ADSORPTION OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTION ONTO MICRO WAVE ASSISTED ACTIVATED CARBON PREPARED FROM PHYILLANTHUS EMBLICA SEEDS

Thenmozhi M[1] , Palanivel C[2]
[1]Assistant Professor, Department of Chemistry,
Krishnasamy College of Science, Arts & Management for Women, Cuddalore.
[2]Associate Professor, Department of Chemistry,
Govt.Arts College, C.Mutlur, Chidambaram, Cuddalore.
Affiliated to Thiruvalluvar University, Serkkadu, Vellore – 632 115.
rthen90@gmail.com[1], palanivelchem@gmail.com[2]

ABSTRACT
Adsorption of Methylene Blue dye ions from aqueous solution onto MWPESAC (Micro Wave assisted Phyillanthus Emblica Seeds Activated Carbon) has been examined. Analytical techniques have been employed to find characteristics of adsorbent materials. The adsorption of Methylene Blue dye ions was conducted in batch system. The effects of pH, adsorbent dosage and initial concentrations of Methylene Blue dye ions and contact time on adsorption efficiency were studied. Optimum adsorption was achieved at a pH 7 and equilibrium was established at 70 min of the process. The equilibrium adsorption data were analysed using three adsorption Kinetics models: Pseudo first order, Pseudo second order and Intra particle diffusion. It is concluded that MWPESAC can be used as an effective adsorbent for removing Methylene Blue dye ions from aqueous solution.

Keywords: *Adsorption, MWPESAC, Methylene Blue dye ions and Kinetic models.*

1.0 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 Phyillanthus Emblica Seeds by Micro Wave assisted $ZnCl_2$ activation for the removal of Methylene Blue dye ions from aqueous solution.

2.0 Materials and Methods

2.1 Preparation of Activated Carbon:

The MWPESAC carbon was prepared from Phyillanthus Emblica Seeds through Micro Wave oven. Firstly; Phyillanthus Emblica Seeds were collected and cut into small pieces. Then the materials were

thoroughly mixed with different % concentration of $ZnCl_2$ solution heating at 700 W in Microwave oven for 10 minutes. After that, the found samples were wash away thoroughly with dilute hydrochloric acid (HCl) and deionized water up to the pH values reached 7.0 and finally dried at 100ºC and stored in desiccators for further studies.

2.2 Preparation of synthetic effluent:

An accurate weight of 1gram of Methylene 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 250 mL iodine flask and 50 mL of Methylene 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. 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 665 nm. To understand the influence of contact time on the percentage removal, experiments were carried out with the dosage of 30 mg/50 mL and with 50 mL of Methylene Blue dye ions solutions of 75, 100, 125 and 150 mg/L [11].

The amount of Methylene Blue dye ions adsorbed in mg/g 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 Methylene 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 Methylene Blue dye ions was calculated using the following equation.

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

3.0 Result and Discussion:

3.1 Effect of adsorbent dosage

The adsorption of Methylene Blue dye ions onto MWPESAC 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 Figure1. 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 30 mg/50 mL of adsorbate solution.

