Academic Sciences

International Journal of Chemistry Research

ISSN- 0976-5689 Vol 3, Issue 1, 2012

Research Article

KINETICS, EQUILIBRIUM STUDIES ON REMOVAL OF IONIC DYES USING A NOVEL NON-CONVENTIONAL ACTIVATED CARBON

A.AGALYA[a]*, P.N.PALANISAMY[b] AND P.SIVAKUMAR[c]

Department of Chemistry, Al-Ameen Engineering College, Erode, Tamilnadu-638104, India, Department of Chemistry, Kongu Engineering College, Erode, Tamilnadu-638052, India, Department of Chemistry, Arignar Anna Govt. Arts College, Namakkal, TN-637001, India. Email: agalarun@rediffmail.com

Received: 3 Nov 2011, Revised and Accepted: 21 Dec 2011

ABSTRACT

The feasibility of activated carbon prepared from *Euphorbia Tirucalli* wood using H_3PO_4 for the removal of Malachite Green (Cationic) and Direct Blue (Anionic) dyes was investigated. The effects of initial dye concentration, contact time, pH and temperature onto ETAC were studied. Equilibrium isotherms and kinetics were investigated and the experimental data fitted well with the Langmuir model. The maximum monolayer adsorption capacities of ETAC were found to be 181.81 mg/g and 138.88 mg/g for MG and DB respectively. The kinetic data obtained were analyzed using pseudo-first order, pseudo-second order and intra particle diffusion models. Thermodynamic parameters were evaluated and suggesting the spontaneous and endothermic nature of physisorption. Activation energy for the adsorption of MG and DB were 12.1402 kJ/mole and 28.8484 kJ/mole.

INTRODUCTION

Dyes are synthetic aromatic organic compounds which have extensive application as colorants for dying and printing in a variety of industries. Discharge of dyes in the environment is worrying for both toxicological and aesthetical reasons because these textile dyes damage the quality of receiving streams and is toxic to food chain organisms[1]. Among the various classes of dyes, basic dyes are the brightest class of soluble dyes used by the textile industry as their tinctorial value is very high[2]. The use of direct dyes has continuously increased in the textile industry and finishing processes since the development of synthetic fibers. Direct dyes posses good affinity for cellulosic fibers and are used widely due to their low cost, excellent color change, good light fastness and ease of application to the material. These dyes are water soluble and contain one or more ionic groups most often sulphonic acid / or amino groups. Many of the direct dyes are highly toxic and potentially carcinogenic[3-4]. Color removal from industrial waste water by adsorption techniques has been of growing importance due to the chemical and biological stability of dyestuffs to conventional water treatment methods and the growing need for high quality treatment[5]. The use of renewable sources as raw material for manufacturing activated carbon is advantageous as these are less expensive to manufacture[6].

In the present study, the adsorptions of three basic dyes namely Basic Green4, Direct Blue have been investigated using ETAC as adsorbent. The kinetic and thermodynamic parameters were calculated to determine the adsorption mechanism. The effect of initial dye concentration, agitation time, pH and temperature has been evaluated to assess the possibility of ETAC for the removal of ionic dyes.

MATERIALS AND METHODS

Adsorbent

Activated carbon prepared from the precursor wood *Euphorbia Tirucalli L.* The wood cut into a pieces of 2 to 3 cm size and dried in sunlight for 10 days. The dried material soaked in a boiling solution of 35% H_3PO_4 for 1 hour and kept at room temperature for 24 hours. The wood material separated, air dried and carbonized in muffle furnace at 550 ºC for 1½ hour. The carbonized material powdered and activated at 800ºC for 10 minutes. The resulting carbon was washed with plenty of water until the residual acid was removed. The dried material was ground well to fine powder and sieved into a particle size of 180 to 300 micron[7].

Adsorbate

The ionic dyes used in this experiment are Basic Green4 has molecular formula: $C_{23}H_{25}ClN_2$ M.Wt: 364.91, λmax: 620nm, Direct Blue, an anionic dye has molecular formula $C_{34}H_{24}N_6Na_4O_{16}S_4$; M.Wt: 992.8, λ_{max} 608 nm. The dyes were used as received without further purification. The structure of Basic Green4 and Direct Blue is presented in Fig.1. A stock solution of dyes (1000 mg/lit) was prepared by dissolving appropriate amount of dye (based on the percentage purity) and suitably diluted as and when required**.** The concentration of the dye was determined using Elico make UV-Vis spectrophotometer at wavelength 620nm for BG4 and 608 nm for DB. All chemicals used were analytical reagent grades and used without further purification.

