

Research Article

Removal of Anionic and Cationic Dyes from Aqueous Solution by Phosphoric Acid Modified Eichhornia Crassipes: Regeneration and Reuse Studies

S Kalai Selvi^{1*} and N Suganthi²

¹Department of Chemistry, Velalar College of Engineering and Technology, Erode

²Department of Chemistry, L.R.G Govt Arts College for Women, Tirupur

Abstract

In the present study Eichhornia Crassipes an aquatic weed was used as a raw material to prepare activated carbon. Batch adsorption studies were carried out using Congo red and Methylene blue dyes at different dilutions with the Eichhornia Crassipes carbon. The effects of different system variables were studied in the batch tests. Kinetics and equilibrium data were studied to develop an efficient and accurate design model for removal of dyes. Results of the kinetic studies show that the adsorption reaction is second-order kinetic model with respect to different concentrations. Elovich model and intra particular diffusion and corresponding constants were calculated and discussed. The Equilibrium sorption data were fitted into by Langmuir, Freundlich, Dubnin–Radushkevich, and Tempkin isotherms. Of the four adsorption isotherm, the R^2 value of Freundlich isotherm model was the highest and fits to both dyes. The important thermodynamic, regeneration and reuse of spent carbon parameters have been obtained.

Keywords: Adsorption, Congo red, Methylene blue, Activated carbon, Isotherm, Thermodynamics

*Correspondence

Author: S Kalai Selvi

Email: kalaiprony@gmail.com

Introduction

In India alone, dyestuff industry produces around 60,000 metric tons of dyes, which is approximately 6.6% of total colorants used worldwide [1]. The soluble dyes and colours in waste water inhibit the process of sunlight penetration and photosynthesis [2]. Methylene blue (MB) is synthetic aromatic complex, used for many textile and dyeing industries. MB damages eye, on gasp causes headache, acute breathing problems, increases sweating and heart rate. On ingest causes abdominal pain, mild bladder irritation, dizziness, vomiting, stomach upset and frequent urination [2]. Congo red is an aromatic water soluble dye, used for many textile, paper and dyeing industries. CR is an acid dye used in testing for hydrochloric acid in gastric contents. It is also used in histological test for amyloidosis (protein misfolding) in which deposits of amyloid proteins are found. CR causes eye irritation, lacrimation (tearing), colour blindness, skin irritation and burns. On inhalation causes severe respiratory problems which even leads to cardiac attack. On ingestion causes diarrhea, infertility, irritation to heart, alteration of platelets count and urinary bladder cancer. In particular, these dyes are synthetic aromatic compounds; which are highly toxic, carcinogenic or mutagenic to life forms [3]. These organic dyes resist to decomposition due to its complex chemical structure. Hence if not treated properly these dyes remain stable in the environment [4]. Consequently their presence in wastewater is unprovoked and it is desirable to remove dye materials from effluents, before it is discharged into the environment.

Many different techniques have applied for the removal of dyes from wastewater including coagulation–flocculation, nanofiltration, micellar enhanced ultrafiltration, photocatalytic degradation, electrochemical degradation, ozonation and biological treatment scheme, Fenton oxidation coupled with biological treatment and adsorption on activated carbon [5-12]. Adsorption has been one of the simple, low cost, easy operative and enhanced techniques for water recovery and re-use to other techniques. Activated carbon is used in air and water purification, in agriculture field as pesticides and insecticides, at oceans and seas for spill cleanup, in metal extraction, in beverages purification, in medical field as detoxifier, at sewage treatment, in air conditioner as air filters, as fuel storage and many other applications. Activated carbon is produced from carbonaceous source materials by Physical or Chemical activation. In Physical activation the source material is carbonized using hot steam / gases at temperatures in the range 600–900 °C, usually in inert atmosphere. In chemical activation, the raw material is impregnated for few hours in certain chemicals such as acid or strong base, or a salt. Then the impregnated material is carbonized at lower

temperatures in the range 450–900 °C. Since the raw material requires lesser time and lower temperature for activation, chemical activation is ideal method than physical activation [13]. Activated carbon is the most widely used adsorbent in the adsorption studies due to its high porosity, increased surface area, internal structure and the surface functional groups. The intrinsic pore network in the lattice structure of activated carbons removes the impurities from gaseous and liquid media. To maintain sustainability, agricultural wastes are measured as significant precursors, as they are low cost, renewable, secure, obtainable at large quantities as readily useable sources. Investigation towards batch and continuous experiments for the treatment of dyestuff water using *Eichhornia Crassipes* roots, livestock sewage sludge, sunflower stalks, eucalyptus barks, sugarcane bagasse pulp, woodsaw dust, orange peel, pomegranate Peels, papaya seeds [14-22] and other biodegradable materials as adsorbent was conducted and resulted in a maximum decolorization.

Eichhornia crassipes (*Water hyacinth*) constitutes an important part of an aquatic ecosystem. The direct effect of *Eichhornia Crassipes* on freshwater bodies is its obnoxious smell. It kills the aquatic biota also and depletes oxygen completely from water streams. All the efforts of scientists and technocrats all over the world to eliminate these weeds by chemical and biological means have met with little success. Invaders (*Eichhornia Crassipes*) can also change the whole ecosystems by altering hydrology, fire regimes, nutrient cycling, and other ecosystem processes. Hence organizations like “The Global Invasive Species Programme” (GISP) is co-ordinated by the “Scientific Committee on Problems of the Environment” (SCOPE), in collaboration with the “World Conservation Union” (IUCN), “CAB International” (CABI), other participating groups and individuals have made a toolkit to restrict the mass of invasive alien species which include *Eichhornia Crassipes*. Due to ecological devastating properties of *Eichhornia Crassipes*, it is used for wastewater treatment. More over the method will become inexpensive if the adsorbent material used were cheaper and does not require any expensive additional pretreatment step. *Eichhornia Crassipes* is a natural adsorbent it is readily available there will no side effect to our earth so it can be an alternative to commercial activated carbon. This has motivated us to take the plant for adsorption studies, which will possibly eradicate the abundance of an invasive organism.

Recovery and reuse of spent (exhausted) activated carbon are economical feasible. Fresh carbon is slightly more efficient than regenerated carbon. But using regenerated carbon reduces the cost of purchase of fresh activated carbon. Re-use of degraded carbon also reduces the amount of generation of wastes which eliminates waste carbon disposal costs. In this work, an attempt was made to remove of CR and MB dyes from textile dye wastewaters using a new adsorbent prepared from *Eichhornia Crassipes* without leaving any secondary pollutant to the environment.

Experimental Procedure

Adsorbate

The CR dye is a secondary diazo dye with molecular formula: $C_{32}H_{22}N_6Na_2O_6S_2$, molecular weight: 696.66 g/mol. The MB dye is a basic cationic dye with molecular formula: $C_{16}H_{18}N_3SCl$, Molecular weight=319.85.

The dyes used for the adsorption study in the present work were CR and MB. The λ_{max} values of the dyes were determined by plotting a graph between absorbance of the dye solution at different wavelengths (**Figure 1**). Since, the maximum absorbance of CR and MB were obtained at 500 nm and 660nm respectively; they were taken as the λ_{max} value of the dyes.

