to activated carbon [6].



Structure of MB

In this study, a try has been made to know the adsorption dynamics of surface modified activated carbons prepared from the barks of *Pterocarpus Marsupium*. The *Pterocarpus Marsupium* tree produces brown woody barks.

Recently, microwave energy has been broadly utilized in the research field and business methods [7]. The microwave irradiation approach has come as an advantageous heating method in place of traditional muffle furnace heating techniques [8-10].

- Interior heating
- Choice of heating
- Extensive heating rates
- Good manage of heating method
- Small gadget size

- Reduced wastage production
- No direct touch among heating supply and heating substances.

2. MATERIAL AND METHODS

2.1. Preparation of Adsorbents

Small pieces of well dried barks were powdered in a pulveriser. 25 g of the powdered barks was mixed with 100mL of phosphoric acid solution of desired concentration (25, 50 and 75 %). To ensure the access of the H_3PO_4acid into the *Pterocarpus Marsupium* Barks, the slurry was kept at room temperature for 24 hours. Then the slurry was subjected to microwave heating under different conditions (450, 600 and 850 watts and 10, 13 and 15 minutes) for simultaneous carbonization and activation. Thus obtained carbonized samples were washed with distilled water at room temperature followed by 0.5 M HCl acid, hot distilled water and cold distilled water until the pH of the washings reach 7. Then the carbon was filtered and dried at 425 K.

H_3PO_4 acid generates more interspaces between carbon layers which gives more surface area and micro porosity to that carbon. H_3PO_4 acid activation causes swelling in the molecular structure of cellulose through electrolytic action, which leads to the breaking of lateral bonds in the cellulose molecules resulting in increased inter and intra voids.

Totally 27 number of activated carbons were prepared by varying preparation parameters. The carbon which is responsible for maximum percentage removal was chosen for further study and the chosen carbon was designated as PBC (*Pterocarpus Marsupium* Barks Carbon). 10 g of the PBCwas mixed with 25% solutions of HCl and also with KOH separately in two containers. They were heated in a microwave oven for 10 minutes. Then the carbons were again washed with hot distilled water and cold distilled water successively. HCl acid treated carbon was and designated as acid treated (Acid modified *Pterocarpus Marsupium* Barks Carbon) APBC and KOH treated carbon was designated as Base modified *Pterocarpus Marsupium* Barks Carbon BPBC.

2.2. Preparation of stock Solution

Analar grade Methylene blue dye belongs to Merck Company was used without in additional purification. 1000 mg/L dye stock solutionof was prepared using double distilled water. The experimental solutions were prepared from the stock solution by appropriate dilution.

2.3. Characterization of prepared carbons

Particle size (µm), Surface area (m^2/g), Pore volume (cm^3/g), Pore size or Pore width (nm), Bulk density (g/mL), Fixed Carbon (%), Moisture content (%) and pHzpc have been determined.

2.4. Adsorption experiments

The effect of parameters studied includes initial concentration of dye solution, adsorbent dose and contact time by batch mode approach due to its simplicity. Pre-determined dose of the adsorbent was taken in 250mL iodine flask having lid and 50mL and pre-determined concentration of the dye solution was poured into the flask. Then the content flask was agitated using rotary shaker (Orbit Company) with 180 rpm for a pre-determined duration. Then the aliquot was centrifuged. Concentration of the centrifugate was measured after necessary dilution using Systronics Double Beam UV-visible spectrophotometer: 2202 on the wave length of 680nm.

The kinetics experiments were carried out for the contact times 5, 10, 20, 40, 60, 80, 100, 120 and 140 minuteswith an operating solution pH of 7.

2.5. Data processing tools

2.5.1. Pseudo First order kinetics

Legergren equation is [11,12] was used for analysing pseudo first order kinetics. Legergren equation is$\log (q_e-q_t)=\log q_e - k_1/2.303 \times t$

Where q_e and $q_t$are the amounts of dye adsorbed (mg/g) at equilibrium and at time t (min), respectively and k_1 is the rate constant for this adsorptiondynamics (l/min).