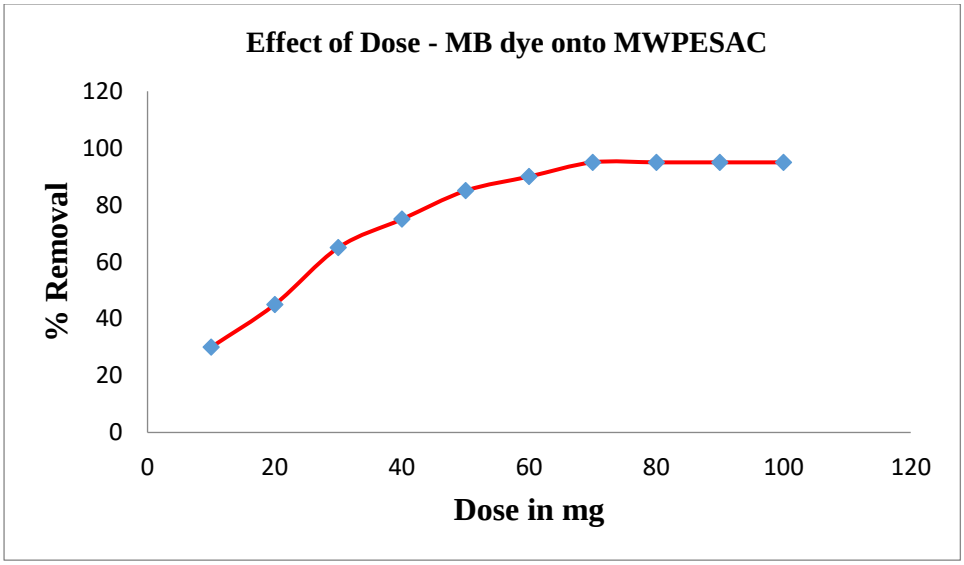

Figure 1: Effect of Dose for MB dye onto MWPESAC

3.2 Effect of Contact time and initial concentration:

The effect of contact time on percentage removal of Methylene Blue dye ions for different initial concentration have been shown in figure 2. Adsorption of Methylene 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 75, 100, 125 and 150 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.

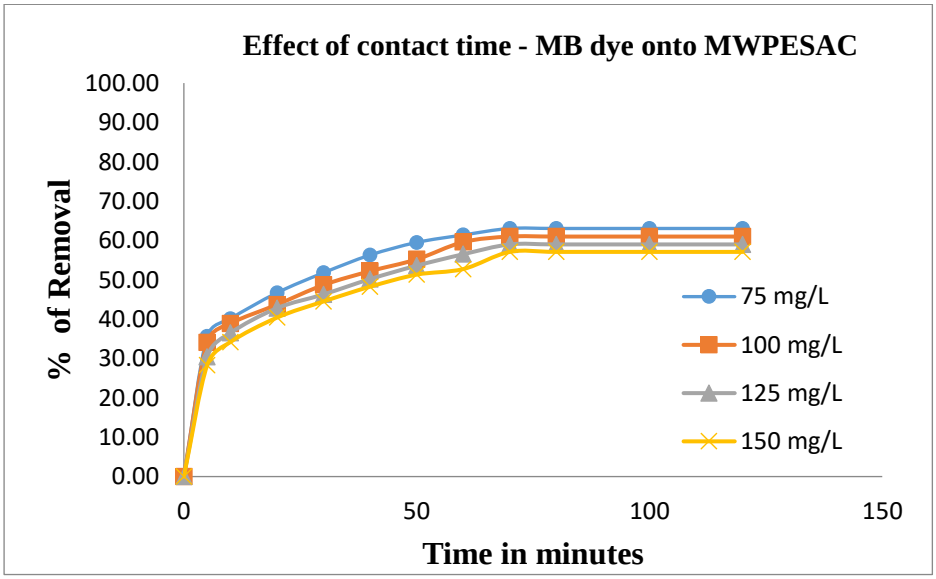

Figure 2: Effect of contact time for MB dye onto MWPESAC

Table 1: Percentage of removal and amount of dye adsorbed

C_i (mg/L)	% of Removal of dye at equilibrium	Adsorbed amount of MB dye at equilibrium (mg/g)
75	63.05	47.29
100	61.00	61.00
125	59.00	73.75
150	57.10	85.65

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 Methylene Blue dye ions the highest dye ions removal efficiency was attained at pH 7, as shown in Figure: 3. Methylene Blue dye ions generates negative charged dye ions when dissolved in water.

When the pH is higher 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.

