Carbon – Science and Technology

Evaluation of dynamics and equilibrium models for the sorption of Basic Violet 3 on activated carbon prepared from Moringa oleifera fruit shell waste

C. Sumithra [(A)], S. C. Murugavel [(B)], S. Karthikeyan [(C, *)]

(A) Department of Chemistry, Tejaa Shakthi Institute of Technology for Women, Karumathampatti, Coimbatore-641659, TN, India.
(B) Department of Basic Sciences, PSG College of Technology, Coimbatore-641004, TN, India.
(C) Department of Chemistry, Chikkanna Government Arts College, College Road, Tirupur-641602, TN, India.

The feasibility of activated carbon prepared from *Moringa oleifera* fruit shell waste to remove Basic Violet 3 from aqueous solution was investigated through batch mode contact time studies. The surface chemistry of activated carbon is studied using Boehm titrations and pH of PZC measurements indicates that the surface oxygenated groups are mainly basic in nature. The surface area of the activated carbon is determined using BET method. The kinetics of Basic Violet 3 adsorption are observed to be pH dependent. The experimental data can be explained by Pseudo second order kinetic model. For, Basic Violet 3, the Langmuir model is best suited to stimulate the adsorption isotherms.

----

1. Introduction :

The industrial processes utilize toxic chemicals for the manufacture of finished products, the unused parts of which escape into the environment as industrial waste-wash [1]. Synthetic dyes have been extensively excreted in the waste water from different industries, particularly from textile, paper, rubber, leather, cosmetic and drug industries which used dyes to colour their products. These dyes rank among the most notorious organic contaminants that are discharged into the environment [2, 3]. Basic violet 3, a member of triphenylmethane group, is extensively used in animal and veterinary medicine as a biological stain, for identifying the bloody figure prints being a protein dye and in various commercial textile operations [4]. It is carcinogenic and has been classified as a recalcitrant molecule since it is poorly metabolized by microbes is non-biodegradable and can persist in a variety of environments [5].

Hence its removal from waste waters before its discharge is essential for environmental safety.

Well known porous materials called activated carbons have wide range of properties and physical forms making them to be prominently used in many applications. They are extensively used in variety of industrial and environmental applications [6, 7]. Adsorption using activated carbon is an effective purification and separation technique used for the removal of dyes from waste water. The following adsorbents sludge biomass [8], fly ash [9], palm kernel fiber [10] were used for the removal of Basic violet 3 from waste waters. Several low cost carbon and non conventional adsorbents have been given. Adsorbents used *Pongamia pinnata* [11], Fly ash [12], *Jatropha curcas* [13], Tree fern [14], *Feronia limonia* [15], *Leucaena leucocephala* [16] etc., The aim of the present work is to investigate the removal of Basic Violet 3 from aqueous solutions by adsorption onto activated

carbon prepared from *Moringa oleifera* fruit shell waste activated carbon (MOAC).

2. Materials and Methods :

2.1. Properties of Basic Violet 3 :

The schematic of the molecular structure of Basic Violet 3 [$C_{25}H_{30}ClN_3$], Molecular weight 407.99 a cationic dye used in the present study is shown in the Figure (1). The pKa of the dye was 9.4 [17].
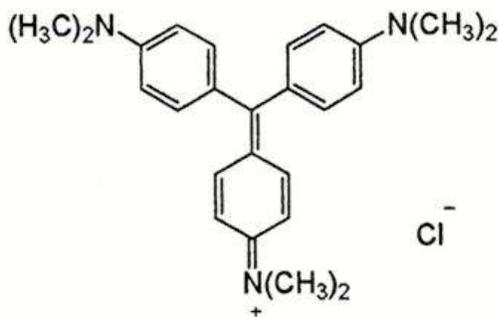

Figure (1) : Schematic of the molecular structure of Basic Violet 3 Dye.

2.2. Preparation and Characterization of Activated Carbon :

Moringa oleifera fruit shell waste is collected and it was dried and cut into small pieces. The pieces were then impregnated with a potassium carbonate solution of known concentration for 24 hours. Then the resultant mass was washed with the excess quantity of water and dried at the 110 ^{o}C for 1 hour. Carbonization of the sample was carried out at 650 ^{o}C in a temperature programmable furnace under N_2 atmosphere. At the end of carbonization, the material in the furnace was left to cool down to ambient temperature under the same N_2 flow rate. The carbon sample thus obtained was washed with pure distilled water and dried in the oven at 120 ^{o}C and then finely grinned [18]. The powdered MOAC was characterized by Scanning Electron Microscopy SEM (HITACHI S 3000N). The content of oxygen–containing functional groups with acidic character and basic character was determined by applying Boehm method [19]. Point of Zero charge describes the shape when the electrical charge density on a surface is null. It is

normally found in relation to the electrolyte pH and pH$_{ZPC}$ value is attributed to the substratum [20].