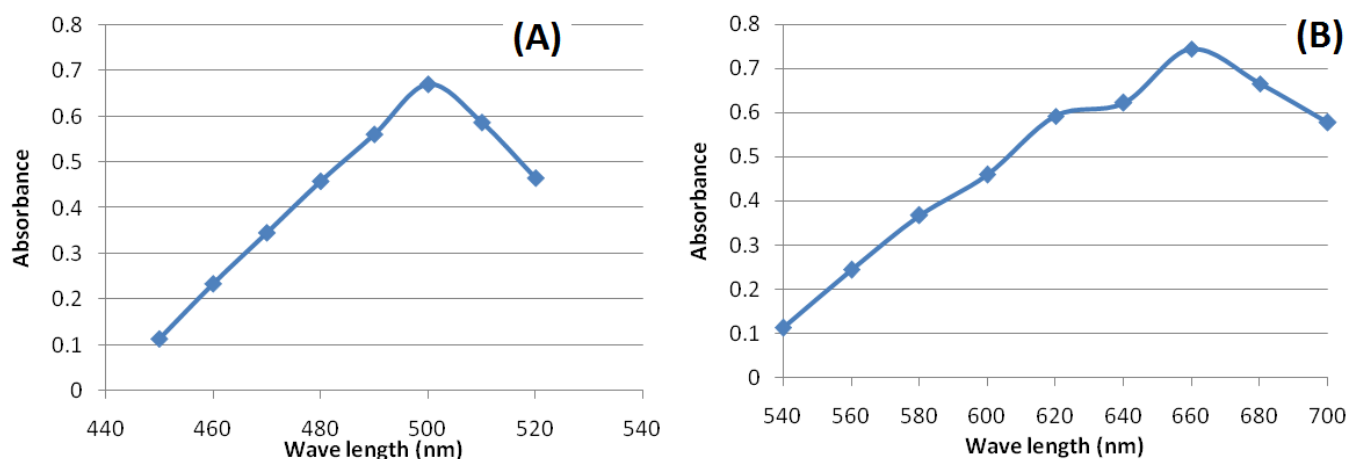


Figure 1 Calibration Curve of (A) Congo red, (B) Methylene blue

Adsorbent preparation

Materials: Eichhornia crassipes has been collected from nearby water sources and treated with 10 % Solution of chloride salts (CaCl_2 , ZnCl_2 , MnCl_2 & NH_4Cl), 10 % solution of sodium sulphates and ammonium sulphates, 10% solution of sodium carbonate, potassium carbonate, dolomite and concentrated phosphoric acid.

Preparation of carbon from Eichhornia crassipes: The collected Eichhornia crassipes was repeatedly washed with water to remove any earthy impurities present in it and dried at 110°C in air oven. The dried Eichhornia crassipes was used for the preparation of various activated carbons by the following procedures listed in **Table 1**.

Table 1 Preparation of carbon by various processes

Name of the process	Reagent Used	Carbonisation process	Drying Process
<i>Pyrolysis Process</i>	-	Carbonised at 400°C for a period of 3 hours and thermally activated in muffle furnace at 800°C for a period of 10 minutes.	-
<i>Carbonization with Chloride salts Process</i>	10 % of calcium chloride, zinc chloride, manganese chloride and ammonium chloride solution		The material obtained was washed well with water and dried at 110°C in hot air oven.
<i>Carbonization with Sulphate salts Process</i>	10 % solution of sodium sulphate and ammonium sulphate.		
<i>Carbonization with carbonate salts process</i>	10 % sodium carbonate and potassium carbonate solution		
<i>Dolomite process</i>	Eichhornia crassipes were sandwiched between two layers of calcium carbonate bed		
<i>Phosphoric Acid Process</i>	1:1 Concentrated Phosphoric acid		

In order to find the most suitable carbon for the detailed study, the carbons thus prepared were subjected to a series of important tests. The carbons prepared by various methods were powered, sieved and particles in the range 75 – 300 μm mesh size were retained for the evaluation of different carbon characteristics.

Analysis of activated carbon

The activated carbon was analysed for its moisture, ash, volatile matter and fixed carbon content, matter soluble in water and acid using the Method IS 1350. Ultimate analysis was done using the Method IS 1350-4-2. Each carbon was separately evaluated and the results of the tests are summarized in **Table 2**.

Table 2 Carbon Characteristics

S.No	Control Tests	Pyrolysis process	Chloride process	Sulphate process	Carbonate process	Dolomite process	Phosphoric acid process
1	Bulk density g/cc	0.57	0.55	0.16	0.6	0.67	0.29
2	Moisture %	4.98	3.56	4.36	6.3	7.81	4.1
3	Ash %	3.39	4.15	3.22	3.68	1.66	1.97
4	Fixed carbon content	96.61	95.85	96.78	96.32	98.34	94.07
5	Matter soluble in water (%)	0.51	0.37	0.57	0.65	0.96	1.11
6	Matter soluble in acid (%)	3.35	2.9	1.75	2.22	0.41	2.35
7	pH	5.72	4.71	4.51	6.44	5.87	5.2
8	Decolorizing power (mg /g)	20.5	23.5	20.41	23.7	22.38	31.50
9	Phenol number (mg)	15.7	16.6	18.3	19.0	16.1	20.0
10	Ion exchange capacity (meq/ g)	0.62	0.516	0.19	0.011	0.36	6.73
11	Iron content [^]	-	-	-	-	-	0.0699
12	Surface area m^2/g	263	156	123	217	120	320

From the Table 2: the carbon characteristics indicated that the carbon obtained by acid process have higher surface area, moderate bulk density and moisture content than other varieties of carbon prepared from *Eichhornia Crassipes* (ECAC), which suggest that extensive adsorption capacity have been introduced by phosphoric acid treatment due microporous structure in carbon.

Ash content values of phosphoric acid activated carbon showed lower values, indicating an increase in fixed carbon content. The carbon derived by acid process is acidic in nature with more ion exchange capacity when compared with other carbons.

The other limitations of the prepared carbons excluding acid process carbon are that they have poor mechanical strength with the result that they cannot be used under column system of treatment. So carbon prepared by acid process was selected for removal of cationic dyes in this study.

Scanning Electron Micrograph

The surface morphology of the prepared activated carbon sample surface was examined using Scanning Electron Micrographs. These micrographs (**Figure 2**) give an appreciation of the porosity of an adsorbent and hence a qualitative assessment of their ability to adsorb the dye molecules in solution. The prepared activated carbon mainly contains considerable micropores, also containing a certain quantity of mesopores. The prepared activated carbon contains redundant pore structure was further proved convincingly by SEM. The images were measured before and after the adsorption of CR and MB onto the adsorbent.

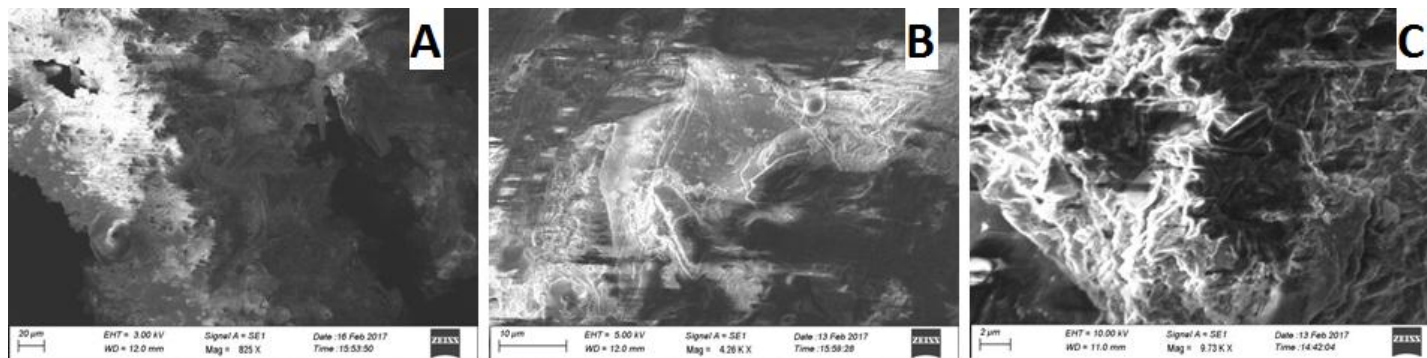


Figure 2 SEM image of (A) ECAC before adsorption, (B) ECAC after adsorption by CR, (C) ECAC after adsorption by MB

Fourier transforms infra red spectra

The FTIR pattern was an important tool to identify some important functional groups, which are capable of adsorbing pollutant ions. FTIR spectroscopy was, therefore, done for preliminary quantitative analysis of major functional groups presented in ECAC. The FTIR spectrum of ECAC, before and after CR and MB adsorption is shown in **Figure 3**.

The FTIR spectra before (BA) and after sorption (AA) of CR and MB were used to determine the vibrational frequency changes in the functional groups present in the adsorbent. The spectra of adsorbents were measured within the range from 600-4000 cm^{-1} wave number. The spectra were plotted using the same scale on the transmittance axis for all the adsorbents before and after adsorption. From the FTIR spectra, it is clear that the adsorbent display a number of absorption peaks, reflecting the complex nature of the adsorbent.