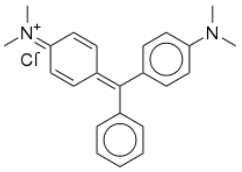

Fig. 1a: Structure of Basic Green4

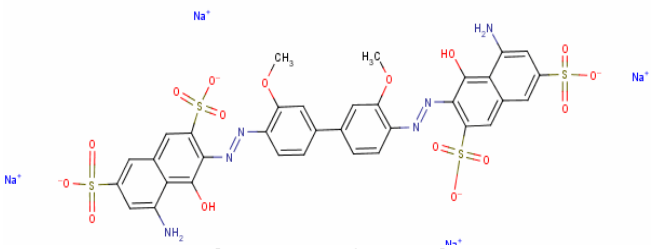

Fig. 1b: Structure of Direct Blue

Characterization Studies

Physico-chemical characteristics of activated carbon prepared from *Euphorbia Tirucalli L* wood were studied as per the standard testing methods[8-9].

Batch Adsorption Experiments

Adsorption experiments of Basic Green4 (BG4) and Direct Blue (DB) onto ETAC were conducted by agitating 100 ml adsorbate solution of known concentration with 0.1 gm weight of adsorbent. The mixture was agitated in a temperature controlled shaker and samples were withdrawn at different time intervals (0-70 min), centrifuged and analyzed for remaining dye concentration.

Equilibrium Isotherm Studies

Equilibrium studies were conducted by agitating 100 ml of dye solution with 0.1 gm of adsorbent at different initial dye

concentration (10-170 mg/lit). After equilibrium, the solution was analyzed for remaining dye concentration. The equilibrium experiments were conducted at different temperatures.

RESULT AND DISCUSSION

Analysis of Adsorbent Characteristics

The Physico-chemical characteristics of activated carbon (ETAC) prepared from *Euphorbia Tirucalli L* wood using H_3PO_4 were summarized in Table.1 and the adsorbent was analyzed for the adsorption of cationic Dye (Basic Green4) and Anionic dye (Direct Blue). The surface morphology of ETAC was examined by Scanning Electron Microscopy (SEM) and shown in Fig.2.

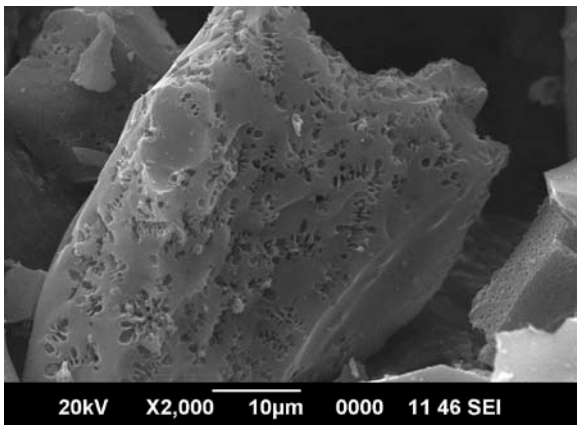

Fig. 2: SEM image of ETAC

Table 1: Physico-chemical characteristics of Adsorbents

S. No	Properties	ETAC
1	pH	6.48
2	Conductivity, µS/cm	0.187
3	Moisture content, %	10.4
4	Ash, %	10.8
5	Volatile matter, %	22.2
6	Bulk density, g/ml	0.56
7	Specific gravity	1.18
8	Porosity, %	52.54
9	Methylene Blue value, mg/g	405
10	Iodine Number, mg/g	932
11	Surface area (BET), m^2/g	857.85

Analysis of Adsorption Parameters

Effect of Initial Dye Concentration

The effect of initial concentration of dye on the percentage removal of BG4 and DB on the ETAC has been studied and shown in Fig.3. On increasing the initial concentration of dye, the percentage removal of dye decreased, although the amount of dye adsorbed per unit mass of adsorbent increased. The decrease in percentage removal is due to the lack of available active sites for adsorption. Similar trend has been reported for the adsorption of Reactive Orange 12 by coir pith activated carbon[10], Reactive Black 5 on activated sludge[11], Reactive Orange on loofa activated carbon[12] and removal of Eosin Y using conducting electro polymers[13]. The results show that the percentage removal of BG4 and DB decreases from 97.87 to 80% and 70.83 to 52.31 % when the initial concentration increases from 25 to 100 mg/lit for ETAC.

Effect of Contact Time

The effect of contact time on adsorption of BG4 and DB onto ETAC has been investigated and shown in Fig.4. The percentage removal was rapid in the beginning, and then slight increase occurs till the adsorption reached equilibrium. The results confirm high and rapid adsorption of BG4 and DB by ETAC.