The N_2 adsorption-desorption isotherms of MOAC were measured at 77 K using N_2 gas sorption analyser (Nova 1000, Quanta Chrome Corporation). From this isotherm, the BET specific surface area (S_{BET}) was determined in the relative pressure range of 0.05 to 0.3 [21]. The t-plot method was applied to calculate the micropore volume and external surface area (Mesoporous surface area). The total pore volume was estimated using liquid volume of adsorbate (N_2) at a relative pressure of 0.99 [22]. All the surface areas were calculated from the nitrogen adsorption isotherms by assuming the area of a nitrogen molecule was 0.162 nm^2.

2.3. Dye Adsorption Measurements :

All reagents used were of AR-grade (E-merk). Different concentration of dye solution of Basic Violet 3 was prepared with distilled water. Batch mode adsorption studies were held out by adding 50 mg of the adsorbent and 50ml of dye solution of certain concentrations, varying pH and temperatures in a thermostated water bath shaker. The samples were withdrawn from the shaker at predetermined time intervals and the solutions were separated from the adsorbent by centrifugation. The concentrations of dyes in the solutions were determined before and after adsorption using Elico UV visible spectrophotometer. The initial dye concentrations in the test solution and contact time were varied to investigate their effect on dynamic and equilibrium studies. The pH of the dye solution was adjusted by using NaOH or HCl solution. The adsorption studies were carried out at different temperatures. The amount of dye adsorbed q (mg/g) and adsorption efficiency was calculated as follows:

$$q = \frac{(c_0 - c_e)v}{m} \tag{1}$$

$$\text{Adsorption Efficiency(\%)} = \frac{(c_0 - c_e)}{c_0} * 100 \tag{2}$$

where, C_o = initial dye concentration (mg/L)
C_e = equilibrium concentration (mg/L)

V = volume of solution (ml)
M = mass of adsorbent (g)
C = residual dye concentration (mg/L)
q = amount adsorbed (mg/g)

3. Results and Discussion :

3.1. Characteristics of Activated Carbon :

The SEM image of the MOAC is presented in the Figure (2). The prepared activated carbon shows the development of porous structure. This might be ascribable to the detrital effect of Potassium carbonate activation process which often results in well-developed internal porosity [23].The oxygen content originates from the oxygenated surface groups. The amount of oxygenated functional groups was obtained by Boehm Titration and is presented in Table (1). This shows that MOAC is rich in basic functional groups.
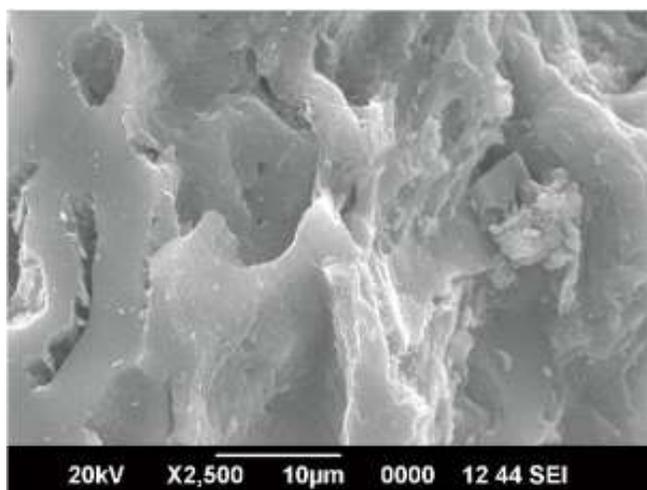

Figure (2) : SEM image of *Moringa oleifera* fruit shell waste activated carbon (MOAC).

No.	Chemical Groups	Concentration mmol/g
1	Carboxyls	2.5
2	Lactones	0.35
3	Bases	5.25

Table (1) : Concentration of surface groups and pHzpc of MOAC.

