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Research Article

ISOTHERM MODELLING - ADSORPTION OF N-BLUE DYE IONS ONTOMICRO WAVE ASSISTED *PTEROCARPUS MARSUPIUM* BARK CARBON

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ABSTRACT

An adsorption N-Blue dye ions from aqueous solution on MWPMBC (Micro Wave assisted *Pterocarpus Marsupium* Bark Carbon) has been investigated. Analytical techniques have been employed to find characteristics of adsorbent materials. The adsorption of N- Blue dye ions was conducted in batch system. The effects of pH, adsorbent dosage and initial concentrations of N- Blue dye ions and contact time on adsorption efficiency were studied. Optimum adsorption was achieved at a pH 3 and equilibrium was established within 70 & 80 min of the process. The equilibrium adsorption data were analysed using four adsorption isotherm models: Langmuir, Freundlich, Temkin, Dubinin-Radushkevich isotherms. It is concluded that MWPMBC can be used as an effective adsorbent for removing N- Blue dye ions from aqueous solution.

Keywords: Adsorption, MWPMBC, N- Blue dye ions, Isotherm model.

1. INTRODUCTION

Dye has always been very essential in nature and environment and it carry on to play a very important role in reporting interesting hues to plants, animals and in the lives of mankind. After the dyeing process, the residual and unspent substances are usually discharged into the environment. Amongst the different industrial wastewaters with different types of colour-causing substances, synthetic textile organic dye wastes occupy a prominent position [1]. The colloidal matter can often be carcinogenic; show allergic reactions; interfere with photosynthesis; clog the pores of the soil; be a breeding ground for bacteria and viruses. It is significant to remove these pollutants from the waste waters before their final disposal [2-4].

Adsorption of organics from solutions on activated carbon is one of the oldest and widespread applications of this material. Earlier studies of activated carbon adsorption were carried out on fatty acids and later extended to a large number of dyes [5].

Treatment technologies are available for the abatement of dye ions from aqueous solutions are precipitation, ion exchange, bioremediation and adsorption. Adsorption is preferred because of it is high efficient, easy to handle and cost effective [6-10].

The present study is undertaken to evaluate the efficiency of an adsorbent prepared from a *Pterocarpus Marsupium* Bark by Micro Wave assisted $ZnCl_2$ activation for the removal of N-Blue dye ions from aqueous solution.

2. MATERIAL AND METHODS

2.1. Preparation of Activated Carbon

The MWPMBC carbon was prepared from *Pterocarpus Marsupium* bark through microwave oven. Firstly; *Pterocarpus Marsupium* barks were collected and cut into small pieces. The material was thoroughly mixed with different concentration of $ZnCl_2$ solution heat-treated at 850 Win Microwave oven for 12 minutes. After that, found samples were washed thoroughly with dilute hydrochloric acid (HCl) and deionized water up to the pH values reached 7.0 and finally dried at 100°C.

2.2. Preparation of synthetic effluent

An accurate weight (1g) of N Blue dye ions was dissolved in 1 L of distilled water to produce the stock solution of synthetic effluent. These stock solutions were then diluted into the required concentrations using distilled water whenever necessary.

2.3. Adsorption Experiments:

Known weight of the adsorbent was taken in 250 mL iodine flask and 50 mL of N blue dye ions solution of known concentration was poured into the flask. Desired pH of the solution was obtained by adding drops of dil. HCl or NaOH solutions. Then the content of the flask was agitated using rotary shaker at 130 rpm for a period of pre-determined duration. Then adsorbent was separated by centrifugation and the concentration of the centrifuge was determined by Double Beam UV-visible Systronics Spectrophotometer: 2202 at 625 nm. To understand the influence of contact time on the percentage removal, experiments were carried out with the dosage of 40 mg/50 mL and with 50 mL of N Blue dye ions solutions of 15, 20 and 25 mg/L [11].

The amount of N Blue dye ions adsorbed in milligram per gram of adsorbent was determined by using the following mass balance equation:

$$q_e = (C_i-C_e)V/W$$

Where C_i and C_e are N Blue dye ions concentrations (mg/L) before and after adsorption, respectively, V is the volume of adsorbate in litre and m is the weight of the adsorbent in grams. The percentage of removal of N Blue dye ions was calculated using the following equation:

$$\text{Removal } (\%) = (C_i-C_e)/C_i \times 100$$

3. RESULTS AND DISCUSSION

3.1. Effect of adsorbent dosage

The adsorption of N Blue dye ions onto MWPMBC was studied by varying the dose of the adsorbent from 10 mg/50 mL to 100 mg/50 mL by taking 50 mg/L of all the adsorbates. The percentage of removal of adsorbate from aqueous solution increased with an increase of carbon dose in all the cases, shown in Fig. 1. This is due to the increased carbon surface area and the availability of more adsorption sites [12]. This was attributed to the increased carbon surface area and the availability of more adsorption sites. Based on these results, the remaining parts of the experiments were carried out with the adsorbent dose of 40 mg/50 mL of adsorbate solution.

