



REMOVAL OF N-BLUE DYE IONS ONTO MICROWAVE ASSISTED *PTEROCARPUS MARSUPIUM* BARK CARBON-KINETICS STUDY

G. Abinaya, S. Sivajiganesan*, V. Nandhakumar, S. Surya

PG & Research Department of Chemistry, A.V.V.M. Sri Pushpam College
(Affiliated to Bharathidasan University), Poondi, Thanjavur (Dt), Tamil Nadu, India

*Corresponding author: avvmsspccsg@gmail.com

ABSTRACT

Removal of N-Blue dye ions from aqueous solution onto MWPMBC (Microwave assisted *Pterocarpus Marsupium* Bark Carbon) has been examined. 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 kinetics models; Pseudo first order, Pseudo second order, Intraparticle diffusion. 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, Kinetic models.

1. INTRODUCTION

Dye has always been very essential in nature and environment and it carry onto 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, ionexchange, bioremediation and adsorption. Adsorption is preferred because it is high efficient, easy to handle and cost effective [6-10].

The present study was undertaken to evaluate the efficiency of an adsorbent prepared from *Pterocarpus*

Marsupium Bark by Microwave assisted ZnCl₂ 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 Micro Wave oven. Firstly; *Pterocarpus Marsupium* bark were collected and cut into small pieces. Then the materials were thoroughly mixed with different percent concentration of ZnCl₂ solution, heat-treated at 850 Win Microwave oven for 15 minutes. Afterwards, the samples were wash thoroughly with dilute hydrochloric acid (HCl) and deionized water till pH values reached 7.0 and finally dried at 100°C.

2.2. Preparation of synthetic effluent

An accurate weight of 1gram of N Blue dye ions were dissolved in 1 L of distilled water to produce the stock solutions 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 250mL iodine flask and 50mL of N blue dye ions solution of known concentration was poured into the flask. Desired

pH of the solution was brought by adding drops of dil. HCl or NaOH solutions. Content of the flask was then agitated using rotary shaker at 180 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 effects of contact time on percentage removal of N Blue dye ions for different initial concentrations have been 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 table 1.

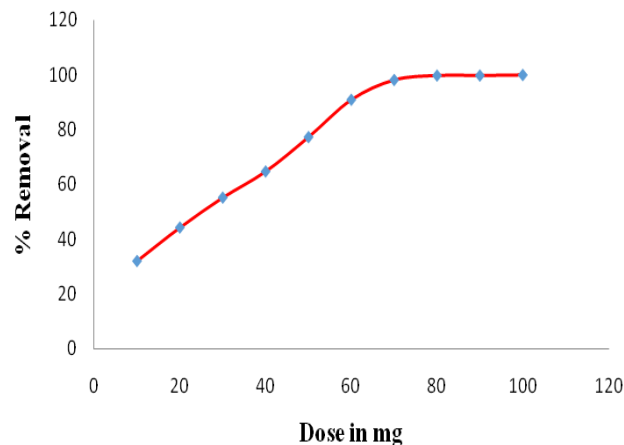


Fig. 1: Effect of Dose - N-Blue dye onto MWPMBC

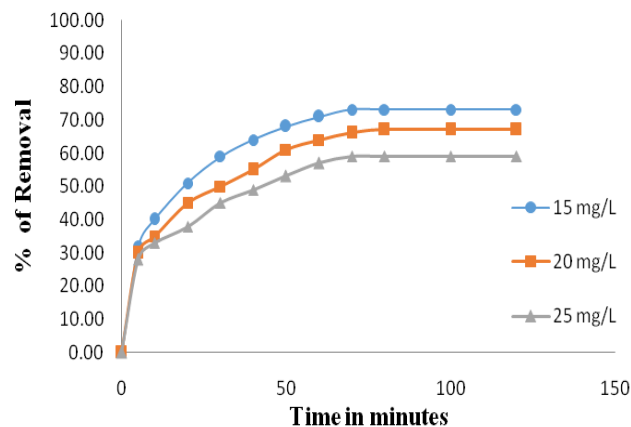


Fig. 2: Effect of contact time for N-Blue dye onto MWPMBC

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

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 was studied ranges in between pH 2-11.

The effect of pH on the % removal of solute from the aqueous phase was detected to be varied 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.

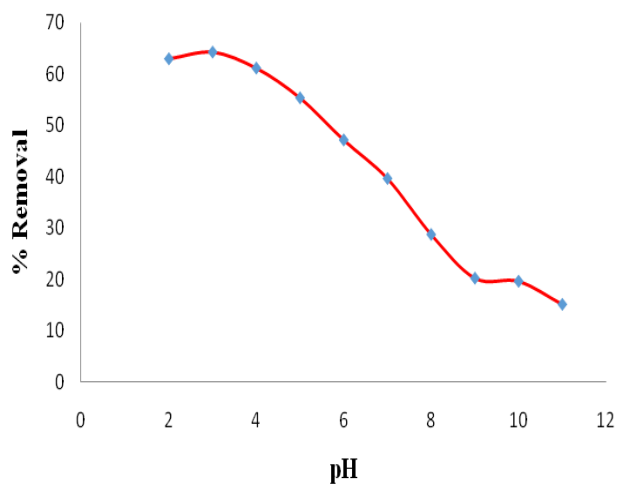


Fig. 3: Effect of pH - N-Blue dye onto MWPMBC

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].