The pH$_{ZPC}$ value of the carbon is calculated from the Figure (3). The value obtained is 8.2 which is in agreement with the rather basic surface chemistry of the carbon materials. At pH<pH$_{ZPC}$, the carbon surface has a net positive charge, while at pH >pH$_{ZPC}$, the surface has a net negative charge. The complete dissociation of the Basic violet 3 takes place above its pKa value and the dye molecule is in its cationic form and acquires a positive charge. This favors the adsorption of dye molecule on to MOAC above pH 9.0. Similar results were shown by Raffiea Baseri et al. [24] for the adsorption of basic dyes on *Thevetia peruviana.*
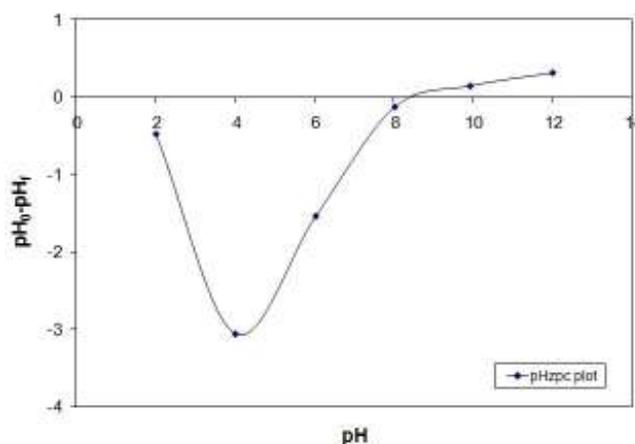

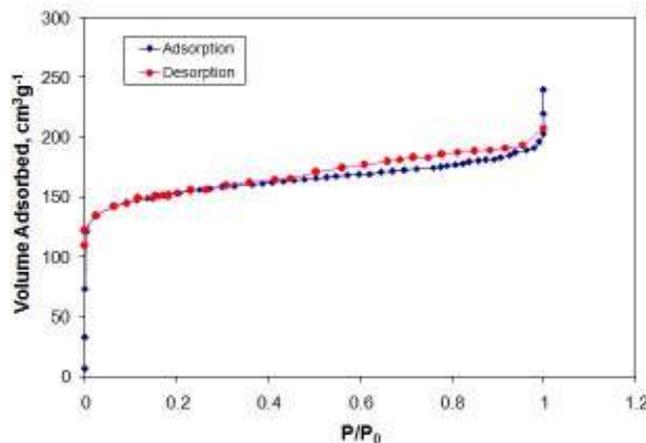Figure (3) : Determination of pHzpc of MOAC.

Figure (4) : Nitrogen adsorption and desorption isotherm of MOAC at 77 K.

The isotherm of nitrogen adsorption at 77 K of the MOAC shown in Figure (4) is supposed to exhibit a combination of Type-I and IV isotherms,

characteristics of co-existence of microporous and mesoporous material. The carbon shows significant nitrogen uptake at low relative pressure. This can be described to the strong interaction between nitrogen molecules and walls with closely spaced pores. The specific surface area of MOAC (S_{BET}) according to the method of Brunauer-Emmet-Teller [21] is 502.89 m^2/g. The total volume of pores (V_{tot}) is equal to 0.3cm^3/g. The micropore volume ($V_{micron)}$ is 0.152 cm^3/g and external surface area (S_{Ext}) 202.15 m^2/g.

3.2 Adsorption Kinetics of Dye:

The kinetic of adsorption have been studied for Basic Violet 3 at pH =9 up to 140 min by varying the initial dye concentration. Three kinetic models were applied to adsorption kinetic data in order to investigate the behavior of adsorption process of Basic Violet 3 onto MOAC: the pseudo-first-order, the pseudo second order and the intra particle diffusion models. A simple kinetic analysis of adsorption, the pseudo first order kinetics and its integrated form, is given by Lagergren [25].

$$log(q_e - q_t) = log\, q_e - \frac{k_1}{2.303} \qquad (3)$$

where k_1 is the pseudo first order rate constant. A plot of log (q_e-q_t) vs time for Basic Violet 3 adsorption on to MOAC enables calculation of the rate constant k_1 and q_e from the slope and intercept of the plot Figure (5).
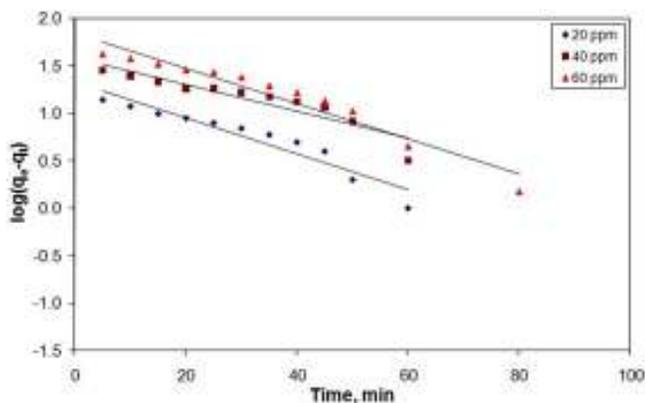