3.2. Effect of Contact time and initial concentration

The effect of contact time on percentage removal of N Blue dye ions for different initial concentration is shown in Fig.2. Adsorption of N Blue dye ions from the solution increases with the time and finally attains equilibrium in 70 to 80 minute for the initial concentrations of adsorbate 15, 20 and 25 mg/L respectively. 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. The percentage of removal and amount of dye adsorbed were given in table1.

Table 1: Percentage of removal and amount of dye adsorbed

C_i (mg/L)	% of Removal of dye at equilibrium	Adsorbed amount of N Blue dye at equilibrium (mg/g)
15	73	10.95
20	67	13.40
25	59	14.75

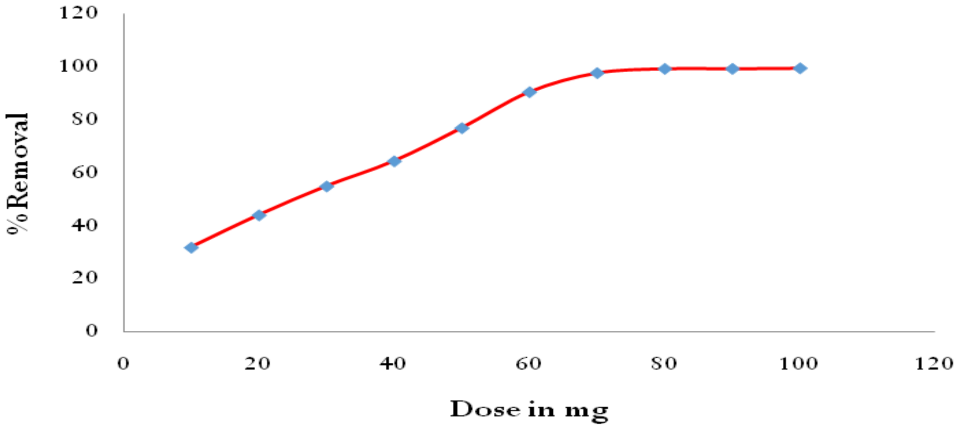

Fig. 1: Effect of Dose- N-Blue dye onto MWPMBC

3.3. Effect of pH

The pH of the solution plays an important role for determining the quantity of solute adsorbed because the pH of the solution affects the functional groups of the activated carbon and also alters the surface charge of the carbon and governs the speciation of the solute. Here adsorption studied ranged in between pH 2-11.

The effect of pH on the % removal of solute from the aqueous phase was detected to be varying for different solutes for the same adsorbent depending upon the nature of the solute.

In the case of N Blue dye ions, the highest dye ions removal efficiency was attained at pH 3, as shown in Fig. 3. N Blue dye generates negative charged dye ions when dissolved in water.

When the pH is lower than pH_{zpc}, the charge on the surface of the adsorbent is positive. At very low pH, the positive charge accumulates on the surface of the adsorbent and facilitates more adsorption of dye anions. Moreover at low pH, the concentration of OH^- ions was very meagre.

3.4. Effect of Temperature

It is well known that temperature plays an important role in the adsorption process. The dye removal increase rapidly from 305, 315, 325 and 335 K this result suggests that the experimental temperature had a greater effect on the adsorption process implying that the surface coverage increased at higher temperatures were shown in Fig. 4. This may be attributed to the increased penetration of metal ions inside micro pores or the creation of new active sites at higher temperatures. This indicates the endothermic nature of the controlled adsorption process. Similar result has been reported in the literature [12].