Table 3 shows the tabulated data for FTIR spectra band assignments for BAAC, AACR, and AAMB samples obtained from **Figure 3**. These spectral lines describe the various changes that occurred in the BAAC, AACR and AAMB samples. The results indicate that some peaks were shifted or disappeared, and the new peaks are also detected in AACR and AAMB samples. These changes observed in the spectrum indicate the possible involvement of those functional groups on the surface of the ECAC in adsorption process.

Point Of Zero Charge (pH_{zpc})

The point of zero charge was determined using the soild addition method. 45ml of KNO_3 solution was transferred to a series of 100ml conical flask. The pH values of the solution roughly adjusted from 2 to 10 by adding either 0.1N HCl or NaOH. The pH of the solution was then accurately noted. Adsorbent (1g) was added to each flask and securely

capped. The suspension was then manually agitated. The pH values of the supernatant liquid were noted. The points of intersection of the resulting curve obtained by plotting a graph between pH_0 Vs ΔpH gives the pH_{ZPC} and was found to be 6 pH (Figure 4).

Table 3 FTIR spectra band assignments for BAAC, AACR and AAMB

Assignment	Band Position in cm^{-1}		
	BAAC	AACR	AAMB
O-H stretching of hydroxyl group	3431.87	3866.34 - 3434.28	3866.34 - 3449.23
C-H stretching in alkanes or alkyl group	2924.59 - 2357.51	2924.11 - 2360.41	2924.59 - 2360.41
C=O stretching of anhydride	1624.56	1693.51 - 1649.63	1693.51 - 1643.85
C=C of aromatic ring		1550.30 - 1462.05	1551.75 - 1462.05
C-N stretching of aliphatic 1° amine	1382.49 - 1030.96	1031.44	-
C-X stretching of carbon halogen group	666.41	669.30 - 643.27	664.48

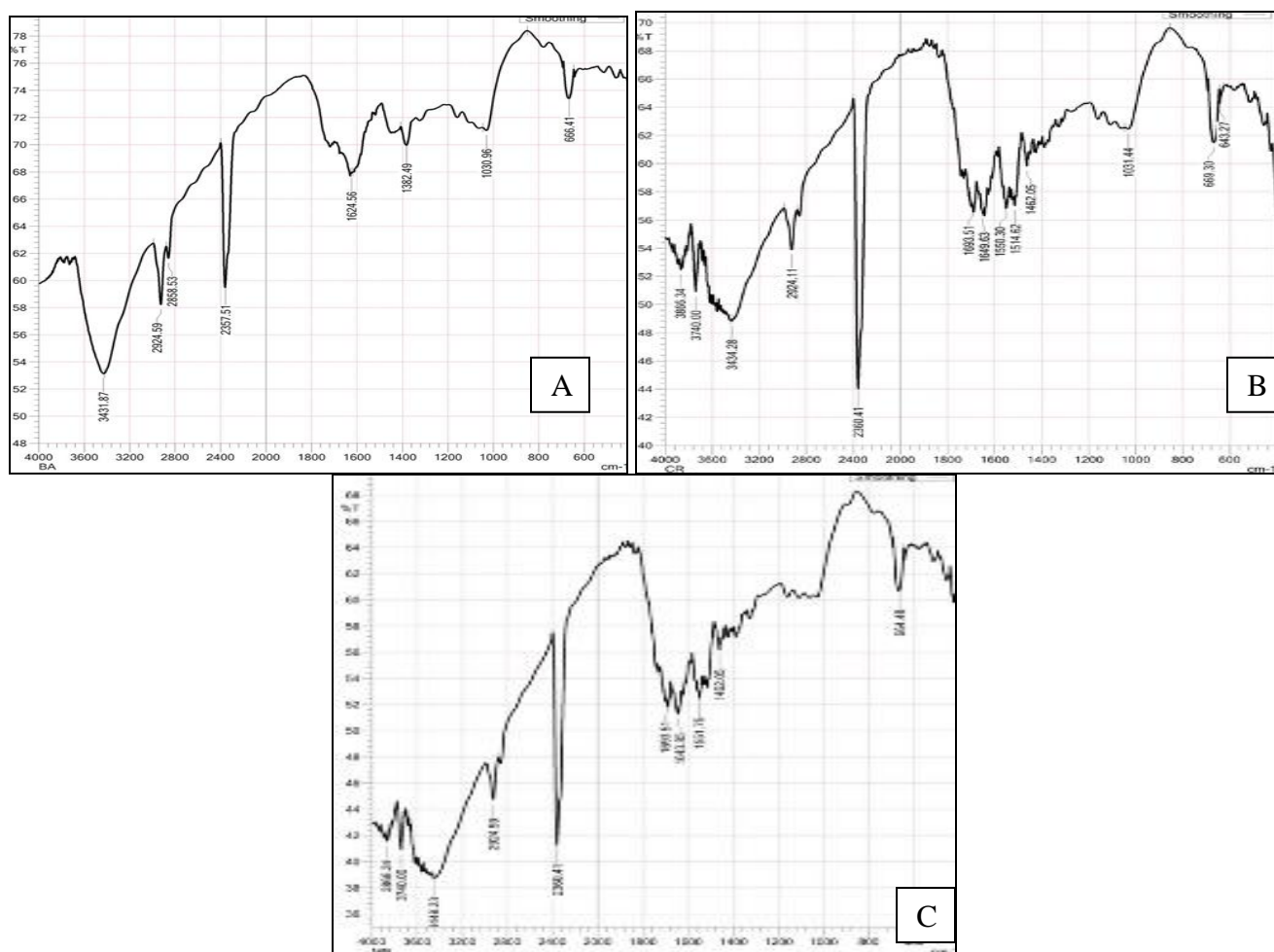


Figure 3 FTIR Spectrum of (A) ECAC before adsorption, (B) ECAC after by CR adsorption, (C) ECAC after by MB adsorption

Batch mode adsorption studies

Preparation of working dye solution

The effects of initial dye concentration, contact time, solution temperature and solution pH on the adsorption uptake for adsorption of CR and MB dyes onto ECAC were studied. Sample solutions were withdrawn at intervals to determine the residual concentration by using UV-VIS spectrophotometer (UV-1800) at 500 and 660nm wavelengths for CR and MB respectively. The amount of dye adsorbed at equilibrium, q_e (mg/g) was calculated via the equation:

$$q_e = \frac{(C_0 - C_e) \times V}{W}$$

where C_0 and C_e are the initial and equilibrium state dye concentrations (mg/l), V is the volume of the solution (l) and W is the mass of the adsorbent used (g).

Adsorption isotherm studies

This was carried out by fitting the equilibrium data to the Langmuir [23], Freundlich [24], Temkin [25], Dubinin–Radushkevich isotherm equations are given below. The applicability and suitability of the isotherm equation to the equilibrium data were compared by judging the values of the correlation coefficients R^2 and normalized standard deviation Δq_e . Linear regression was carried out by using Microsoft Excel worksheet to determine the isotherm parameters.

Isotherm Model	Equation
Langmuir Isotherm	$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$
Freundlich Isotherm	$\log q_e = \log k + \left(\frac{1}{n}\right) \log C_e$
Temkin Isotherm	$q_e = B(\ln A + \ln C_e)$
Dubinin-Radushkevich Isotherm	$\varepsilon = RT \ln \left(\frac{1}{1 + C_e} \right) \& E = \frac{1}{\sqrt{2\beta}}$

Batch kinetic studies

Kinetic and equilibrium models Pseudo-first-order [26], pseudo-second-order [27], Elovich-chemisorption and intra-particle diffusion model [28] kinetic equations are given below.

Kinetic Model	Equation
Pseudo-First Order Equation	$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$
Pseudo-Second Order Equation	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$
Elovich Model	$q_t = \frac{1}{\beta[\ln(\alpha\beta)]} + \frac{\ln t}{\beta}$
Intra-Particle Diffusion	$q_t = k_{id} \sqrt{t} + C$

Thermodynamic Parameters

The activation energy for the adsorption of selected dyes onto prepared adsorbents was evaluated using the following form of Arrhenius equation.

$$\ln k_2 = \ln A - \frac{E_a}{RT}$$

Where, k_2 (g/mg/min) is the rate constant derived from pseudo-second order kinetic model, E_a (kJ/mol) is the Arrhenius activation energy of adsorption and A is the Arrhenius factor, R is the gas constant which is equal to 8.314 J/mol/K, and T (K) is the system temperature.