Figure (5) : Influence of initial dye concentration on pseudo first order plots for Basic Violet 3 adsorption.
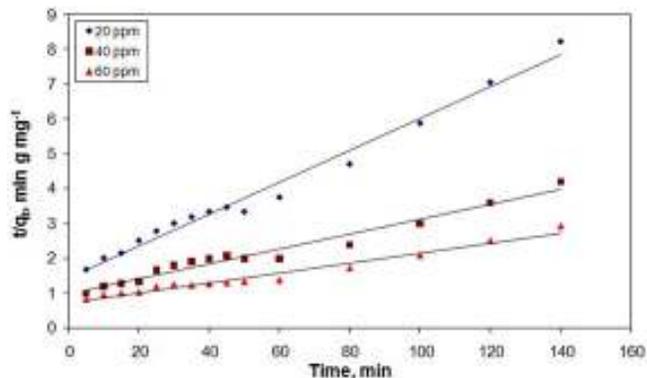

Figure (6) : Influence of initial dye concentration on pseudo second order plots for Basic Violet 3 adsorption.

To describe dye adsorption, the modified pseudo second order kinetic equation [26] is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \qquad (4)$$

where, k_2 is the pseudo second order rate constant. A plot of t/q_t vs t for Basic Violet 3 adsorption onto MOAC is shown in Figure (6), which enables calculation of the rate constant k_2 which in turn is used to calculate the initial sorption rate h as follows
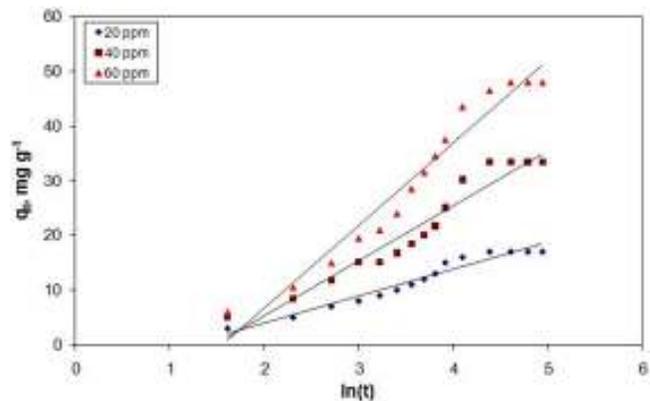
$$h = k_2 q_e^2 \qquad (5)$$

Figure (7) : Influence of initial dye concentration on Weber Morris plots for Basic Violet 3 adsorption

For a solid – liquid adsorption process, the solute transfer is normally characterized by external mass transfer or intra-particle diffusion or both. The intra-particle diffusion model proposed by Weber and Morris [27] was used to identify the mechanism involved in the adsorption process.

$$q_t = k_{id}t^{0.5} + C \qquad (6)$$

where k_{id} (mg/g min$^{0.5}$) is the rate constant of the intra-particle diffusion model and C (mg/g) reflects the boundary layer effect. The k_{id} and C can be determined from the slope and intercept of the plot q_t vs $t^{0.5}$ and is shown in Figure (7) for Basic violet 3 adsorption.
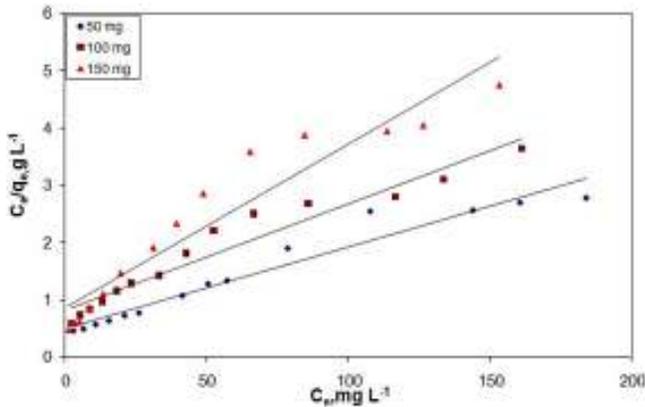