2.5.2. Pseudo Second order kinetics

Ho equation is [13]

$t/q_t = 1/ k_2.q_e^2 + 1/q_e\, t$

The initial adsorption rate, h (mg/(g min)), as $t \rightarrow 0$ can be defined as

$h = k_2 q_e^2$

The initial adsorption rate (h), the equilibrium adsorption capacity (q_e), and the second-order constants k_2 (g/ (mg min)) can be determined experimentally from the slope and intercept of plot of t/q_tversus t.

2.5.3. Intra particle diffusion

Weber-Morrris equation is [14]

$q_t = k_p t^{1/2} + C$

Where $k_p$is the intra-particle diffusion rate constant, a plot of $q_t$versus $t^{1/2}$ should be a straight line with a slope

k_p which is the rate constant for intra particle diffusion and intercept C is the thickness of the boundary film.

2.5.4. Test for kinetics models

The Mean of sumoferrorsquaresisas follows;

MSSE (%) = $\sqrt{\sum[(q_e)_{exp}-(q_e)_{cal}]^2}$ / N

Where N is the number of data points, $(q_e)_{exp}$is the experimental q_e, $(q_e)_{cal}$ is the calculated q_e [12].

3. RESULTS AND DISCUSSION

3.1. Optimization of adsorbent preparation parameters

The prepared 27 carbons prepared under orthogonal array of experiments were subjected to remove MB dye from aqueous solution with 20 mg of the adsorbent, 50 mL of MB dye solution of concentration of 100mg/Land 1 hour agitation time. Percentage of removal increased with the increase of radiation time, radiation power and concentration of H_3PO_4 solution. Based on results, 50% H_3PO_4 solutions, radiation power 850 watts, radiation time 15 minutes and impregnation time 24 hours were chosen as optimum conditions.

3.2. Effect of contact time for different initial concentrations

The percentages of removal of MB from aqueous solution with respect to different contact times and with different initial concentrations were shown in Fig. 1-3.