Effect of pH

The pH of the dye solution plays an important role in the adsorption process. The effect of initial pH on the adsorption of BG4 and DB on to the ETAC has been investigated and shown in Fig.5. The maximum percentage removal of BG4 occurs at pH 8-9 and DB occurs at 3-4. In alkaline medium, the carbon surface become negative which enhances the positively charged cationic dyes[14]. In acidic medium, the surface of the adsorbent is positively charged due to higher concentration of H^+ ions, so the electrostatic attraction between adsorbent and DB (anionic dye), is enhanced.

Effect of Temperature

The effect of temperature on dye adsorption has been studied at 30, 35, 40 and 45º C. The results indicated that the amount of dye adsorbed at equilibrium increases with increasing temperature. The equilibrium adsorption increased from 92.19 to 98.44 % and 62.86 to 74.29 % for BG4 and DB, indicates that the adsorption is endothermic process.

Adsorption Kinetics

A study of adsorption kinetics is desirable as it provides information about the mechanism of adsorption, which is important for the validation of the efficiency of the process. In the present work, the kinetic data obtained from batch studies have been analyzed by using pseudo-first order, second order and intra particle diffusion models.

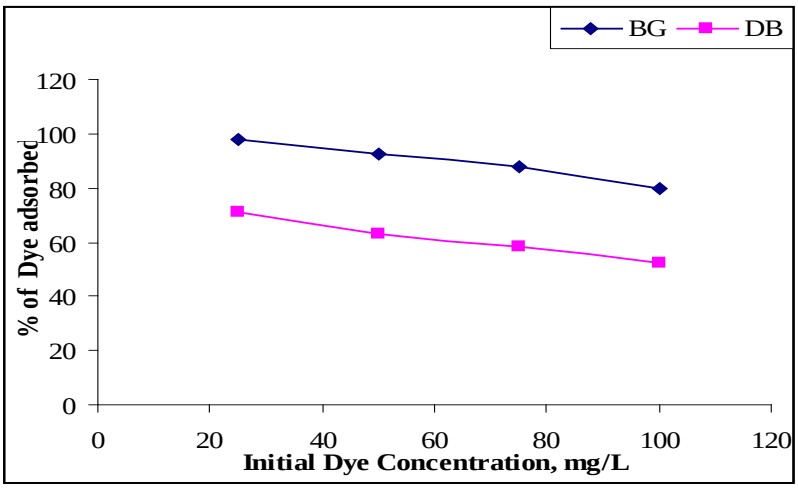

Fig. 3: Effect of Initial Dye Concentration

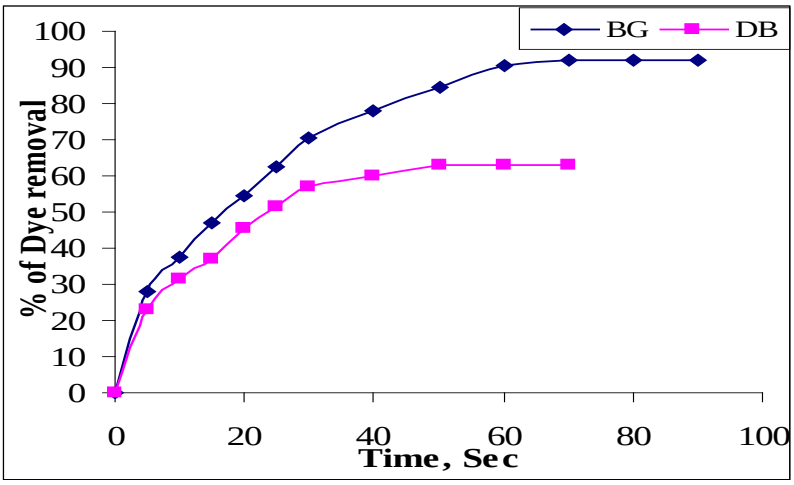

Fig. 4: Effect of Contact time

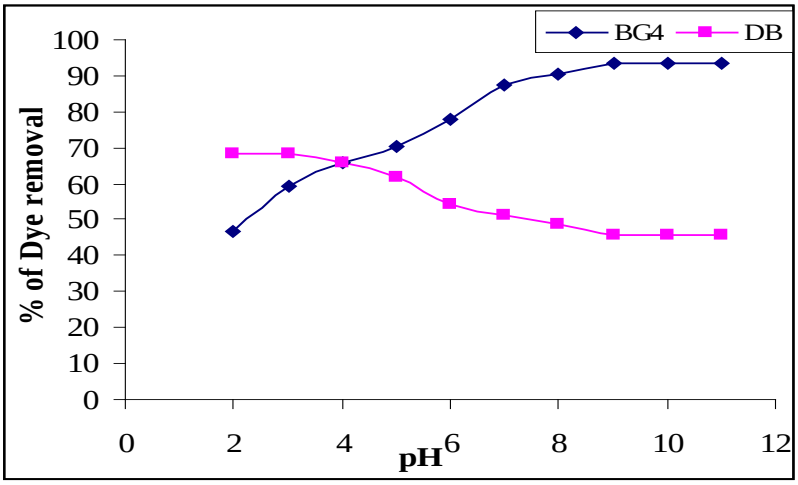

Fig. 5: Effect of pH

Pseudo-First Order Model

The pseudo-first order equation of Lagergren [15] is generally as follows

$$\frac{dq}{dt} = k_1(q_e - q_t) \qquad \ldots (1)$$

The integrated form of equation

Error! Bookmark not defined. $$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

... (2)

The amount of dye adsorbed at equilibrium q_e and first order rate constant k_1 calculated from intercept and slope of the plot $\log(q_e\text{-}q_t)$ vs time and the results are summarized in table 2. From the values of r^2, it is clear that pseudo first order equation does not fit well for whole range of adsorption process, as it is applicable for the initial stages of adsorption processes[16].

Pseudo-Second Order Model

The second order equation for the equilibrium adsorption is expressed[17] as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e 2} + \frac{t}{q_e} \qquad \ldots (3)$$

The r^2 values obtained for various initial dye concentrations were above 0.98 indicating that the second order kinetic model describes very well for adsorption of both cationic and anionic dyes onto ETAC. The values of second order rate constant k_2 and q_e were calculated from the intercepts and slopes of the plot of t/q_t vs t and the results are presented in table 2.