The Activation for the adsorption and the Arrhenius factor were calculated from the plot of $\ln k_2$ Vs $1/T$. The thermodynamic parameters were evaluated using the following mathematical relationship.

$$K_c = \frac{C_{ads}}{C_{sol}}$$

$$\Delta G^0 = -RT \ln K_c$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

Where, K_c is the equilibrium constant, C_{ads} is the amount of dye (mg/L) adsorbed on adsorbent at equilibrium, C_{sol} is the equilibrium concentration of dye (mg/L) in the solution, T is the solution temperature in K and R is a gas constant (8.314 J/mol/K). The values ΔH^0 and ΔS^0 were evaluated from the slope and intercept of Arrhenius plot of $\ln K_c$ Vs $1/T$.

Result and Discussion

Point of Zero Charge

The results of point of zero charge of *Eichhornia Crassipes* Activated Carbon was obtained by plotting a graph between pH_o Vs ΔpH (**Figure 4**) and was found to be 6 pH.

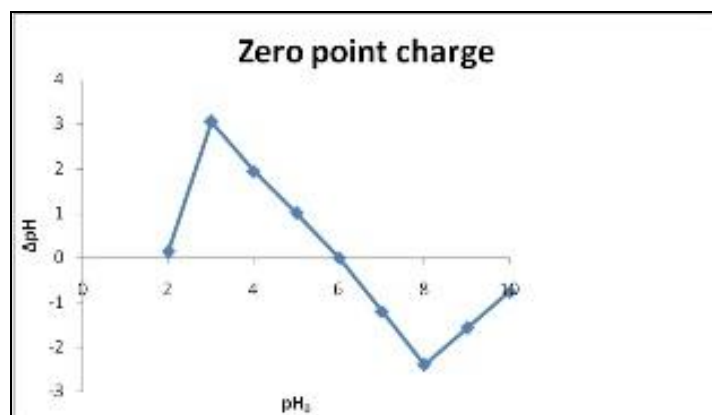


Figure 4 Point of Zero Charge

Effect of Initial Concentration and Agitation Time

The effect of agitation time on the removal of CR and MB dyes by ECAC at various initial dye concentrations (80, 100, 120 and 140mg/L) with a carbon dosage of 100mg/100 ml were presented in **Figure 5**. The amount of dye adsorbed at various intervals of time indicated that the removal of dye initially increases with time. On increasing initial concentration, the actual amount of dye adsorbed per unit mass of adsorbent also increased. It meant that the adsorption is highly dependent on the initial concentration of dyes.

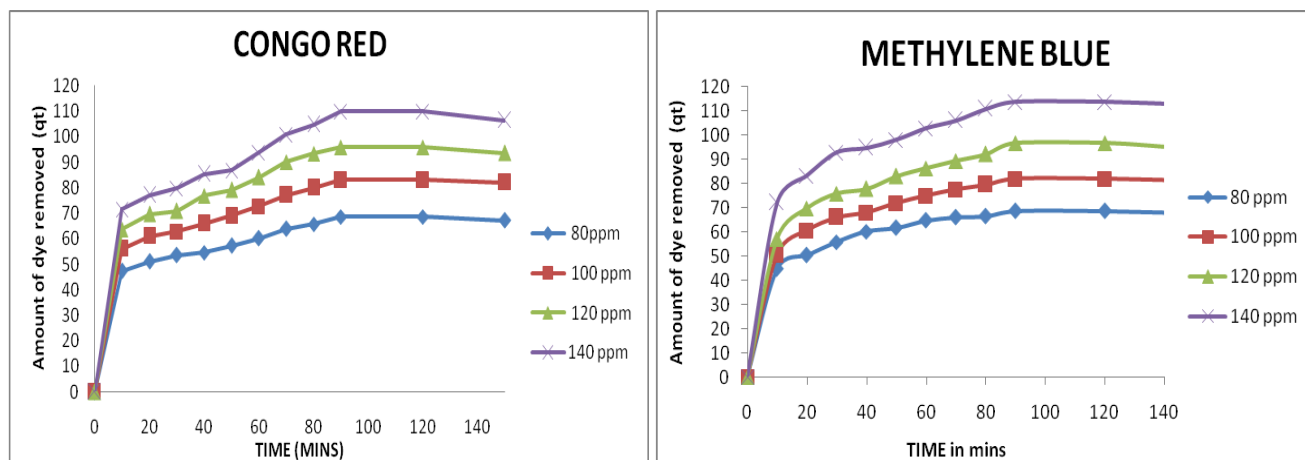


Figure 5 Effect of Agitation Time

Effect of Carbon Dosage

The effect of carbon dosage on the percentage of dye removal with dye concentrations (100 mg/L) at a various carbon dosage of 50 to 300 mg were presented in **Figure 6**. The removal of dye increased with increasing carbon dosage. From the result, it was clear that maximum colour is removed at high carbon dosage (300mg). The increase in the percent removal of dye with the increasing carbon dosage is due to the increase number of carbon particles. But 10g/L was taken as optimum carbon dosage for further studies.

Effect of pH

The effect of pH of the solution (pH from 2 to 12) on the adsorption of dyes (CR and MB) of concentration 100 mg/L by the activated carbon with a carbon of dosage 100 mg was determined. The result showed (**Figure 6**) that an increase in the solution pH led to an increase in the colour removal for MB. It meant that on increasing pH, the availability of negatively charged groups at the adsorbent surface sites necessitated the adsorption of basic dyes.

Effect of Temperature

The effect of temperature on colour removal by (CR and MB) dyes was investigated at a different temperature 25°C, 30°C, 40°C and 50°C with the dye concentrations 100 mg/L at fixed carbon dosage of 100 mg, it was found that the percentage of colour removal increased with increasing temperature which indicating the process to be endothermic in nature. The maximum adsorption was observed at 50°C. Increasing the temperature increases the rate of diffusion of the adsorbed molecules across the boundary layer and the internal pores of the adsorbent particles (**Figure 6**).