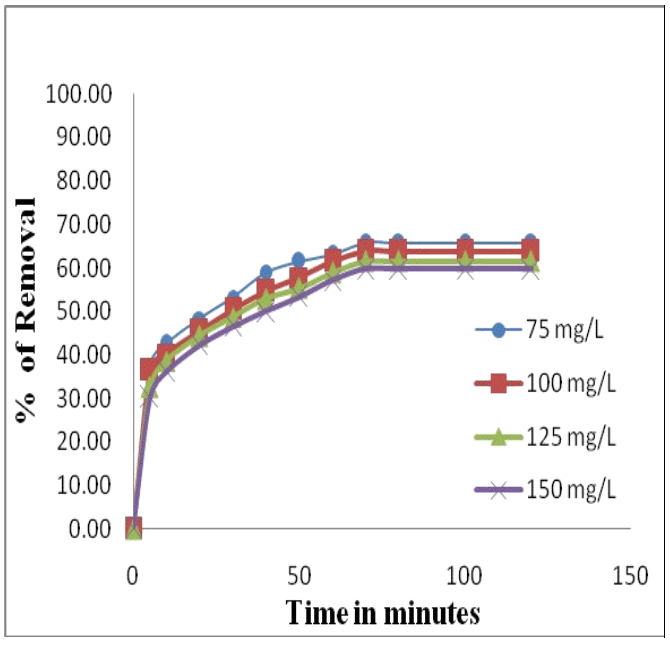


Fig. 1: Effect of contact time MB dye onto PBC

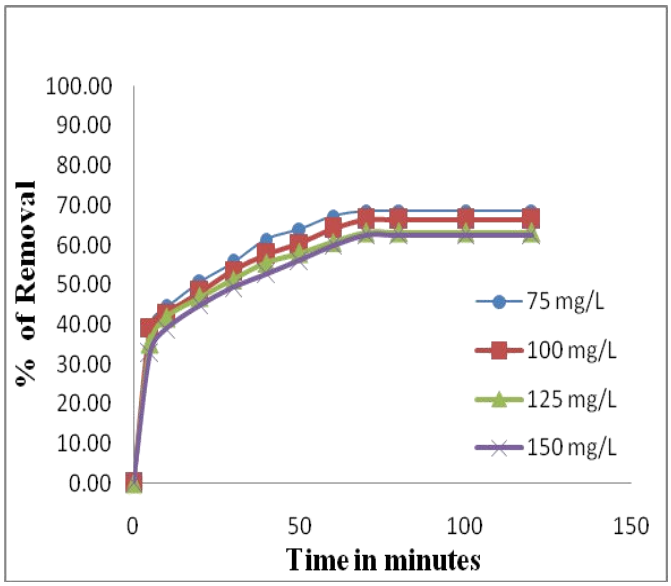


Fig. 2: Effect of contact time MB dye onto APBC

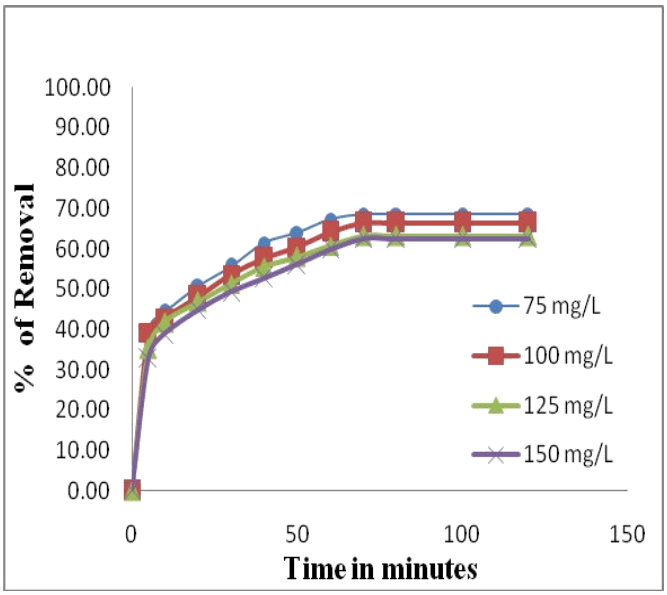


Fig. 3: Effect of contact time MB dye onto BPBC

The rapid uptake of the adsorbates in the initial stages is noticed as revealed by the curves. The percentage of removal increased with the increase in contact time and decreased with the increase of initial concentration of the dye. However the amount of dye adsorbed on the adsorbent increased with the increase of initial concentration of the dye solution as depicted in the Fig. 1-3. The time to attain equilibrium was found to increase when the initial concentration of the dye was increased were given in the table 1. The percentage of removal as well as the quantity adsorbed at equilibrium was found to be high for BPBC when compared to other carbons.

Table 1: Results for $C_i$vs % Removal and $C_i$vs qe

Ci	Temp	PBC		APBC		BPBC	
		% Removal	qe	% Removal	qe	% Removal	qe
75	305	65.74	49.31	64.50	48.38	68.51	51.38
	315	66.29	49.72	65.05	48.79	69.06	51.79
	325	66.83	50.13	65.59	49.20	69.60	52.20
	335	67.42	50.57	66.18	49.64	70.19	52.64
100	305	63.84	63.84	62.40	62.40	66.42	66.42
	315	64.51	64.51	63.07	63.07	67.09	67.09
	325	65.18	65.18	63.74	63.74	67.76	67.76
	335	65.91	65.91	64.47	64.47	68.49	68.49
125	305	61.45	76.81	60.40	75.50	63.21	79.01
	315	62.19	77.74	61.14	76.43	63.95	79.94
	325	62.95	78.69	61.90	77.38	64.71	80.89
	335	63.80	79.75	62.75	78.44	65.56	81.95
150	305	59.81	89.72	57.10	85.65	62.56	93.84
	315	60.08	90.13	57.37	86.06	62.83	94.25
	325	60.36	90.54	57.65	86.47	63.11	94.66
	335	60.65	90.98	57.94	86.91	63.40	95.10

3.3. Kinetic models

The adsorption kinetics shows the evolution of the adsorption capacity through time and it is necessary to identify the types of adsorption mechanism in a given system. Plots of different kinetic models applied were given in the Figs. 4-12 and the kinetic parameters calculated were given in the Tables 2-4.