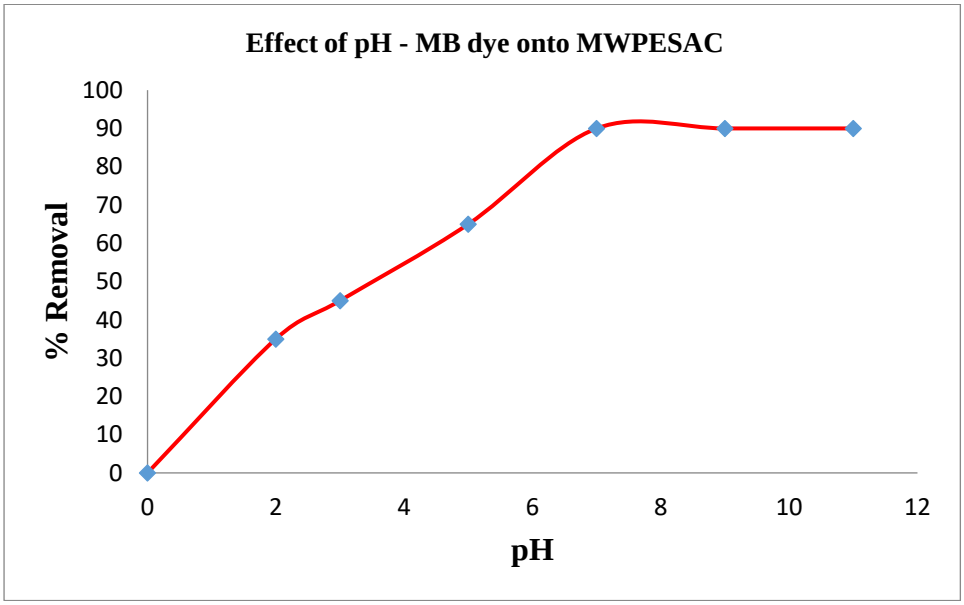

Figure 3: Effect of pH for MB dye onto MWPESAC

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 figure: 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].

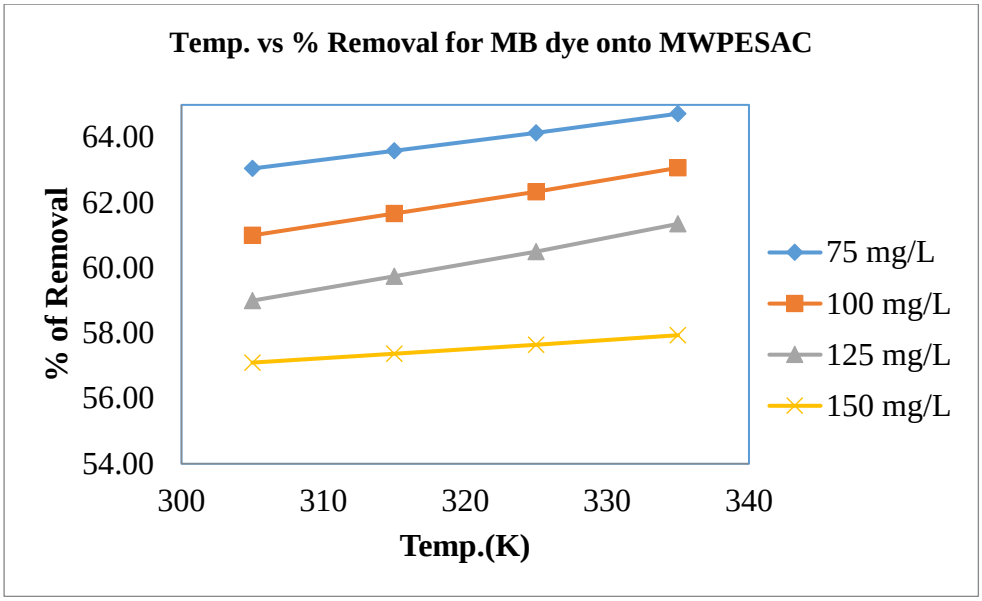

Figure 4: Temperature vs % Removal for MB dye onto MWPESAC

4.0 Kinetic Models

4.1 Pseudo First order kinetics

Legergren equation is [13]

$\log (qe-qt) = \log qe - k1 /2.303 \times t$

Where qe and qt 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).