The value of k_2 decreases with increase in dye concentration due to decrease in available vacant sites for adsorption. Based on the values of co-relation co-efficient, the second order kinetic model was more suitable to describe the adsorption process for cationic dye adsorption than pseudo-first order model.

Intra Particle Diffusion Model

The pseudo-first order and second order kinetic models could not identify the diffusion mechanism, so that the kinetic results were further analyzed using intra particle diffusion model[18]. In batch mode adsorption process there is a possibility that the transport of dye molecules from the solution into the pores of the adsorbent is the rate controlling step.

$$t^{1/2} = k_{id} + C \qquad \ldots (4)$$

This possibility was tested by plotting a graph between qt and $t^{1/2}$ at different initial dye concentration and shown in Fig. 6a and 6b. All the plots have initial curved portion followed by an intermediate linear portion. The initial portion is related to mass transfer and linear part is due to intra particle diffusion. The values of k_{id} for all

concentrations studied were determined from the slopes of respective plots and the results are presented in table 2. If the intra particle diffusion was the only rate controlling step, the plot passed through the origin, if not the boundary layer diffusion controlled the adsorption to some degree[19]. But the plots obtained were not linear over the whole time range, implying that more than one process affected the adsorption ie the mechanism of removal of ionic dyes is complex and both surface adsorption as well as intra particle diffusion contribute to the rate determining step.

Table 2: Kinetic Model values for adsorption of Basic Dyes onto ETAC

Dyes	Concn mg/L	First Order Kinetics			Second Order Kinetics			Intra Particle Diffusion model	
		k_1 (min^{-1})	q_e(cal) (mg/g)	r^2	k_2 X 10^{-4} (g/mgmin)	q_e(cal) (mg/g)	r^2	k_{id} (mg/g min)	r^2
	25	0.0587	47.19	0.9859	13.5943	57.14	0.9983	5.1370	0.9130
BG4	50	0.0594	108.81	0.9349	4.4762	114.94	0.9936	10.1944	0.9641
	75	0.0548	150.00	0.9667	2.6715	169.49	0.9945	14.8601	0.9639
	100	0.0571	196.56	0.9685	1.6596	217.39	0.9891	18.7876	0.9585
	25	0.0705	36.94	0.9900	16.2548	43.86	0.9921	4.4566	0.9418
DB	50	0.0769	67.9	0.9810	10.0603	76.92	0.9922	7.8533	0.9338
	75	0.0804	98.67	0.9800	7.0313	107.53	0.9915	11.0129	0.9317
	100	0.0705	112.56	0.9886	4.9206	131.57	0.9912	13.3735	0.9454