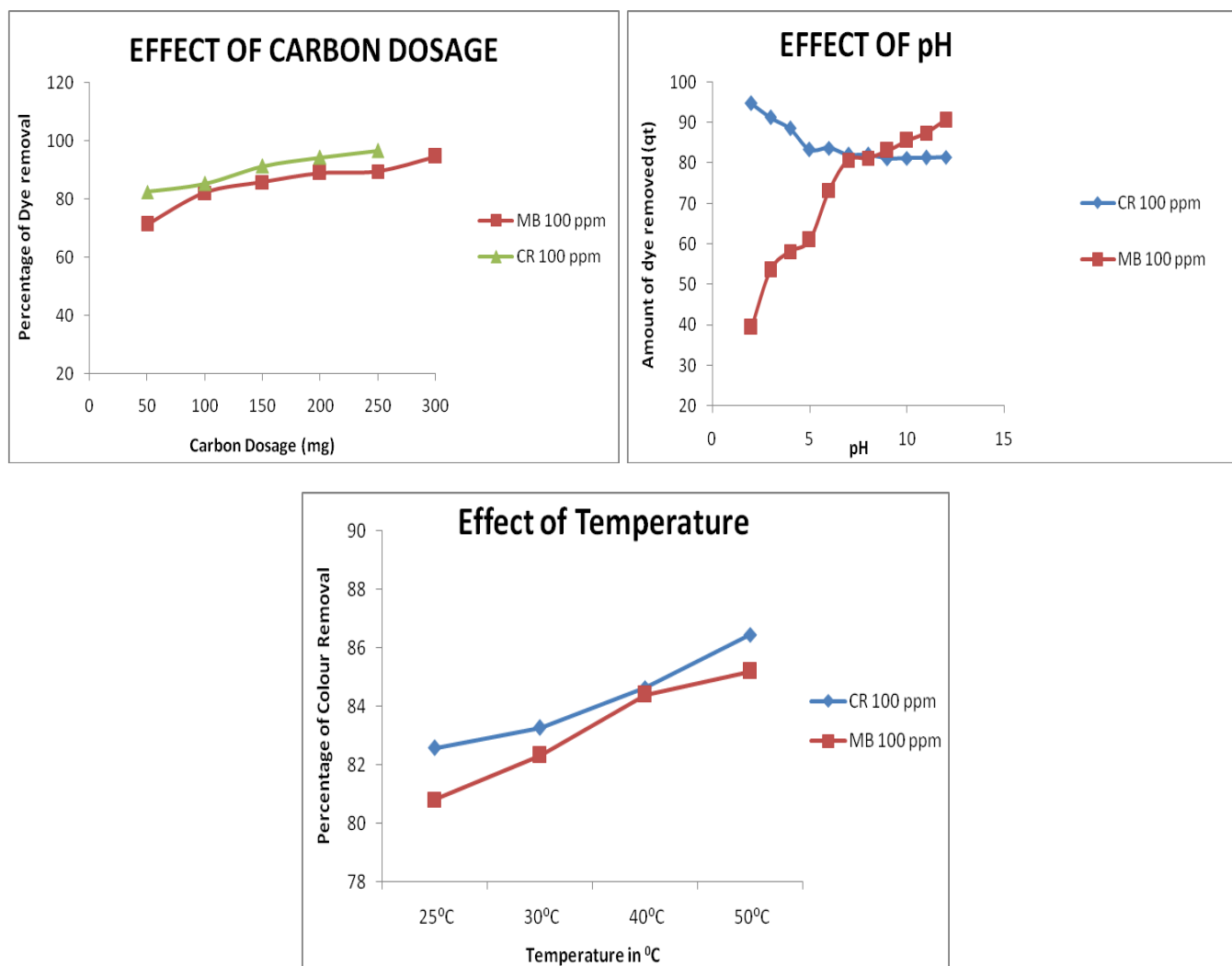


Figure 6 Effect of Carbon dosage, pH, and Temperature

Analysis of Adsorption Kinetics

The study of adsorption kinetics is significant as it provides valuable insights into the reaction path ways and the mechanism of the reactions. Four kinetic models are used to explain the mechanism of the adsorption of CR and MB dyes onto prepared ECAC.

The Lagergen pseudo-first order kinetics and pseudo-second order kinetics plots for the adsorption of dyes CR and MB onto ECAC were showed in **Figures 7** and **8** respectively. The calculated K_1 , K_2 values and their corresponding linear regression correlation coefficient values are represented in **Table 4**. The obtained R^2 values for the pseudo second-order model are higher than the pseudo first-order model. This shows that the adsorption of CR and MB onto ECAC is well-fitted to the pseudo second-order kinetic model compared to the pseudo first-order model. The calculated q_e values also well agreed with experimental q_e values for pseudo second-order kinetic model. This indicates that the adsorption process depends on both the adsorbent and adsorbate concentrations in the solutions.

The Elovich kinetic plot is shown in **Figure 9**. The Elovich parameters are represented in **Table 5**. The calculated ' α ' and ' β ' parameters used to estimate the reaction rate. The obtained R^2 values for the carbon for all the concentrations are considerably high. But the calculated constants α and β fails to obey the conditions for MB onto ECAC. In case of CR the calculated constants α and β obeys the conditions, but R^2 values obtained for all the concentrations are considerably low. This suggests that the Elovich model doesn't fit to describe the present adsorption mechanism.

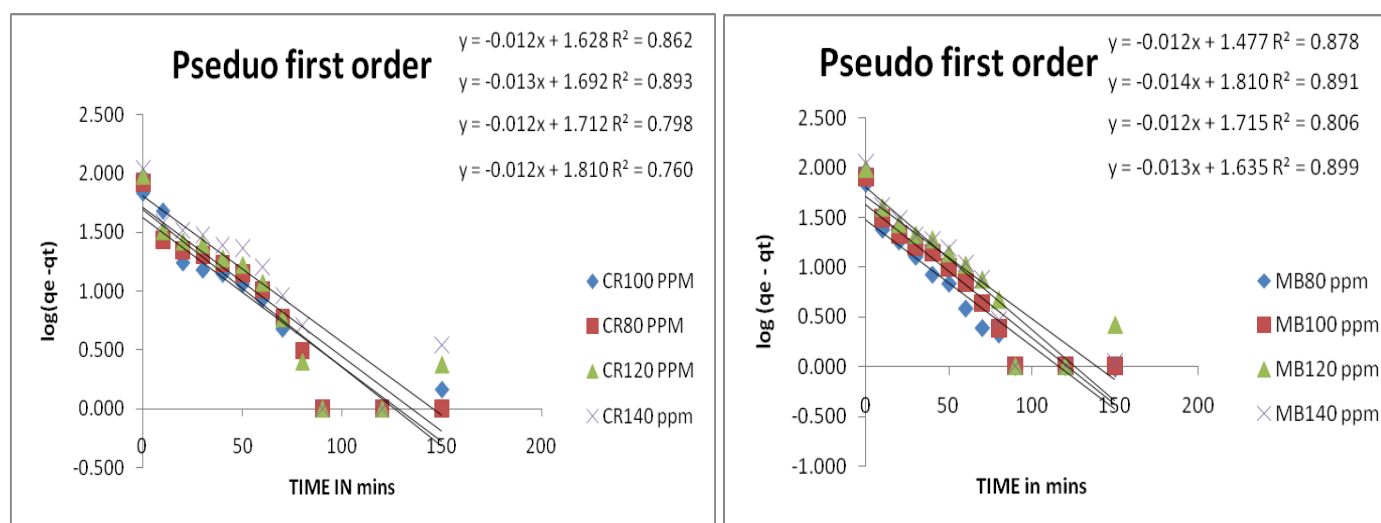


Figure 7 The pseudo-first order kinetics of CR and MB onto ECAC

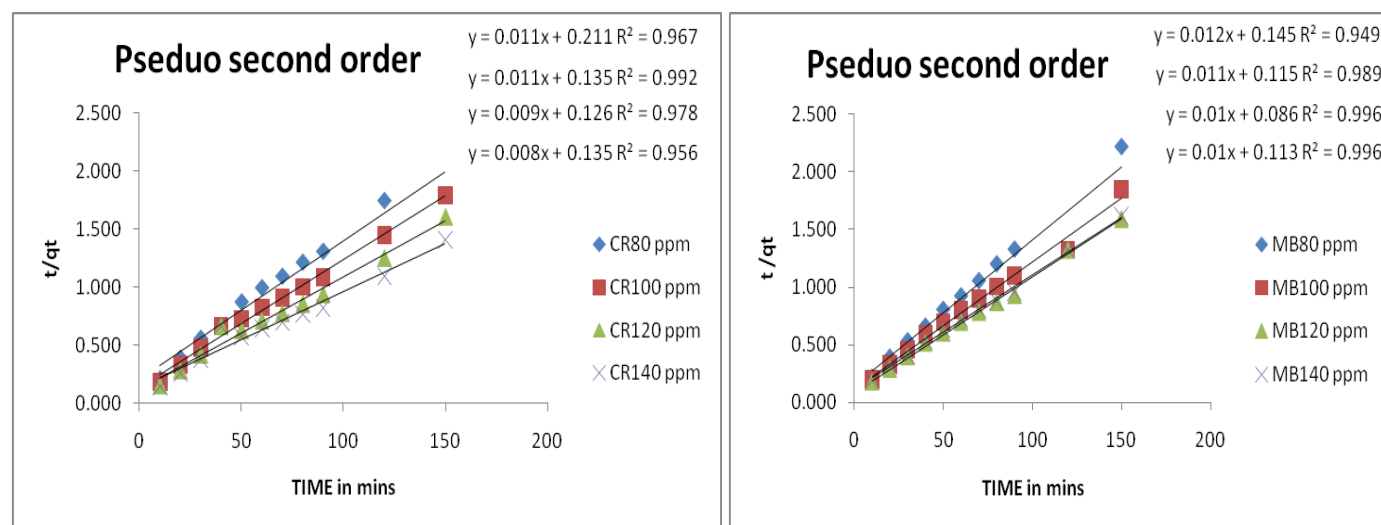
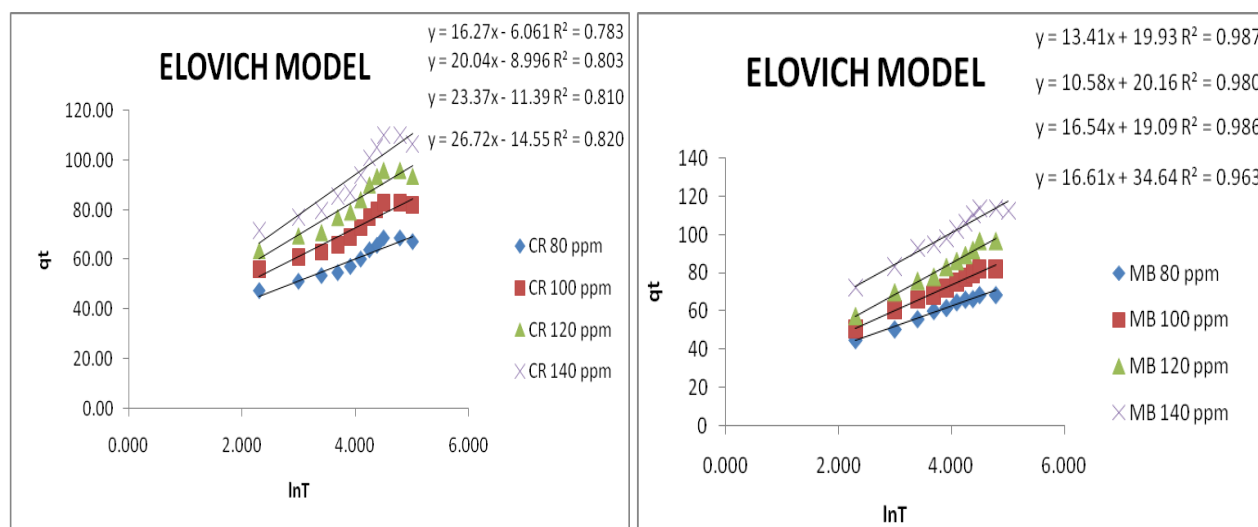