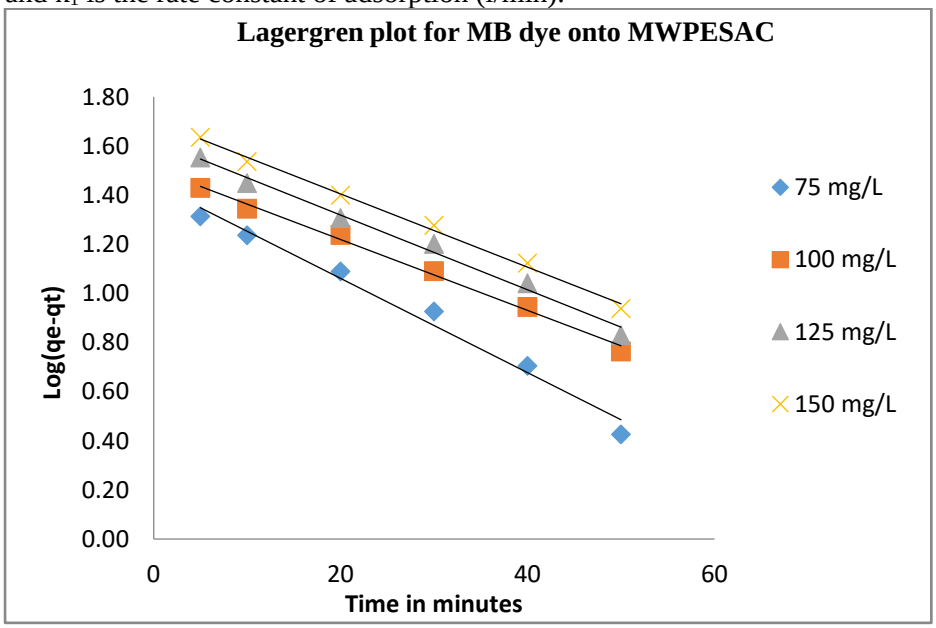

Figure 5: Lagergren plot for MB dye onto MWPESAC

4.2 Pseudo Second order kinetics

Ho equation is [14]

$t/qt = 1/ k_2.qe^2 + 1/qe\ t$

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

$h = k_2 qe^2$

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

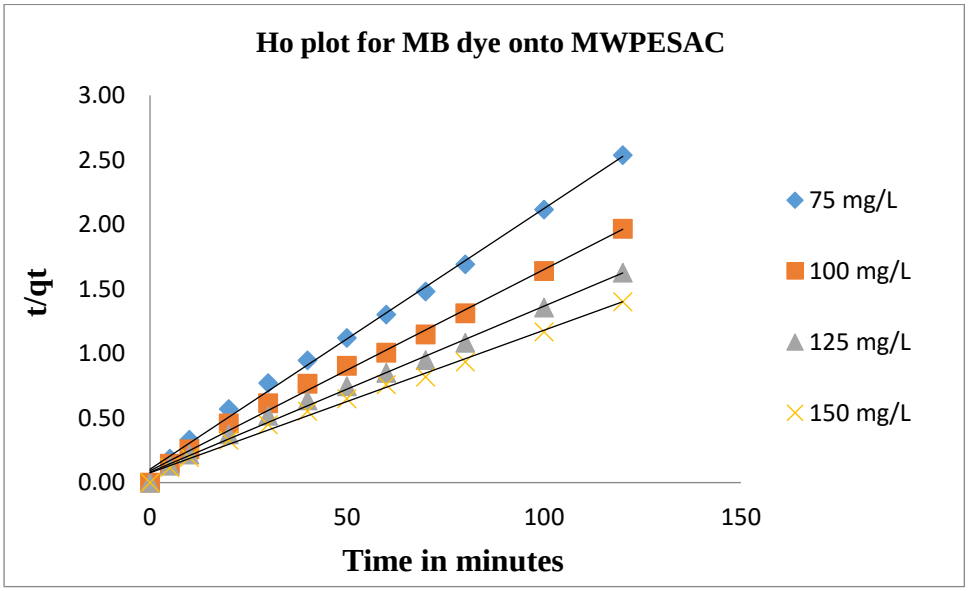

Figure 6: Ho plot for MB dye onto MWPESAC

4.3 Intra particle diffusion

Weber–Morris equation is [15]