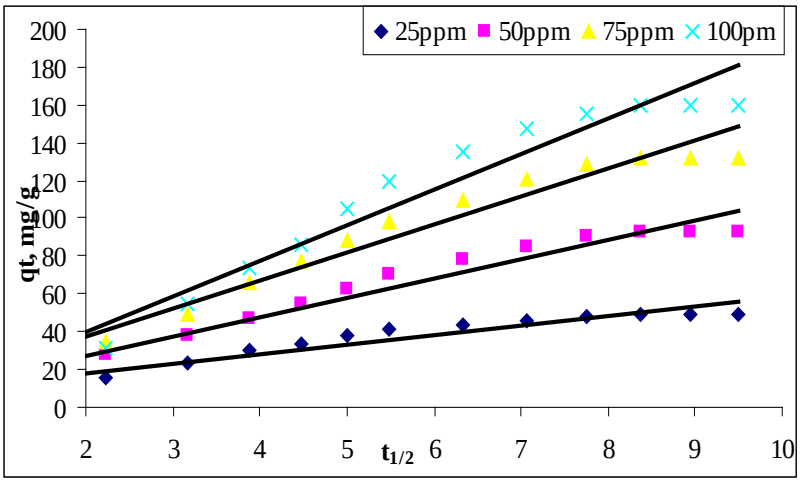

Fig. 6a: Intra particle diffusion model for adsorption of BG4

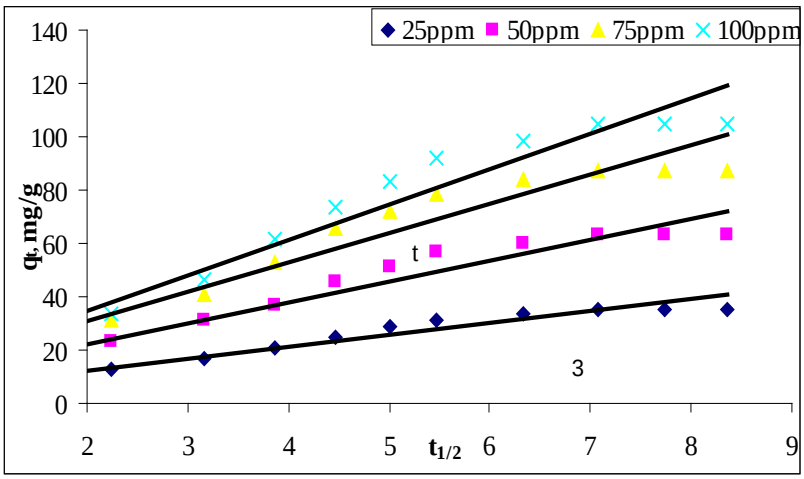

Fig. 6b: Intra particle diffusion model for adsorption of DB

Langmuir Isotherm

The Langmuir isotherm equation is based on the assumption that the maximum adsorption corresponds to a saturated monolayer of adsorbate dye molecule on the adsorbent surface. The energy of adsorption is constant and there is no transmigration of the adsorbate in the plane of the surface[22]. The linearised form of Langmuir isotherm is presented by the equation.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{C_e}{Q_0} \quad \ldots (5)$$

Where, C_e is the equilibrium concentration (mg/L), q_e is the amount of dye adsorbed at equilibrium (mg/g) and Q_0 (mg/g) and b_L (L/mg) are Langmuir constants related to adsorption capacity and energy of adsorption respectively. Fig. 7a and 7b showed the Langmuir plot for BG4 and DB respectively. The values of Q_0 and b_L calculated from the slopes and intercepts of the linear plots of Ce/q_e vs Ce and the results are presented in table 3. The results show that the value of adsorption efficiency Q_0 and adsorption energy b_L of ETAC increases with increasing the temperature suggests that the maximum adsorption corresponds to a saturated monolayer of dye molecules on adsorbent. The maximum adsorption capacity Q_0 varies from 181.81 to 192.30 mg/g for BG4 and 138.88 to 147.05 mg/g for DB while increasing the temperature from 30ºC to 45ºC.

Adsorption Isotherm

Isotherms are the equilibrium relation between the concentration of the adsorbate on the solid phase and in the liquid phase. It is the most important data to understand the mechanism of adsorption systems. In this study, Langmuir[20] and Freundlich[21] isotherm models were used to describe both cationic and anionic dye equilibrium.