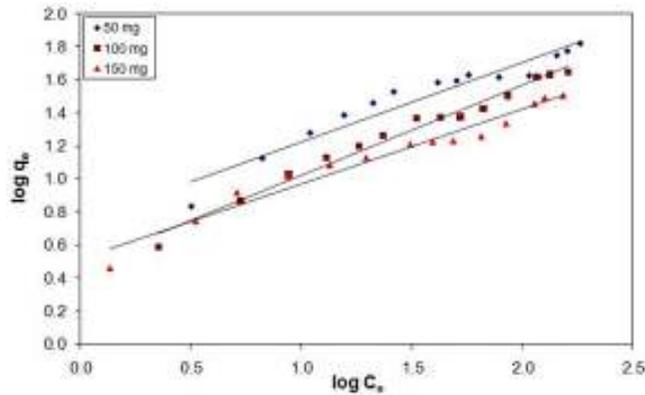Figure (8) : Influence of carbon dosage on Langmuir plots for Basic Violet 3 adsorption

Figure (9) : Influence of carbon dosage on Freundlich plots for Basic Violet 3 adsorption.

Table (2 & 3), summarizes the parameters and coefficients of the pseudo first order, pseudo second order and Weber Morris model. The results show that the correlation coefficients for the pseudo second order and Weber Morris model has high value for adsorbent. According to the intra particle diffusion model, the plot of uptake should be linear if intra particle diffusion is involved in the adsorption process and if the line passes through the origin then intra particle diffusion is the rate controlling step. When the plot doesn't pass through the origin, this is an indicative of boundary layer control. This shows that the intra particle diffusion alone is not the rate limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously.

Concentration	Pseudo First Order Values		Weber Morris Model	
	k_{Lager} x 10^{-2} min^{-1}	R^2	K_{id}, mg g^{-1} min$^{-0.5}$	R^2
20 ppm	0.0435	0.9069	1.406	0.9746
40 ppm	0.0387	0.7481	4.2454	0.919
60 ppm	0.0431	0.9364	4.5374	0.8824

Table (2) : Kinetic model values for adsorption onto MOAC.

Concentration	Pseudo Second Order Values			
	q_e mg g^{-1}	k_2 x10^{-3} g mg^{-1} min^{-1}	h mg g^{-1} min^{-1}	R^2
20 ppm	21.83	1.46	0.6958	0.9838
40 ppm	46.73	0.464	1.013	0.9611
60 ppm	69.93	0.281	1.374	0.9683

Table (3) : Kinetic model values for adsorption onto MOAC.

3.3. Adsorption Isothrems :

In this work, adsorption isotherm data of Basic Violet 3 dye were fitted with the Langmuir and Freundlich models, for variation in Activated carbon (MOAC) dosage, which are most widely used. The isotherm fits were compared through the coefficient of correlation (R^2) and were reported in Table (4 & 5).

Carbon	Langmuir Isotherm		
Dosage (mg)	b_L, L mg^{-1}	Q_0, mg g^{-1}	R^2
50	0.0289	71.94	0.981
100	0.0239	54.94	0.9844
150	0.0401	35.09	0.9815

Table (4) : Parameters of Langmuir adsorption isotherms for adsorption onto MOAC.

Carbon	Freundlich Isotherm			
Dosage (mg)	1/n	n	k_f mg g^{-1}	R^2
50	0.4824	2.073	5.554	0.9316
100	0.5467	1.829	2.986	0.9815
150	0.4533	2.206	3.272	0.962

Table (5) :Parameters of Freundlich adsorption isotherms onto MOAC.

The Langmuir model **[28]** assumes that the solid surface carries a limited number of sites that are characterized by equal energy of adsorption, independent of the degree of coverage and thus indicating a monolayer adsorption. The linearized form of the Langmuir equation is described by equation (7).

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (7)$$

where, Q_o is the maximum adsorption capacity, b is the Langmuir binding energy coefficient. The b and Q_o can be calculated from the intercept and slope of the linear plot of C_e/q_e against C_e as shown in Figure (8).

It is obvious that the Langmuir adsorption isotherm is more fitted to describe the adsorption equilibrium ($R^2 > 0.98$).Therefore, monolayer coverage of Basic Violet 3 onto MOAC particles is taken up with the maximum adsorption capacity of 71.94 mg/g.