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

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

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

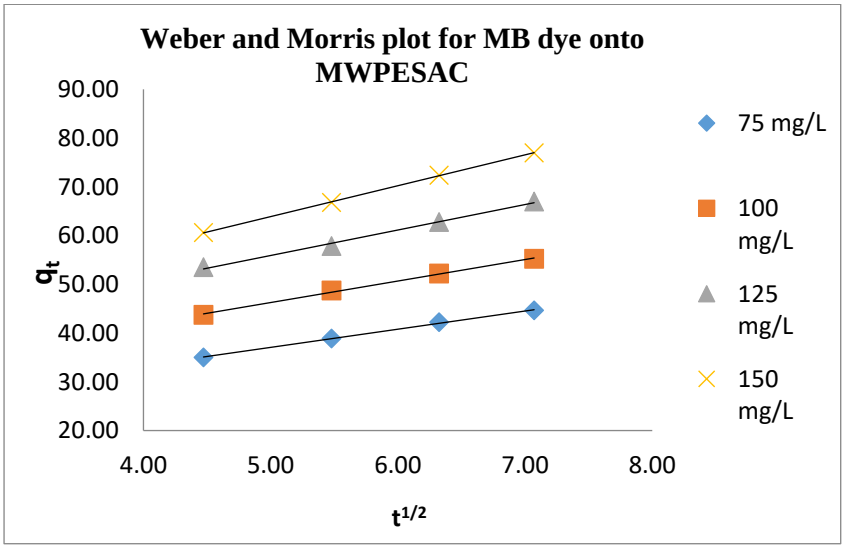

Figure 7: Weber and Morris plot for MB dye onto MWPESAC

4.4 Test for kinetics models

The sum of error squares is given as follows;

$MSSE = \sqrt{\Sigma} [(qe)exp - (qe)cal]^2 / N$

Where N is the number of data points, (qe)exp is the experimental qe, (qe)cal is the calculated qe [16].

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

Adsorbent	**Concentration mg/L**	**K_1 min^{-1}**	**q_e(Cal) mg/g**	**q_e(Exp) mg/g**	**R^2**	**MSSE**
MWPESAC	75	0.0421	27.6630	47.29	0.9860	16.11
	100	0.0350	41.9662	61.00	0.9897	
	125	0.0343	50.4429	73.75	0.9957	
	150	0.0332	32.1662	85.65	0.9947	

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

Adsorbent	**Concentration mg/L**	**$k_2 \times 10^{-4}$ g/mg.min**	**q_e(Cal) mg/g**	**h**	**R^2**	**MSSE**
MWPESAC	75	0.0037	48.54	08.65	0.9959	0.60
	100	0.0026	62.11	10.05	0.9941	
	125	0.0020	75.19	11.36	0.9940	
	150	0.0016	84.75	11.17	0.9924	

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

Adsorbents	**Concentration mg/L**	**kp (mg/g.min)**	**R^2**
MWPESAC	75	3.7295	0.9985
	100	4.4115	0.9971
	125	5.2269	0.9953
	150	6.3338	0.9998

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 0.0332 to 0.0421. The pseudo first order theoretical adsorption capacity (qe_{cal}) values,

obtained from the intercept of the linear plots, were compared with the experimental adsorption capacity (qe_{exp}) values. The initial sorption rate h increases directly with the increase of initial MB dye concentration at each temperature for adsorbent, while an inverse relationship exists between the overall sorption rate and initial MB dye concentration for adsorbent.

The analysis of the results obtained in the present study with two kinetic models is presented in Table 2 & 3 and shown in Figures 5 & 6. Between 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 (qe_{cal}) and experimental adsorption capacity (qe_{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). The Kp values were found to increase with an increase of MB dye concentration that reveals the rate of adsorption governed by the diffusion of adsorbed MB dye within the pores of the adsorbent, which were given in Table 4 and shown in Figure 7. Present results show that pore diffusion limits the overall rate of MB dye adsorption [18].

5.0 Conclusion:

This is concluded that MWPESAC can be used effectively for the removal of Methylene Blue dye ions from aqueous solution. The adsorption of MB dye ions onto MWPESAC increased with the increasing of initial concentration of adsorbate. The adsorption of adsorbate onto adsorbent was pH-dependent process with the maximum removal efficiency at the initial pH of 7.0. Adsorption processes for adsorbate was found to follow the pseudo second-order kinetics rate expression. The MSSE confirmed the intra particle diffusion as the rate-limiting step in the dye adsorption process.