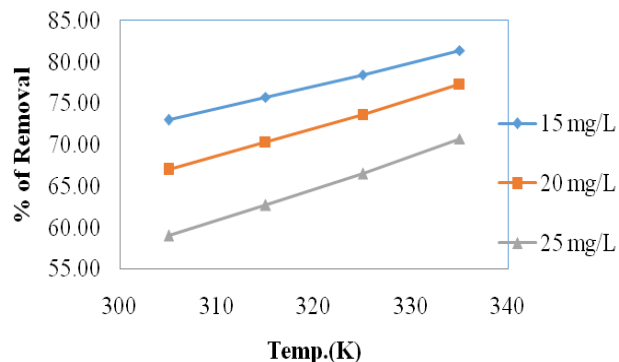


Fig. 4: Temperature vs % of removal for N-Blue dye onto MWPMBC

3.5. Kinetic Models

3.5.1. Pseudo First order kinetics

Legergren equation is [13]:

$$\log(q_e - q_t) = \log q_e - k_1 / 2.303 \times t$$

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 of adsorption (l/min).

3.5.2. Pseudo Second order kinetics

Ho equation is [14]:

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

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_t versus t .

3.5.3. Intra particle diffusion

Weber-Morris equation is [15]:

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

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.

3.5.4. Test for kinetics models

The sum of error squares is given as 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 [16].

In practice, kinetic studies were carried out in batch reactions using various initial sorbate concentrations. Sorption kinetic models have been proposed to clarify the mechanism of sorption from aqueous solution to on an adsorbent. Several adsorption kinetic models have been established to understand the adsorption kinetics and rate-limiting step. These include pseudo-first and second-order rate model, Weber and Morris [17] sorption kinetic models. The first order rate constant, k_1 (min^{-1}) ranged from 0.0398 to 0.0493. The pseudo first order theoretical adsorption capacity ($q_{e, \text{cal}}$) values, obtained from the intercept of the linear plots, were compared with the experimental adsorption capacity ($q_{e, \text{exp}}$) values. The initial sorption rate “h” increases directly with the increase of initial N-Blue dye concentration at each temperature for MWPMBC adsorbent, while an inverse relationship exists between the overall sorption rate and initial N-Blue dye concentration for MWPMBC adsorbent.

The analysis of the results obtained in the present study with two kinetic models is presented in table 2 & 3 and shown in fig. 5 & 6. Among the first order and second order, second order kinetic model seems to best describe the above adsorption system as it has R^2 value which was very close to unity. Moreover, the difference between calculated adsorption capacity ($q_{e, \text{cal}}$) and experimental adsorption capacity ($q_{e, \text{exp}}$) values of second order is little when compared to the first order kinetic model. Statistically, it is tested with the tool mean sum of error squares (MSSE) [20]. The K_p values were found to increase with an increase of N-Blue dye concentration that reveals the rate of adsorption governed by the diffusion of adsorbed N-Blue dye within the pores of the adsorbent, which were given in table 4 and shown in fig. 7. Present results show that pore diffusion limits the overall rate of N-Blue dye adsorption [18].

Table 2: First order Kinetic parameters for the removal of N-Blue dye onto adsorbents

Concentration mg/L	K_1 min^{-1}	$q_e(\text{Cal})$ mg/g	$q_e(\text{Exp})$ mg/g	R^2	MSSE
15	0.0493	9.00	11.67	0.9855	1.55
20	0.0417	10.82	14.39	0.9631	
25	0.0398	11.38	15.80	0.9608	

Table 3: Second order Kinetic parameters for the removal of N-Blue dye onto adsorbents

Concentration mg/L	$k_2 \times 10^{-4}$ g/mg.min	$q_e(\text{Cal})$ mg/g	h	R^2	MSSE
15	0.0124	11.6686	1.69	0.9946	0.54
20	0.0084	14.3885	1.73	0.9914	
25	0.0080	15.7978	2.00	0.9911	

Table 4: Intra Particle diffusion parameters for the removal of N-Blue dye onto adsorbents

Concentration mg/L	k_p (mg/g.min)	R^2
15	0.9780	0.9908
20	1.2175	0.9880
25	1.4243	0.9923