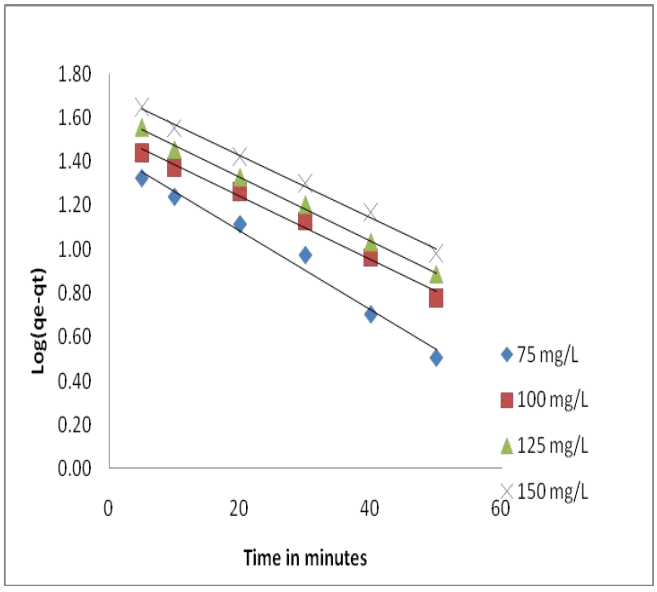


Fig. 4: Lagergren plot for MB dye onto PBC

Between the pseudo first order and pseudo second order, second order kinetic model seems to best describe the above adsorption system as it has R^2 values very close to unity. Moreover, difference between q_e (cal) and q_e (exp) values of pseudo second order is small when compared to pseudo first order kinetic model. Statistically it is tested with the tool mean sum of error squares (MSSE). The Δq_e and M SSE values were given in the Tables 2 & 3, from which it was concluded second order kinetic model was more appropriate rather than first order kinetic model.

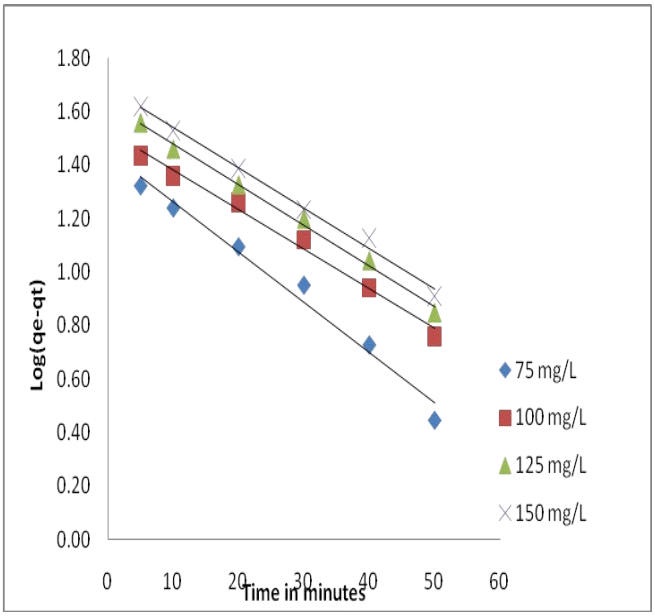


Fig. 5: Lagergren plot for MB dye onto APBC

Table 2: Pseudo first order Kinetic parameters for the removal of MB dye onto adsorbents

Adsorbents	Concentration mg/L	K_1 min^{-1}	q_e(Cal) mg/g	q_e(Exp) mg/g	R^2	MSSE
PBC	75	0.0415	27.80	49.31	0.9819	17.19
	100	0.0336	41.84	63.84	0.997	
	125	0.0327	51.25	76.81	0.9944	
	150	0.0332	33.78	89.72	0.9911	
APBC	75	2.7360	28.18	48.38	0.9794	16.19
	100	0.0350	42.67	62.40	0.9945	
	125	0.0348	48.98	75.50	0.9931	
	150	0.0341	33.77	85.65	0.9885	
BPBC	75	0.0408	28.26	51.38	0.9851	18.67
	100	0.0359	41.05	66.42	0.9945	
	125	0.0327	51.25	79.01	0.9944	
	150	0.0336	33.63	93.84	0.9943	