Figure 8 The pseudo-second order kinetics of CR and MB onto ECAC

Table 4 Kinetics model's constant and their correlation coefficients

Kintetic studies	Initial conc (mg / L)	Congo Red				Methylene Blue			
		qe expt (mg / l)	qe calculated (mg / l)	k ₁ / k ₂ (min-1)	R ²	qe expt (mg / l)	qe calculated (mg / l)	k ₁ / k ₂ (min-1)	R ²
Pseudo first order	80	68.67	42.462	0.028	0.599	68.58	29.992	0.0276	0.87
	100	83.00	49.204	0.030	0.818	82.02	64.565	0.0322	0.89
	120	95.96	51.523	0.028	0.680	96.74	51.880	0.0276	0.80
	140	109.92	64.565	0.028	0.885	113.77	43.152	0.0299	0.89
Pseudo second order	80	68.67	90.909	0.0006	0.967	68.58	83.333	0.0010	0.94
	100	83.00	90.909	0.0009	0.992	82.02	90.909	0.0011	0.98
	120	95.96	111.111	0.0006	0.978	96.74	100.000	0.0012	0.99
	140	109.92	125.000	0.0005	0.956	113.77	100.000	0.0009	0.99

**Figure 9** Elovich Kinetic Model Plot of CR and MB onto ECAC**Table 5** Kinetics model's constant and their correlation coefficients

	Initial conc (mg / L)	Congo Red			Methylene Blue		
		α mg/g/min	β mg/g	R ²	α mg/g/min	β mg/g	R ²
Elovich Model	80	11.21	0.061	0.783	59.26	0.070	0.987
	100	12.79	0.050	0.803	71.10	0.090	0.980
	120	14.36	0.043	0.810	52.44	0.060	0.986
	140	15.50	0.037	0.820	133.64	0.060	0.963
Intra Particle Diffusion		K_{id}		R²	K_{id}		R²
	80	2.215		0.978	4.476		0.974
	100	3.061		0.972	4.209		0.981
	120	3.972		0.928	4.897		0.974
	140	4.049		0.957	5.471		0.918

Test of Kinetics Model

Intra-Particle Diffusion Studies

The intraparticle diffusion plots were shown in **Figure 10**. At each concentration the linear plot did not pass through the origin. Such deviation of straight lines from the origin may be due to the difference in rate of mass transfer in the initial and final stages of adsorption. This shows that both intra particle diffusion and film diffusion had simultaneously occurred in adsorption processes. Alike results were explained elsewhere by [29]. The high correlation

coefficient value represented in **Table 5** proved that both the film and pore diffusion played a significant role for the adsorption of CR and MB onto the prepared activated carbon ECAC.

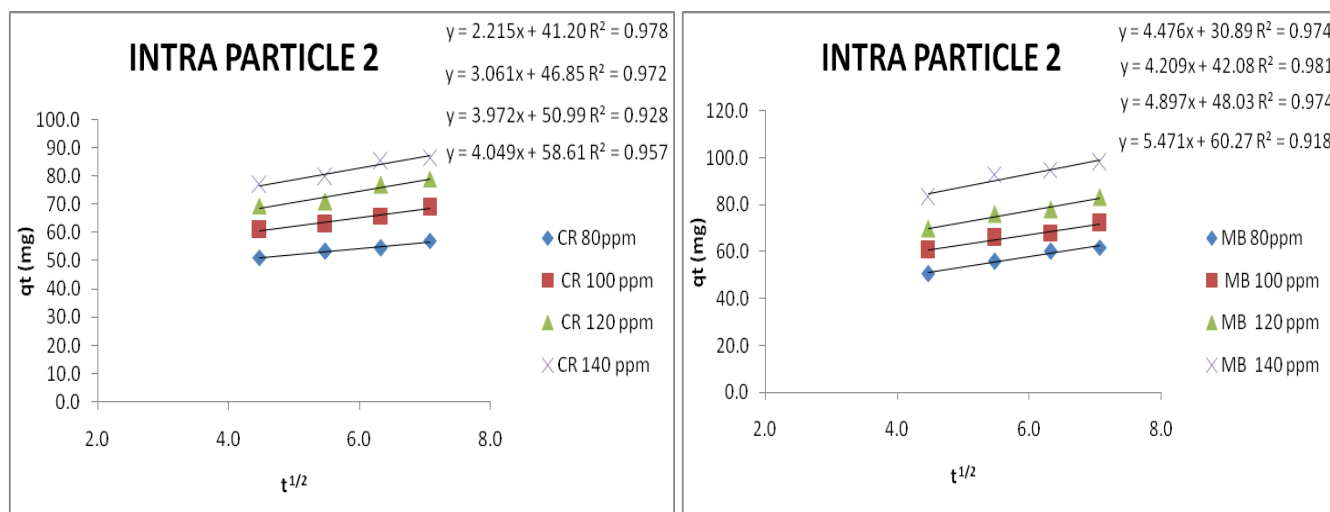


Figure 10 Intra Particle Diffusion plot of CR and MB onto ECAC

Adsorption Isotherms

Adsorption isotherms provide an approximate estimation of adsorption capacity of the adsorbent.

Langmuir Isotherm

The linear plot of C_e/q_e Vs C_e suggests the applicability of the Langmuir isotherms as shown in **Figure 11**. The values of Q_0 and b were determined from slope and intercepts of the plots and are presented in **Tables 6** and **7**.

The constant Q_0 (mg/g) is a measure of maximum adsorption capacity of the adsorbent under the experimental conditions and b (L/mg) is a constant related to the energy of adsorption. The value of R_L indicates the shape of the isotherm to be unfavorable, linear, favourable or irreversible. R_L values for the present study data fall between 0 and 1, which suggest that the adsorption of CR and MB on the adsorbent is favourable.