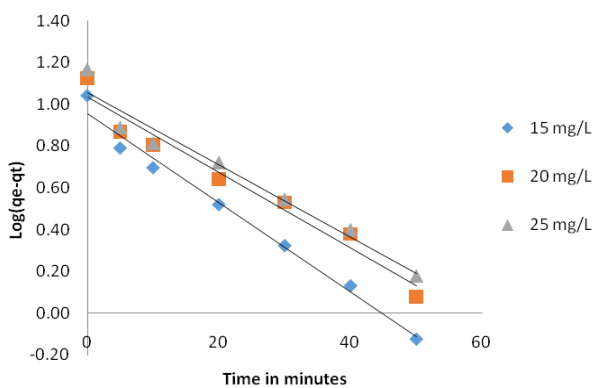


Fig. 5: Lagergren plot for N-Blue dye onto MWPMBC

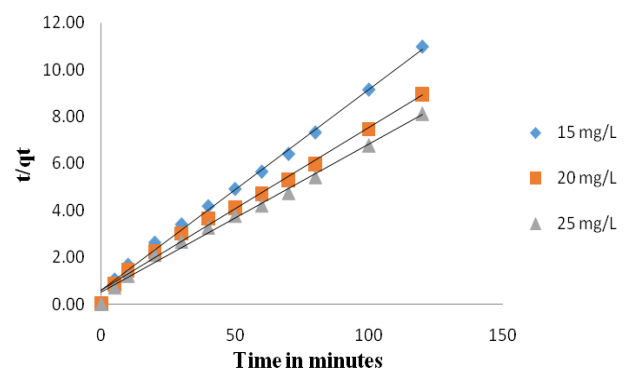


Fig. 6: Ho plot for N-Blue dye onto MWPMBC

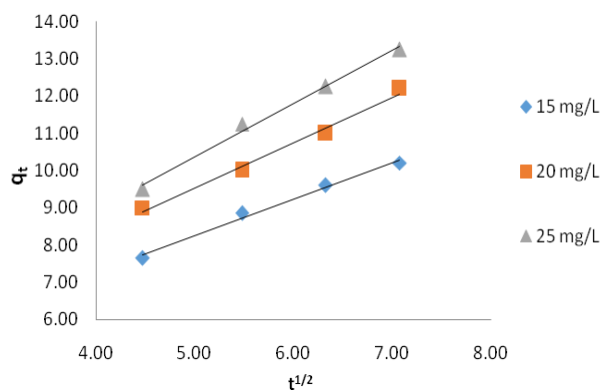


Fig. 7: Weber and Morris plot for N-Blue dye onto MWPMBC

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 of N-Blue dye onto adsorbent was pH-dependent process with the maximum removal efficiency at the initial pH of 3.0. Adsorption processes for N-Blue dye was found to follow the pseudo second-order kinetics rate expression. The MSSE confirmed the intraparticle diffusion as the rate-limiting step in the dye adsorption process.

Conflict of interest

None declared

5. REFERENCES

- Vijayraghavan NS, *Science Tech. Entrepreneur*, 1999; **7**:3.
- Mahajan SP, "Pollution Control in Process Industries", Summer Report, 5. IIT Bombay.
- Whitaker and Hillock; "Dyeing and Coal tar Dyestuff", 1949; **5th ed.** 1.
- Edwaed, M. *Developments in Waste Water Treatment Methods*, 2003; **27**.
- Bansal M. Ph. D. Thesis, Panjab University, Chandigarh, 1997; 2 & 12.
- Hasan S, Ghosh TK, Viswanath DS, Boddu VM, *Journal of Hazardous Materials*, 2008; **152**:826-837.
- Arivoli S. Ph. D. Thesis, Gandhigram Rural University, Gandhigram. 2007.
- Paul Chen J, Wu Shunnian Wu, Kai Hau Chong, *Carbon*, 2003; **41**:1979-1986.
- Vijayaraaghavan K, Jegan J, Palanivel K, Velan M, *J. Chem. Engg.* 2005; **106**:177-184.
- Sekaran G, Shanmugasundaram KA, Mariappan M, Raghavan KV. *J. Chem. Technol.* 1995; **2**:311.
- Selvarani K, PhD. Thesis, Regional Engineering College, Thiruchirapalli, 2000.
- Sych NV, Trofymenko SI, Poddubnaya OI, Tsyba MM, Sapsay VI, Klymchuk DO, Puziy AM, *Applied Surface Science*, 2012; **261**:75-82.
- Ali MMS, EL-SAI N, GIRGIS BS, *International Journal of Computational Engineering Research*, 2014; **04**:70-78.
- Javier Blanco Castro, R Pablo. Bonelli, Elsa G. Cerrella, Ana Cukierman L, *Ind. Eng. Chem. Res.* 2000; **39**:4166-4172
- Lagergren S, Svenska BK. Zurtheorie der sogenannten adsorption geloesterstoffe. *Vetenskap-sakad. Handl.* 1982; **24**, 1, 1898.
- McKay G, Ho YS, *Process Biochemistry*, 1999; **34**:451.
- Weber Jr WJ, Morris JC, *Journal of the Sanitary Engineering Division, American Society of Civil Engineers* 1963; **89**:31.
- Ramesh K, Rajappa A, Roopa, NandhakumarV, *Int. J. Curr. Res. Chem. Pharma. Sci.*, 2014; **1**:28-36.