Table 3: Pseudo second order Kinetic parameters for the removal of MB dye onto adsorbents

Adsorbents	Concentration mg/L	k_2 $\times 10^{-4}$ g/mg.min	q_e(Cal) mg/g	H	R^2	MSSE
PBC	75	0.0037	51.5464	9.86	0.9962	1.95
	100	0.0025	67.1141	11.21	0.9945	
	125	0.0020	80.6452	13.21	0.9934	
	150	0.0015	95.2381	13.97	0.9934	
APBC	75	0.0038	50.7614	9.77	0.9964	1.80
	100	0.0025	65.7895	10.95	0.9944	
	125	0.0020	79.3651	12.72	0.9944	
	150	0.0018	90.0901	14.31	0.9947	
BPBC	75	0.0037	53.7634	10.57	0.9963	1.85
	100	0.0026	69.4444	12.56	0.996	
	125	0.0023	82.6446	15.43	0.9942	
	150	0.0016	99.0099	15.60	0.9942	

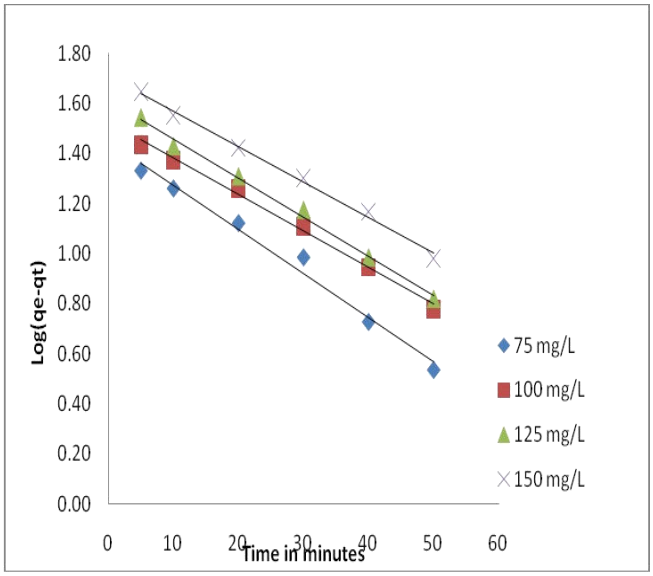


Fig. 6: Lagergren plot for MB dye onto BPBC

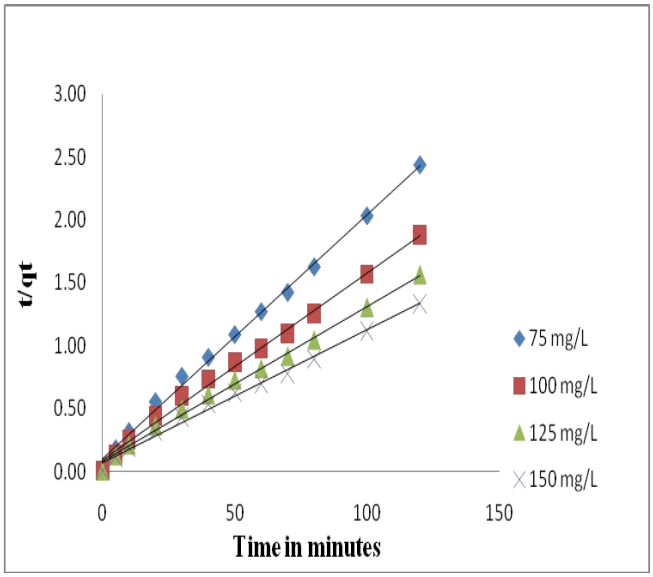


Fig. 7: Ho plot for MB dye onto PBC

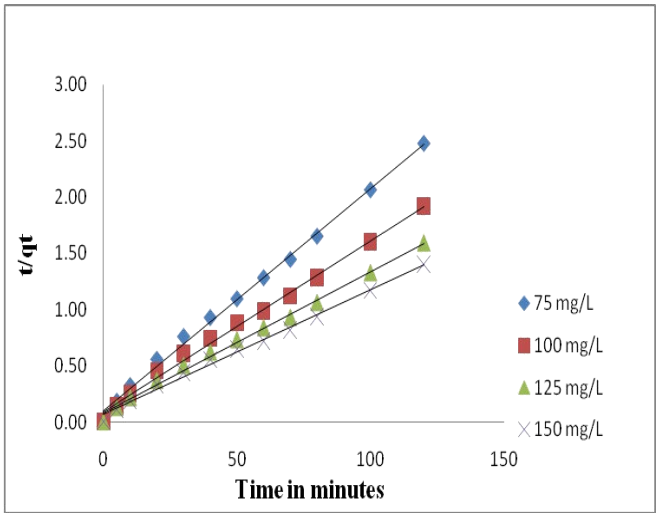


Fig. 8: Ho plot for MB dye onto APBC

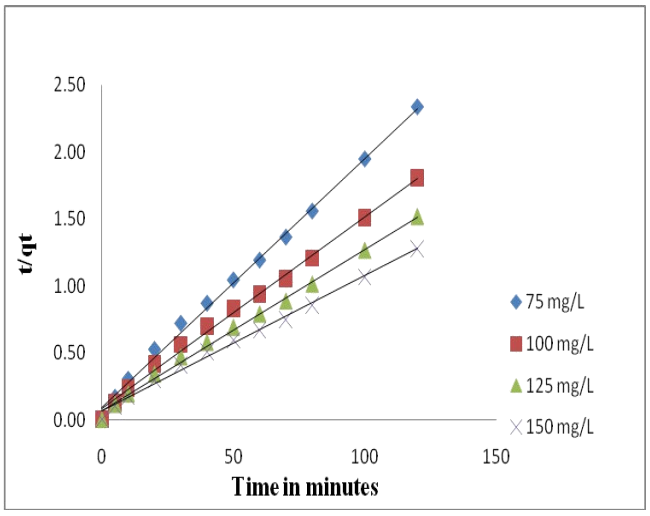


Fig. 9: Ho plot for MB dye onto BPBC

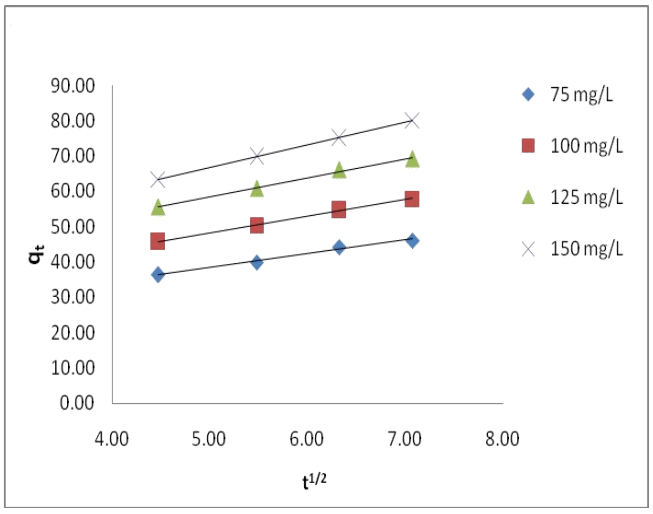


Fig. 10: Weber and Morris plot for MB dye onto PBC