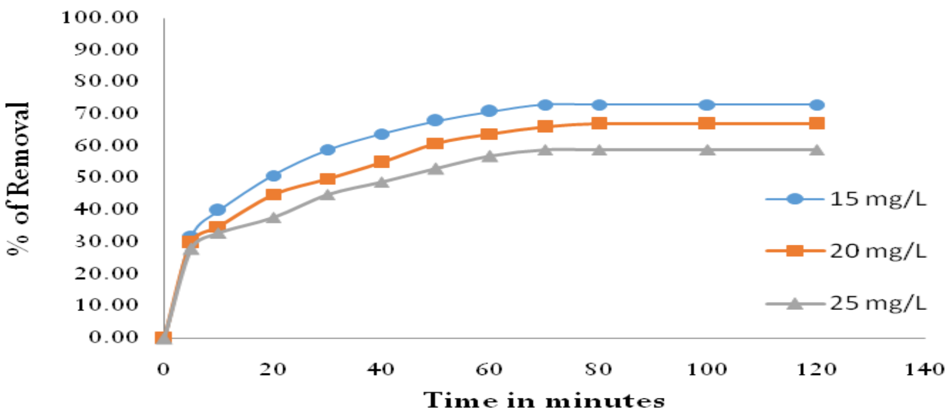

Fig. 2: Effect of contact time for N-Blue dye onto MWPMBC

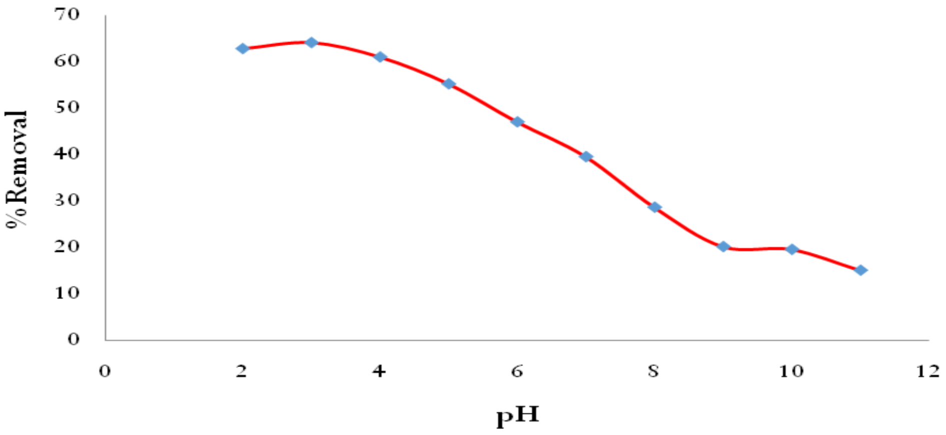

Fig. 3: Effect of pH - N-Blue dye onto MWPMBC

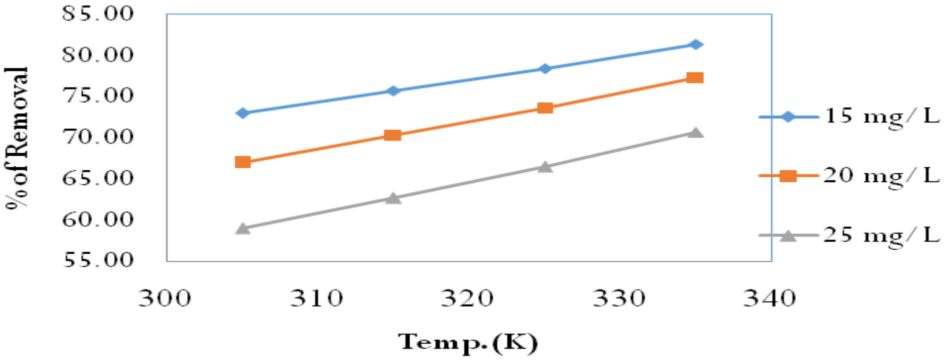

Fig. 4: Temperature vs % of Removal for N-Blue dye onto MWPMBC

3.5. Isotherm studies

The equilibrium between the two phases (liquid and solid state) is rationalized by absorption isotherm. The equilibrium data obtained from the experiments were processed with the following isotherm equations such as Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich adsorption isotherm models. Inference obtained from each isotherm are discussed herein.

3.5.1. Langmuir isotherm:

The Langmuir isotherm describes the monolayer adsorption onto a surface containing a finite number of identical binding sites [13-17]. The linearized form of the Langmuir equation is given as

$$C_e/q_e = 1/q_m b + C_e/q_m$$

Where 'q_m' is the maximum adsorption capacity for monolayer coverage, 'b' is a coefficient related to the affinity between the sorbent and the sorbate [18-14]. Dimensionless equilibrium parameter 'R_L' is defined by the following equation [19-15].

$$R_L = 1/(1 + bC_0)$$

Where; $C_0$is that the initial concentration of the adsorbate in the solution. The separation factor R_L value indicates the nature of the adsorption process as given below:

R_L value	Nature of the process
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

3.5.2. Freundlich isotherm

The Freundlich isotherm is an empirical model based on adsorption onto a heterogeneous surface. The linearized form of the Freundlich isotherm [20-16] is expressed as:

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

Where,

'K_f' (mg/g) is the constant indicative of the relative adsorption capacity and 'n' value related to intensity adsorption.