The Freundlich isotherm **[29]** is an empirical equation and is one of the most widely used isotherms for the description of multi-site adsorption. The linear form as follows:

$$log\,q_e = \frac{1}{n}log\,C_e + log\,k_f \qquad (8)$$

where K_f and n are the Freundlich isotherm constants indicating the adsorption capacity and adsorption intensity respectively. The K_f and n can be calculated from the intercept and slope of the linear plot of log q_e against log C_e Figure (9). The value of $n > 1$ indicates favorable and heterogeneous adsorption of Basic Violet 3 onto MOAC.

4. Conclusions:

The adsorption of cationic dye, Basic Violet 3 onto porous activated carbon prepared from *Moringa oleifera* fruit shell waste Activated Carbon was studied. The characterization of the surface chemistry of activated carbon (MOAC) by Boehm method has shown the presence of Basic groups at the surface of MOAC. The rates of adsorption of the dye on MOAC were measured and it was observed that the process followed pseudo second order kinetic model. The equilibrium adsorption isotherms of Basic violet 3 onto MOAC were measured as a function of carbon dosage variation. The adsorption capacity obtained was 71.94 mg/g for Basic Violet 3 at the carbon dosage of 50 mg. The Langmuir model gives the best fit for the adsorption of Basic Violet 3 onto MOAC.

Acknowledgement :

References :

[1]　Z. Akshu, Process Biochem. 40 (2005) 997.

[2]　S. D. Khattri, M. K. Singh, Water Air Soil Pollut. 120 (2000) 283.

[3]　P. Monash, G. Pugazhenthi, Adsorption 15 (2009) 390.

[4]　S. Senthilkumar, P. Kalaamani, C. V. Subburaam, J. Hazard. Mater. 136 (2006) 800.

[5] C. C. Chen, H. J. Liao, C. Y. Cheng, C. Y. Yen, Y. C. Chung, Biotechnol. Lett. 29 (2007) 391.

[6] Z. Hu, M. P. Srinivasan, Microporous & Mesoporous Mater. 43 (2001) 267.

[7] N. R. Khalili, M. Campbella, G. Sandi, J. Golas, Carbon 38 (2000) 1905.

[8] K. H. Chu, K. M. Chen, Process Biochem. 37 (2002) 1129.

[9] S. Wang, Y. Boyjoo, A. Choueib, Chemosphere 60 (2005) 1401.

[10] G. O. El–Sayed, Desalination 272 (2011) 225.

[11] S. Karthikeyan, B. Sivakumar, N. Sivakumar, J. Chem. 7 (2010) S175.

[12] P. B. Nagarnaik, A. G. Bhole, G. S. Natarajan, Indian J. Environ. Hlth. 45 (2003) 1.

[13] S. Karthikeyan, K. Sakthivel, C. Kannan, Rasayan J. Chem. 4 (2011) 519.

[14] Yuh-Shan Ho, Water Res. 37 (2003) 2323.

[15] S. Karthikeyan, P. Sivakumar, J. Environ. Nanotechnol. 1 (2012) 5.

[16] S. Karthikeyan, A. Baburajendran, Nature Environ. Pollut. Technol. 9 (2010) 461.

[17] R. W. Sabnis, Hand Book of Acid- Base indicators, Taylor and Francis group (2007) 108.

[18] W. J. Hassler, Purification with activated carbon. Chemical publishing company, New York, 2nd Edn. (1974).

[19] Boehm, Advances in catalysis. Vol. 16, Academic press, New York (1966) 179.

[20] Arvind Kumar, B. Prasad, I. M. Mishra, J. Hazard. Mater. 152 (2008) 589.

[21] S. Brauner, P. H. Emmet, E. Teller, J. Am. Chem. Soc. 60 (1938) 309.

[22] A. Allwar, J. Appl. Chem. 2 (2012) 9.

[23] J. C. Collins, M. F. H. Zain, F. S. Dek, Malaysia J. Anal. Sci. 10 (2006) 1.

[24] J. RaffieaBaseri, P. N. Palanisamy, P. Siva Kumar, Indian J. Chem. Technol. 19 (2012) 311.

[25] S. Lagergren, ZurTheorie Der Sogennten Adsorption GelosterStoffe, Hand linger 24 (1898) 1.

[26] Y. S. Ho, G. Macy, Adsorpt. Sci. Technol. 18 (2000) 639.

[27] W. Weber, J. Morris, J. Sanit-Eng. Div. Am. Soc. Civ. Eng. 89 (1963) 31.

[28] R. Akkaya, U. Ulusoy, J. Hazard Mater. 51 (2008) 380.

[29] C. Kannan, B. Sivakumar, P. Nithya, S. Karthikeyan, Indian J. Sci. 4 (2013) 45.