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter R_L [23] that is defined by the following equation

$$R_L = \frac{1}{(1+bC_0)} \qquad \ldots (6)$$

Where, Co is the initial solute concentration. The R_L value indicated the type of adsorption isotherm to be either unfavourable (R_L >1), favourable (R_L<1), linear (R_L=1) or irreversible (R_L=0). Langmuir model is more appropriate to explain the nature of adsorption of ionic dyes onto ETAC

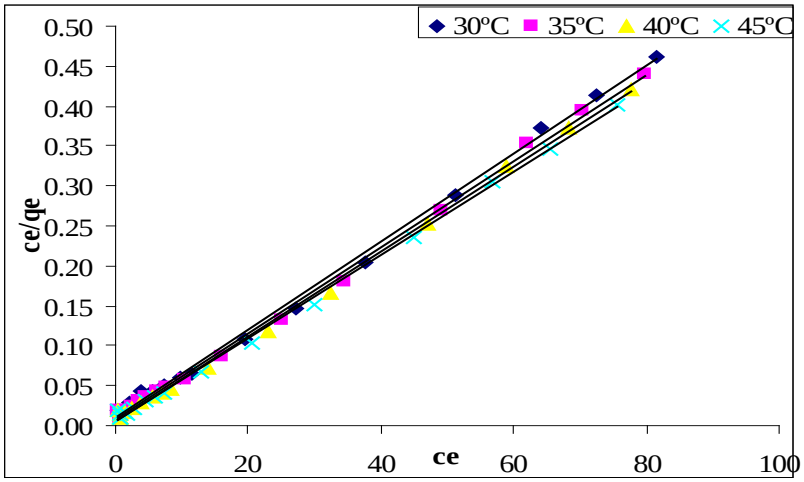

Fig. 7a: Langmuir plot for the adsorption of BG4

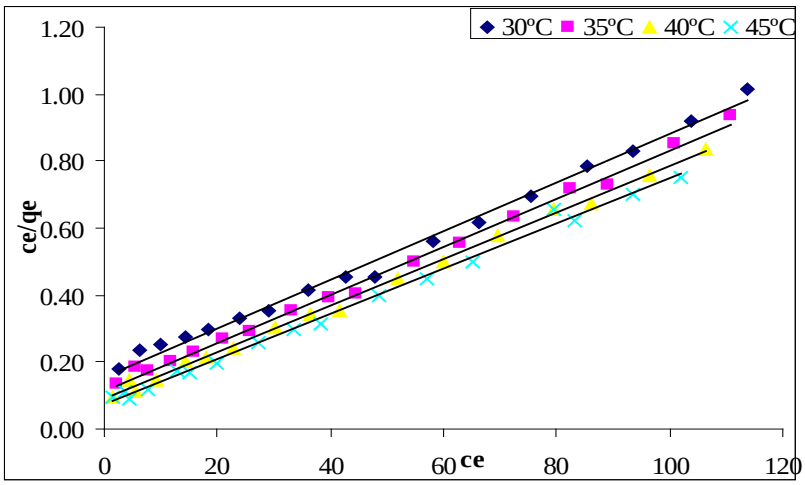

Fig. 7b: Langmuir plot for the adsorption of BG4

Table 3: Comparison of the coefficients of Isotherm parameters of BG4 and DB

Dyes		Isotherm Models					
	Temp	Langmuir			Freundlich		
	ºC	Q_0	b			k_f	
BG4		(mg/g)	(L/mg)	r^2	n	($mg^{1-1/n}$ $L^{1/n}g^{-1}$)	r^2
	30	181.81	0.5188	0.9974	3.5149	64.7142	0.8079
	35	185.18	0.7105	0.9979	3.7950	72.9457	0.7956
	40	188.67	0.8688	0.9982	4.0112	79.7994	0.7620
	45	192.30	0.8965	0.9983	4.040	85.7235	0.7237

	30	138.88	0.0457	0.9941	2.1477	14.7978	0.9182
DB	35	138.88	0.0618	0.9960	2.3753	19.4043	0.9057
	40	142.85	0.0794	0.9976	2.6130	24.6547	0.9003
	45	147.05	0.0949	0.9951	2.7902	29.2348	0.8930

Freundlich Isotherm

The Freundlich isotherm is an empirical equation derived to model the multilayer adsorption and for the adsorption on heterogeneous surfaces.

$$\log q_e = \log K_f + \frac{1}{n}\log c_e \qquad \ldots (7)$$

Where, K_f and 1/n are Freundlich constants related to the adsorption capacity and adsorption intensity of the adsorbent respectively. The q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/g), Ce is the equilibrium concentration of adsorbate (mg/L). The values of K_f and 1/n are calculated from intercept and slopes of linear plot of log q_e vs log c_e (Fig. not shown) and the results are presented in table 3. The value of 1/n is below one for all three dyes studied indicating that the adsorption of ionic dyes on ETAC is favourable. But it poorly fits with the experimental data with correlation coefficient 0.8079 to 0.7237 for BG4, 0.9182 to 0.8930 for DB.