3.5.3. Tempkin isotherm

Tempkin isotherm adopts that the temperature of sorption in the film reductions linearly with the attention due to the sorbate/sorbent interactions. Moreover, the drop in heat of absorption is not logarithmic, as stated in the Freundlich expression. The linear form of Tempkin equation is [21].

$$q_e = RT/b_T \ln a_T + RT/b_T \ln C_e$$

Where, b_T is the constant associated to the temperature of sorption (J/mg) and a_T the equilibrium binding constant equivalent to the maximum binding energy (L/g) The constants a_T and b_T were calculated from the slopes and intercepts of q_e versus $\ln C_e$

3.5.4. Dubinin-Radushkevich isotherm:

The Linear form of Dubinin-Radushkevich isotherm is [22]

$$\ln q_e = \ln q_D - B\varepsilon^2$$

Where q_D is the theoretical enrichment potential (mg/g) B is a constant relative to the average free energy of sorption per mole of sorbate (mol^2/J^2) and ε is polanyi energy, which is related to equilibrium as given below

$$\varepsilon = RT \ln (1+1/C_e)$$

The Q_D and B constants were calculated from the straight line slope and intercept obtained from the plot of $\ln q_e$ versus ε^2. The average free energy of sorption E calculated from B using the following equation [23].

$$E = 1/(2B)^{1/2}$$

E is a parameter used in forecasting the type of sorption. An E value less than 8 kJ/mol is a suggestion of physic-sorption.