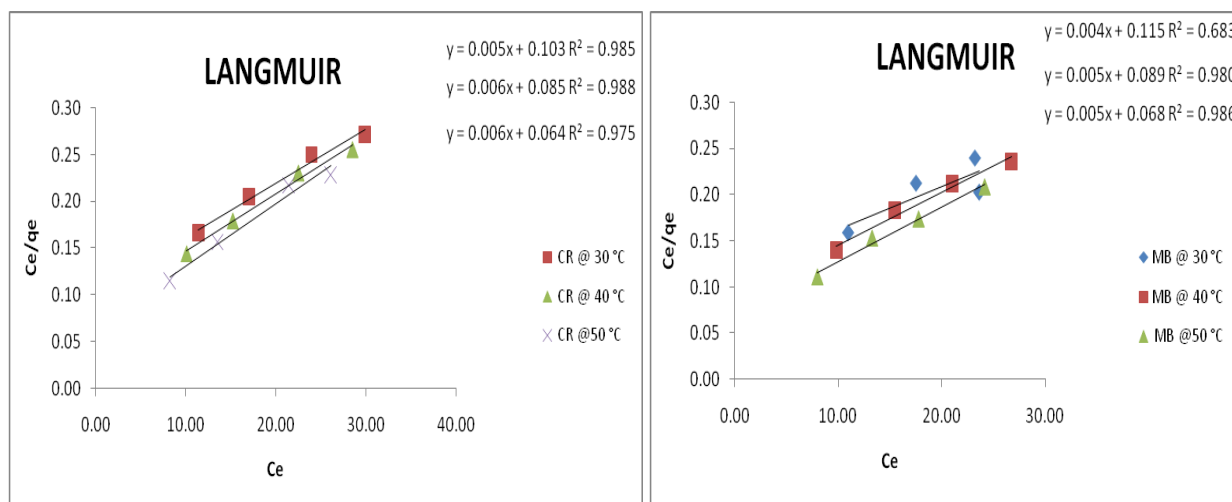


Figure 11 Langmuir Isotherm plot of CR and MB onto ECAC

Freundlich Isotherm

The linear graph of $\log q_e$ Vs $\log C_e$ is shown in **Figure 12**. The values of Freundlich isotherm parameters are given in **Tables 6** and **7**, which shows that the values of bond energies (K_f) were increased with temperature. A graph plotted from the Langmuir isotherm model and Freundlich isotherm model yielded a straight line with higher R^2 regression co-efficient value. This indicates the surface of the ECAC contains heterogeneous moieties which are uniformly

distributed on the surface. The magnitude of exponent $1/n$ gives an indication about the favorability of adsorption; the value of $1/n$ should be in the range of $0-1$. In the present study, the values of $1/n$ were within the range and also $n > 1$, indicates that the adsorption is physical in nature [29].

Table 6 Isotherms Statistical Parameters / Constants for CR

Temp. (°C)	Langmuir isotherm				Freundlich isotherm		
	B (L/mg)	Q_0 (mg/g)	R^2	R_L Value	ϵ (KJ/mole)	N	R^2
30	0.04854	200.00	0.985	0.163	21.3796	2.0921	0.996
40	0.07059	166.667	0.988	0.118	25.5270	2.2936	0.994
50	0.09375	166.667	0.975	0.092	32.2107	2.6525	0.977
Temp. (°C)	Temkin isotherm			Dubinin-Radushkevich isotherm			
	α (A) (L/g)	β (B) (J/mg)	R^2	β (mole ² /J ²)	ϵ (KJ/mole)	X_m	R^2
30	0.44	41.68	0.984	-0.011	6.7420	111.29	0.923
40	0.59	38.66	0.986	-0.008	7.9057	111.63	0.929
50	0.96	34.02	0.957	-0.005	10.000	109.85	0.883

Table 7 Isotherms Statistical Parameters / Constants for MB

Temp. (°C)	Langmuir isotherm				Freundlich isotherm		
	B (L/mg)	Q_0 (mg/g)	R^2	R_L Value	K_f (mg/L)	N	R^2
30	0.03478	250.00	0.683	0.213	22.2844	2.1505	0.992
40	0.05618	200.00	0.980	0.144	23.5505	2.1142	0.994
50	0.07353	200.00	0.986	0.114	28.7078	2.2883	0.993
Temp. (°C)	Temkin isotherm			Dubinin-Radushkevich isotherm			
	α (A) (L/g)	β (B) (J/mg)	R^2	β (mole ² /J ²)	ϵ (KJ/mole)	X_m	R^2
30	0.47	40.58	0.978	-0.01	7.0711	109.74	0.890
40	0.51	42.25	0.979	-0.008	7.9057	112.97	0.897
50	0.72	40.01	0.982	-0.005	10.000	114.34	0.890