Thermodynamic parameters

Activation Energy

The second order rate constant of the dye adsorption is expressed as a function of temperature by Arrhenius relationship.

$$\ln k_2 = \ln A - \frac{Ea}{RT} \qquad \ldots (10)$$

Where Ea and A refers to Arrhenius activation energy and Arrhenius factor obtained from the slope and intercepts of a graph by plotting $\ln k_2$ vs 1/T shown in Fig. 8. The activation energies were found to be 12.1403kJ/mole and 28.8484 kJ/mole for BG4 and DB respectively. The minimum value of Ea (12.1403 kJ/mole) for sorption of BG4 onto ETAC indicated the higher adsorption due to lesser energy barrier. The physisorption usually have energies in the range of 5-40 kJ/mole, while higher activation energies 40-800 kJ/mole suggests chemisorption[24]. The activation energy < 40 kJ/mole for both the dyes indicates the diffusion controlled physisorption.

The thermodynamic parameters such as change in standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) can be determined by using VantHoff equation

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad \ldots (8)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad \ldots (9)$$

Where, T is the absolute temperature and K_L (L/g) is the standard thermodynamic equilibrium constant. By plotting a graph of $\ln K_L$ vs 1/T, the values of ΔS^0 and ΔH^0 can be estimated from the slopes and intercepts (Fig. not shown). The results are given in table 4. The positive values of ΔS^0 confirming physical adsorption nature and increased randomness at the solid-solution interface during adsorption and indicate affinity of the dye onto adsorbents[25]. The value of enthalpy of a sorption process may be used to distinguish between chemical and physical adsorption[26-27]. For chemical adsorption enthalpy value ranges from 83-830 KJ/mole[28].

Table 4: Thermodynamic Parameters at different Temperatures

Dye	Temp°C	ΔGº kJ/mol	ΔHº kJ/mol	ΔSºkJ/K/mol	Ea kJ/mole	ΔH_X kJ/mole
	30	-11.6152				
BG4	35	-12.3456	32.6460	0.1460	12.1402	51.4802
	40	-13.0760				
	45	-13.8064				
	30	-4.7143				
DB	35	-5.4909	42.3432	0.1553	28.8484	19.2311
	40	-6.2674				
	45	-7.0439				

Isosteric Heat of Adsorption

It is the basic requirements for the characterization and optimization of an adsorption process and also very important for equipment and process design.

The isosteric heat of adsorption at constant coverage is calculated using Clausius- Clapeyron equation[29].

$$\ln Ce = \frac{\Delta H_X}{RT} + K \qquad \ldots (10)$$

Where Ce is the equilibrium dye concentration in solution (mg/L), ΔH_X is the isosteric heat of adsorption (kJ/mole). The isosteric heat of adsorption is calculated from the slope of the plot lnCe versus 1/T. The magnitude ΔH_X of provides an information about the nature and mechanism of the process. For physical adsorption ΔH_X should be below 80 kJ/mole and for chemical adsorption it ranges between 80 and 400 kJ/mole[30] . The values of ΔH_X for the adsorption of BG4 and DB onto ETAC are 51.4802 kJ/mole and 19.2311 kJ/mole which are within the range of physisorption and suggested that the adsorption process is physisorption.

CONCLUSION

The present study confirmed that the activated carbon prepared from *Euphorbia Tirucalli L* wood was found to be suitable adsorbent for the removal of ionic dyes. Removal of ionic dyes is pH dependent and maximum removal occurs at pH 8-9 for cationic dyes (MG) and 3-4 for anionic dyes (DB). The kinetic studies revealed that the adsorption data was controlled by both surface adsorption and intra particle diffusion. The experimental adsorption equilibrium data were in good agreement with Langmuir model. The determination of thermodynamic parameters indicates the spontaneous and endothermic nature of adsorption process. The activation energy for cationic dye BG4 is 12.1402 and anionic dye is 28.8484 kJ/mole which was below 40 kJ/mole and also isosteric heat of adsorption indicates the physical nature of adsorption process. Based on the results obtained in this study, it can be concluded that ETAC is an effective, economic and alternative adsorbent for the removal of dyes.

ACKNOWLEDGEMENT

The second and third authors thank UGC, New Delhi for providing financial assistance under major research project scheme to carryout this research work.

REFERENCES

1. Tan IAW, Ahamed AL and Hameed BH. Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies. Desalination. 2008; 225: 13-28.
2. Mckay G. Adsorption of dye solution from aqueous solution with activated carbon. J Chem Technol Biotechnol. 1982; 32: 759.