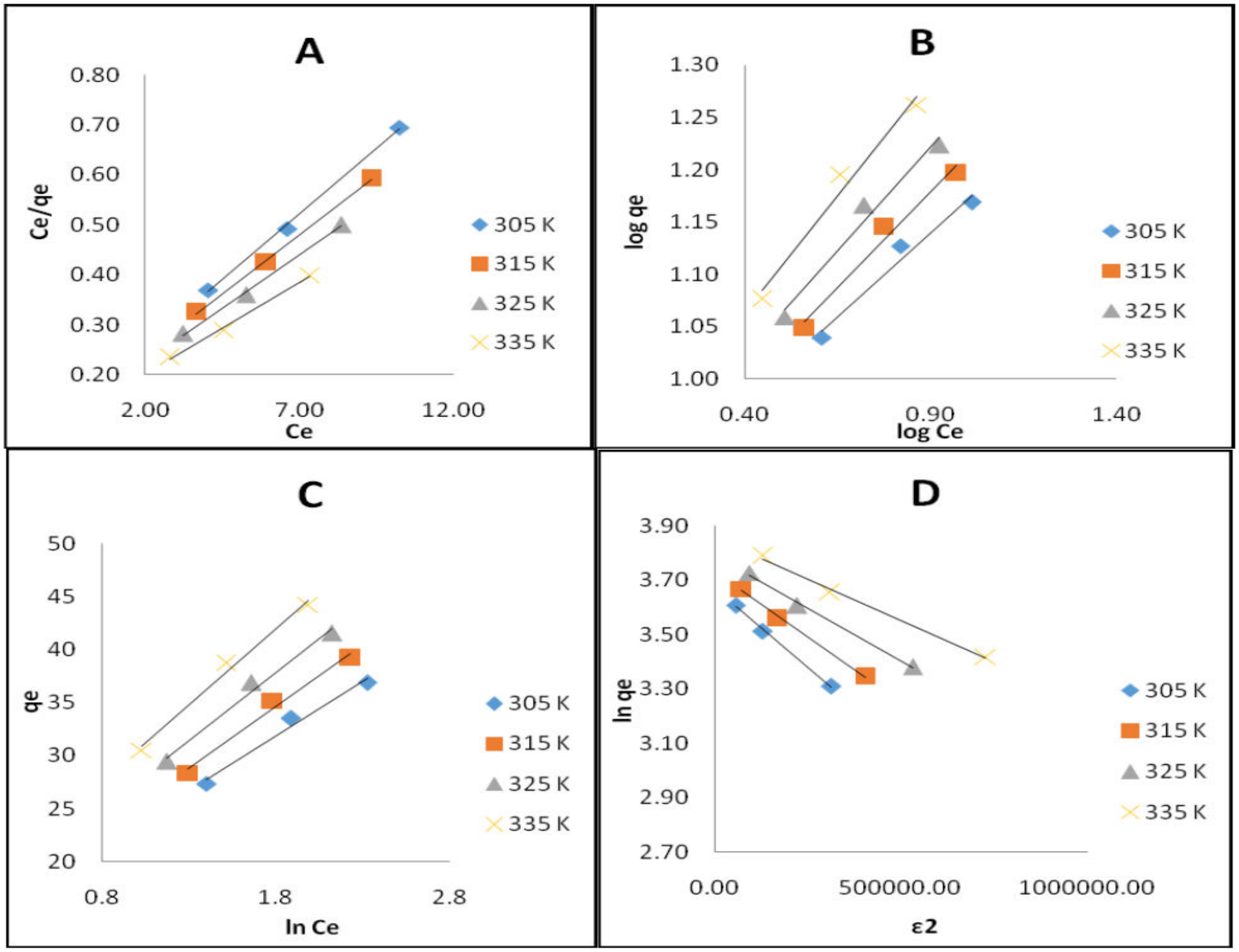

Fig. 5: [A, B, C & D] Langmuir, Frendlich, Temkin & Dubinin-Raduskevich Isotherms for N-Blue dye ions onto MWPMBC

Table 2: Results of various isotherms plots for the adsorption of NBlue dye ions onto MWPMBC

Isotherms	**Temp (K)**	**Parameters and their results**			
		Q_0 (mg/g)	**b**	**R_L**	**R^2**
Langmuir	305	19.011	0.345	0.1618	0.9985
	315	21.186	0.314	0.1750	0.9987
	325	23.419	0.305	0.1399	0.9979
	335	27.100	0.289	0.1875	0.9967
Freundlich		n	k_f (mg/g^{-1})		R^2
	305	3.1008	7.0746		0.9705
	315	2.7480	7.0909		0.9772
	325	2.5113	7.3063		0.9760
	335	2.2467	7.6878		0.9768

		B_1 (J/mg)	K_T (L/g)	R^2
Temkin	305	195.78	3.1535	0.9817
	315	211.46	3.1913	0.9847
	325	227.39	3.3400	0.9872
	335	246.88	3.6722	0.9889
Dubinin Raduskevich		q_D(mg/g)	E (kJ/mol)	R^2
	305	644.7318	0.5239	0.9979
	315	607.1921	0.5222	0.9970
	325	560.5170	0.5203	0.9961
	335	522.6292	0.5169	0.9955

3.5.5. *Analysis of Isotherms*

3.5.5.1. Langmuir isotherm

In the present study Q_0 value ranges from 19.01 to 27.10, as the temperature increases the monolayer adsorption capacity also found to increase. This kind of results were obtained in various similar studies [24].The separation factor R_L values in between 0 to 1 indicates the favourable adsorption.R^2 values of isotherm ranged "between" 0.9987 to 0.9967.R^2 values were close to unity which reached to good fitting intoLangmuir isotherm.

3.5.5.2. Frendlich Isotherm

The values of n were between 1 and 10 which indicates cooperative adsorption [25]**.** The R^2 value was low compared to Langmuir, Temkin and D-R isotherms.

3.5.5.3. Temkin Isotherm

B_1-Temkin constant is related to the heat of adsorption. This B_1 value increased from 195.78 to 246.88as the temperature of adsorption increased. Temkin parameter K_T value give on idea about nature of adsorption [26]. In our present study the K_T values ranged from 3.1535 to 3.6722 which indicate the adsorption is physical nature. The R^2 value waslow compared to Langmuir and D-R isotherms.

3.5.5.4. Dubinin-Raduskevich

The activation energy E value ranges from 0.5239 to 0.5169. It was indicate that physic sorption [27]. The R^2 value was very low when compared to Langmuir isotherms. In general the fitting data in isotherm equation were in the following order Langmuir > Dubinin-Raduskevich>Temkin>Frendlich.

4. CONCLUSION

This is concluded that MWPMBC can be used effectively for the removal of N Blue dye ions from aqueous solution. The adsorption of N Blue dye ions onto MWPMBC increased with the increasing of initial concentration of N Blue dye ions. The adsorption equilibrium data was well described by the Langmuir isotherm when compared to other three isotherms such as Freundlich, Temkin and Dubinin-Radushkevich.

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