6.0 Acknowledgement

The authors greatly acknowledge the Principal, Research supervisor and Head, Department of Chemistry of Govt. Arts College, C. Mutlur, Chidambaram, Cuddalore for the support rendered for the completion of the work.

7.0 Conflict of Interest

The authors declare no conflict of interest.

8.0 References:

[1] Gupta, V.K and Suhas, A.I.,. Application of low-cost adsorbents for dye removal--a review. J. Environ. Manage. 2009, 90, 2313– 42.

[2] Hameed, B.H. and El-Khaiary, M.I.,. Equilibrium, kinetics and mechanism of malachite green adsorption on activated carbon prepared from bamboo by K_2CO_3 activation and subsequent gasification with CO_2. J. Hazard Mater. 2008, 157-344.

[3] Hesler, J.C., Recovery and Treatment of Metal Finishing Wastes by Ion Exchange Plating. 1955, 42, 1019-1029.

[4] Intidhar Jabir Idan, Siti Nurul Ain Binti Md & Jamil,. Removal of Reactive Anionic Dyes from Binary Solutions by Adsorption onto Quaternized Kenaf Core Fiber. International Journal of Chemical Engineering, 2017, Article ID 9792657, 13.

[5] Jafar Ahamed, A., and Shajudha Begum, A. Adsorption of copper from aqueous solution using low cost adsorbent. Arch. Appl. Sci. Res., 2012, 4, (3):1532-1539.

[6] Kadirvelu, K., Thamaraiselvi, K., Namasivayam, C. Adsorption of nickel (II) from aqueous solution onto activated carbon prepared from coir pith. Separation and Purification Technology. 2001, 24, 497–505.

[7] Kavitha, D. and Namasivayam, C. Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. Bio resource Technology. 2007, 98, 14–21.

[8] Li, W., Zhang, L.b., Peng, J.h., Li, N. and Zhu, X.y.,. Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbo. Ind Crops Prod., 2008, (27), 341-347.

[9] Martin, M.J., Adriana, A., Balaguer, D.M., Rigola, M. Towards waste minimization in WWTP: Activated carbon from biological sludge and its application in liquid phase adsorption. Journal of Chemical Technology and Biotechnology. 2002, 77, 825-833.

[10] McKay, G. and Ho, Y.S., Pseudo-Second Order Model for Sorption. Processes Bio chem., 1999,.34, 451- 465.

[11] Mekala Suneetha,. Removal of fluoride from polluted waters using active carbon derived from barks of Vitex negundo plant. Journal of Analytical Science and Technology, 2015, 6, 15, 2-19.

[12] Mishra, A. and Bajpai, M., The flocculation performance of Tamarindus mucilage in relation to removal of vat and direct dyes. Bio resource Technol. 2006, 97, 1055–1059.

[13] Murty, M.N., Surender Kumar.,. Water Pollution in Indian. Economic Appraisal, India Infrastructure Report. 2011, 285–298.

[14] Namasivayam, C., Kavitha, D. IR, XRD and SEM Studies on the Mechanism of Adsorption Of Dyes and Phenols by Coir Pith Carbon from Aqueous Phase. Microchemical Journal. 2006, 82, 43–48.

[15] Norman, L.M., Cha, C.Y.,. Preparation and characterization of activated carbon from wood via microwave-induced $ZnCl_2$ activation. Chem. Eng. Commun. 1996, 40, 87.

[16] Palanisamy, P.N., Agalya, A. and Sivakumar,P. Effciency of activated carbon and white charcoal from textile dyeing industry in synthetic wastewater. Indian Journal of Chemical Techonology., 2011, 20, 245-251.

[17] Ravikumar, M.N.V., Sridhari, T.R., Bhavani, K.D. and Dutta, P.K. Decolorization of Dyeing Wastewater Using Polymeric Absorbents - An Overview. Colorage. 1998, 40, 5–34

[18] Ray, A.B., Selvakumar, A., Tafuri, A.N.,. Removal of selected pollutants from aqueous media by hardwood mulch. Journal of Hazardous Materials. 2006, 136, 213-218.