3. Kaushik CP, Tuteja R, Kausik N and Sharma JK. Minimisation of organic chemical load in direct dyes effluent using low cost adsorbents. Chem Eng J. 2009; 155: 234.
4. 4.Bayramoglu G and Arica MY. Biosorption of benzidine based textile biomass of Trametes vesicolor. J Hazard Mater. 2007; 143: 135.
5. Basar CA. Applicability of the various adsorption models of three dye adsorption onto activated carbon prepared waste Apricot. J Hazard Mater. 2006; 135, 232-241.
6. Hameed BH, Din ATN and Ahamed AL. Adsorption of Methylene blue onto Bamboo-based activated carbon: Kinetics and Equilibrium studies J Hazard Mater. 2006; 7, 49-55.
7. Sivakumar P and Palanisamy PN. Low-cost non-conventional activated carbon for the removal of Reactive Red 4: Kinetic and isotherm studies. Rasayan J Chem. 2008; 4, 871-883.
8. Hsieh CT and Teng H. Liquid-phase adsorption of phenol onto activated carbons prepared with different activation levels: J.Colloid.Interf.Sci. 2000; 230, 171-175.
9. Ilhan U, Kinetics of the adsorption of Reactive dyes by Chitosan. Dyes Pigments. 2006; 70, 76-83.
10. Santhy K and Selvapathy P. Removal of reactive dyes from wastewater by adsorption on coir pith activated carbon. Bioresour Technol. 2006; 97, 1329.
11. Gulnaz O, Kaya A and Dincer S. The reuse of dried activated sludge for adsorption of reactive dye. J Hazard Mater. 2006; B134, 190.
12. Abdelwahab O. Evaluation of the use of loofa activated carbons as potential adsorbents for aqueous solutions containing dye. Desalination. 2008; 222, 357.
13. Ansari R and Mosayebzadeh Z. Removal of Eosin Y. An Anionic dye, from aqueous solutions using Conducting Electroactive Polymers. Iranian Polymer J. 2010; 197, 541.
14. Helfferich F. Ion Exchange, McGraw-Hill Book Company, Inc., New York, 1963.
15. Langergren S. Zur theorie der sogenannten adsorption geloster stoffe, K.Sven, Veternskapsakad. Handl. 1898; 24, 1.
16. Chiou MS and Li HY. Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads. J Hazard Mater. 2002; 93, 233.
17. Ho Y S and Mckay G. Pseudo-second order model for sorption processes. Proc Biochem. 1999; 34, 451.
18. Weber Jr WJ and Morris JC. Kinetics of adsorption on carbon from solution. J.Sanitary Eng.Div.ASCI. 1963; 89, 31-60.
19. Cheung WH, Szeto YS and Mckay G. Intra particle diffusion processes during Acid dye adsorption onto Chitosan. Bioresour Technol. 2007; 98, 2897-2904.
20. Langmuir I. The adsorption of gases on plane surface of glass, mica and platinum. J Am Chem Soc. 1918; 40, 1361.
21. Freundlich HMF. Over the Adsorption in solution. J Phy Chem. 1906; 57, 384.
22. Gong R, Jin Y, Chen J, Hu Y and Sun J. Removal of Basic dyes from aqueous solution by sorption on phosphoric acid modified Rice straw. Dyes Pigments. 2007; 73, 332-337.
23. Vermeulen T. Pore and solid diffusion kinetics in fixed bed absorption under constant pattern conditions. Ind Eng Chem Fund. 1996; 5, 221.
24. Nollet H, Roels M, Lutgen P, Meeran PVD and Verstraete. Removal of PCBs from waste water using fly ash. Chemosphere. 2003; 53, 655.
25. Kelleher BP, O'Callaghan M, Leahy MJ, Dwyer TFO and Leahy JJ. The use of fly ash from the combustion of poultry litter for the adsorption of Chromium (III) from aqueous solution. J Chem Technol Biotechnol. 2002; 77, 1212.
26. Budhraja J and Singh M. Spectrophotometric study of adsorption of Bromo thymol Blue on charcoal and phosphates of Fe and Al. J Indian Chem Soc. 2004; 81, 573 .
27. Doula M, Ieannou A and Dimirkou A. Thermodynamics of Copper Adsorption-Desorption by Ca-Kaolinite. Adsorption. 2000; 6, 325-335.
28. Gopal V and Elango KP. Studies on Defluoridation of water using Magnesium titanate. Indian J Chem Technol. 2010; 17, 28-33.
29. Anirudhan TS and Radhakrishnan PG. Thermodynamics and Kinetics of adsorption of Cu (III) from aqueous solutions onto a new cation exchanger derived from Tamarind Fruit shell. J Chem Thermodynamics. 2008; 40, 702.
30. Dogan M and Alkan M. Removal of Methyl Violet from aqueous solution by perlite. J Colloid Interf Sci. 2003; 267, 32.