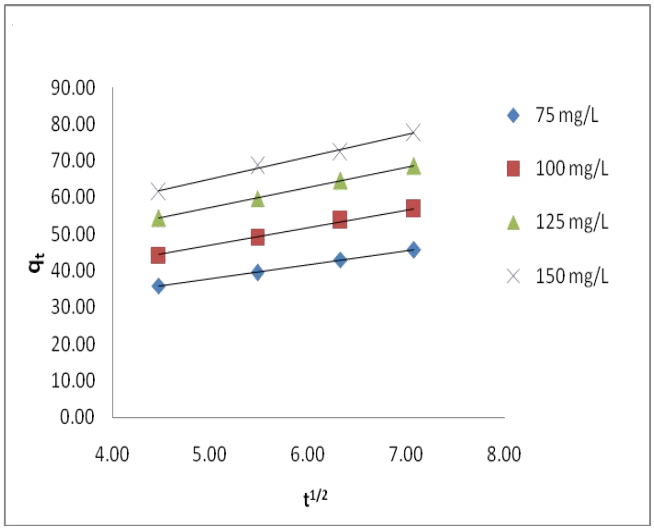


Fig. 11: Weber and Morris plot for MB dye onto APBC

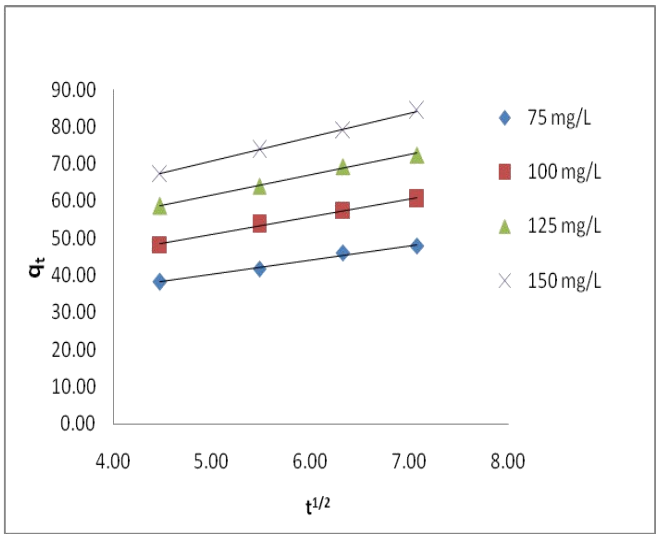


Fig. 12: Weber and Morris plot for MB dye onto BPBC

Table 4: Intra Particle diffusion parameters for the removal of MB dye onto adsorbents

Adsorbents	Concentration mg/L	k_p (mg/g.min)	R^2
PBC	75	3.93	0.9872
	100	4.73	0.9992
	125	5.37	0.9957
	150	6.44	0.9996
APBC	75	3.77	0.9983
	100	4.87	0.9975
	125	5.45	0.9999
	150	6.07	0.9921
BPBC	75	3.92	0.9882
	100	4.73	0.9947
	125	5.41	0.9952
	150	6.44	0.9996

Figs.10-12 show the final liner portions of plots drawn between mass of dye adsorbed per unit mass of adsorbent (q_t) versus $t^{1/2}$. These linear plots are attributed to the pore diffusion which is the accessible sites of adsorption. This is attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. The values of k_p obtained from the slopes of straight lines are listed in Table 4.

4. CONCLUSION

Microwave assisted H_3PO_4 activated carbons (PBC, APBC and BPBC) were prepared from *Pterocarpus Marsupium barks* found to have good capacity of adsorption. Experimental data indicated that PBC, APBC and BPBC were effective in removing MB dye from aqueous solution. Equilibrium adsorption was achieved in about 70 minutes for the dosage of 20 mg/50 mL of solution at room temperature of 305 K for the initial concentration of dye solutions ranging from 75 to 150 mg/L. Kinetic studies revealed that the process of adsorption follows pseudo second order kinetics. Adsorption studies inferred that KOH surface modified carbon was more effective than other adsorbents for the adsorption of MB dye. Order of best fitting kinetic model according to increasing R^2 value and MSSE was found as Second Order>First Order.

Carbons	Average R^2		MSSE	
	First Order	Second Order	First Order	Second Order
PBC	0.9911	0.9944	17.19	1.95
APBC	0.9889	0.9950	16.19	1.80
BPBC	0.9921	0.9952	18.67	1.85

Conflict of interest

None declared

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