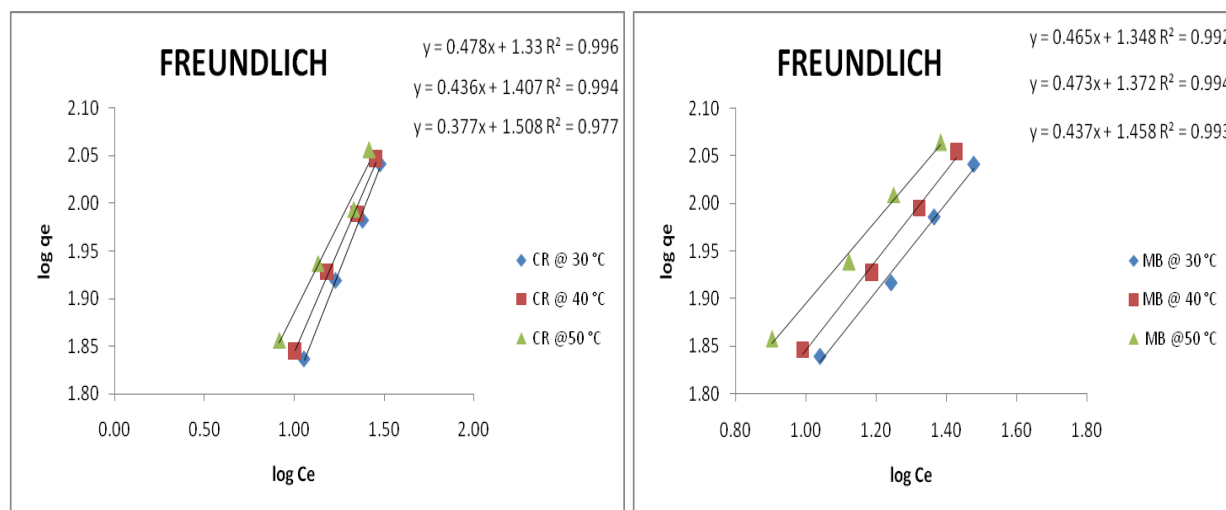


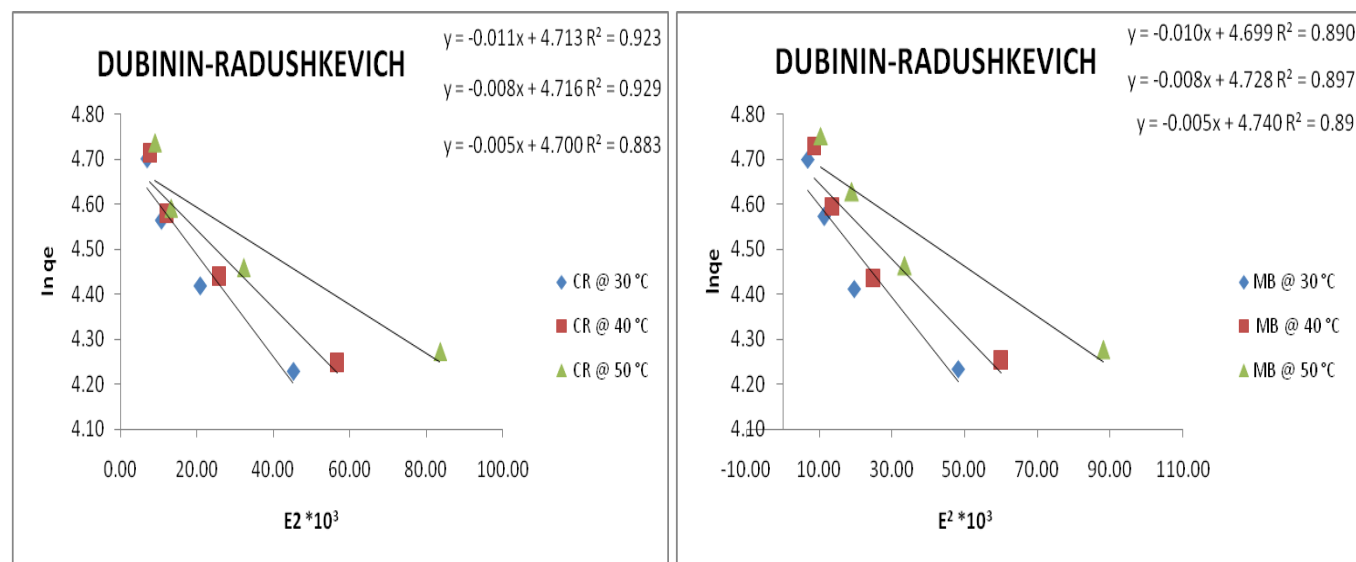
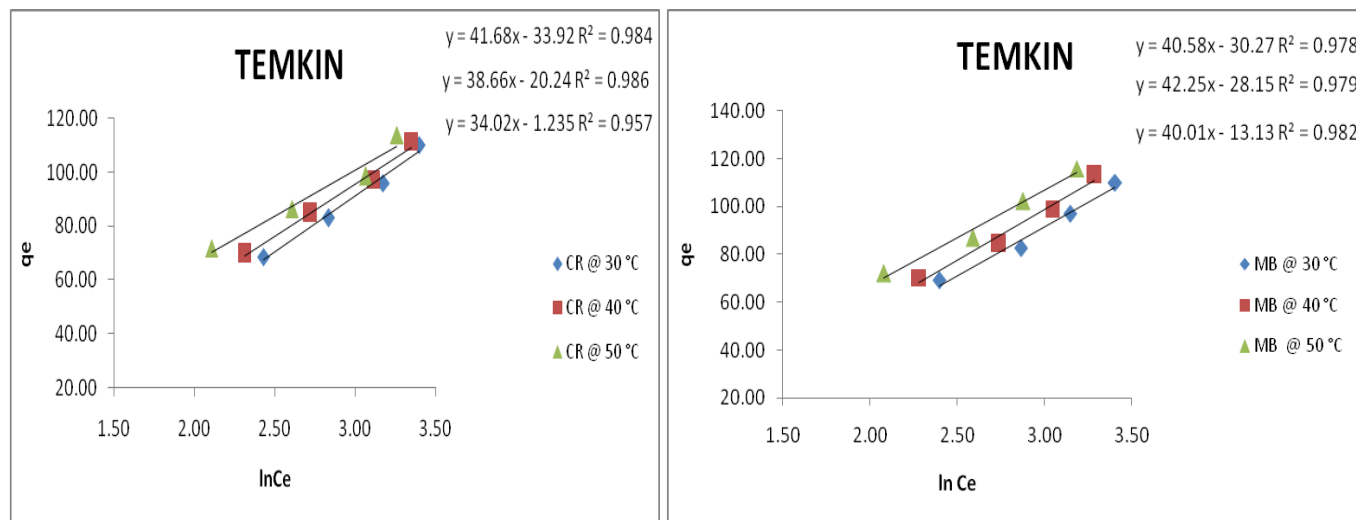
Figure 12 Freundlich isotherm plot of CR and MB onto ECAC

Temkin Isotherm

The values of the Temkin A constants and B calculated from the intercept and slope respectively and correlation coefficients are listed in Tables 6 and 7 from the linear plot of $\ln C_e$ Vs q_e (**Figure 13**). The maximum binding energy (A) is increased with raise in temperature. The value of B is varied with raise in temperature. The obtained R^2 values were nearer to 1. Temkin isotherm model also fits the present adsorption system for both CR and MB.

Dubinín-Radushkevich Isotherm

A plot of $E^2 \times 10^{-3}$ versus $\ln q_e$ gives a linear trace (**Figure 14**) and the constants X_m , E and β calculated from the slope and intercept respectively are listed in **Tables 6 and 7**. The mean free energy of adsorption E is calculated. Based on the energy of activation one can predict whether an adsorption is physisorption or chemisorption. If the energy of activation is $< 8 \text{ kJ mol}^{-1}$, the adsorption is physisorption and if the energy of activation is 8 to 16 kJ mol^{-1} , the adsorption is chemisorption in nature. Results of E obtained indicate that the adsorption of CR and MB dyes on ECAC were physisorption at low temperature (30°C & 40°C) and chemisorption at high temperature (50°C).

*Thermodynamic Parameters*

The ΔS° , ΔH° , and ΔG° values obtained from the plot of $1/T$ vs $\ln k$ (**Figure 15**) at different temperatures for various initial dye concentrations were presented in **Tables 8 and 9**. Generally, when the ΔG value is between 0 and -20 KJ/mol , then the adsorption is physisorption; while, when a ΔG value is more negative and is ranging from -80 to -400 KJ/mol , then the adsorption is chemisorptions [30]. The positive values of ΔH° show the endothermic nature of adsorption and it governs the possibility of chemisorptions rather than physisorption at higher temperature. The positive value of enthalpy changes ΔH° for the process confirms the adsorption of CR and MB on the surface of prepared activated carbon is endothermic in nature. The negative ΔG° values indicate the feasibility of the adsorption

process at all temperatures studied. The positive ΔS° values indicate that the increasing randomness at the surface of the adsorbent among the adsorption process.

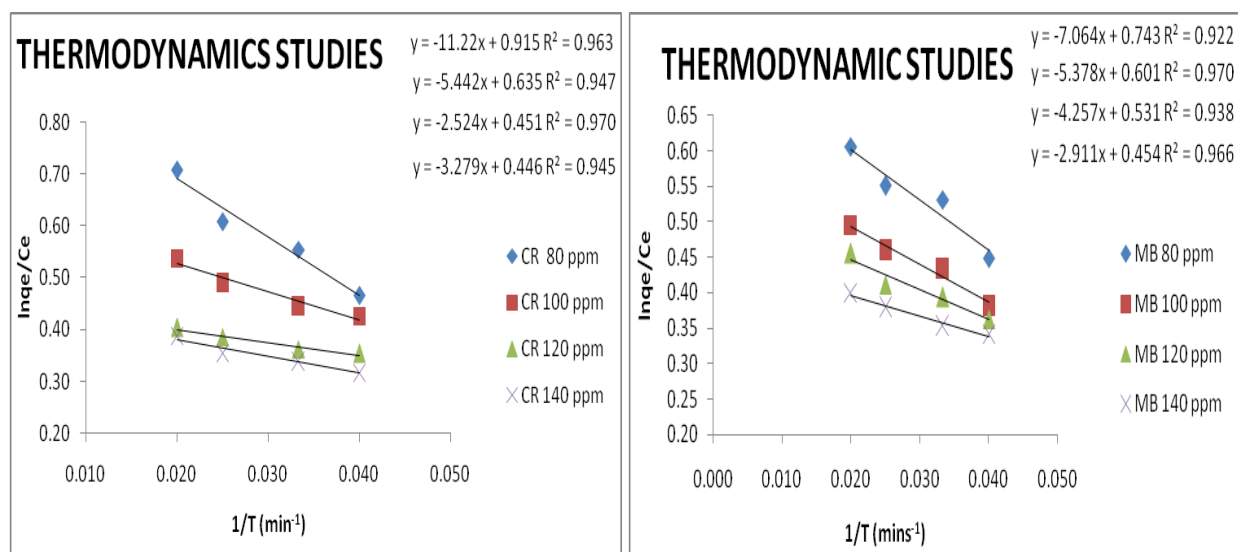


Figure 15 Arrhenius Plot for calculation of Thermodynamic parameters of CR and MB

Table 8 Thermodynamic Parameters of CR

Initial dye concentration, (mg/L)	ΔS° (KJ/mol/K)	ΔH° (KJ/mol)	ΔG° (KJ/mol)			
			298K	303K	313K	323K
80	7.6073	93.2831	-2173.7	-2211.73	-2287.8	-2363.88
100	5.2794	45.2448	-1528.01	-1554.41	-1607.2	-1660
120	3.7496	20.9845	-1096.4	-1115.15	-1152.64	-1190.14
140	3.7080	27.26161	-1077.74	-1096.28	-1133.36	-1170.44

Table 9 Thermodynamic Parameters of MB

Initial dye concentration, (mg/L)	ΔS° (KJ/mol/K)	ΔH° (KJ/mol)	ΔG° (KJ/mol)			
			298K	303K	313K	323K
80	6.177	58.730	-1782.11	-1812.99	-1369.92	-1415.57
100	4.997	44.713	-1444.31	-1469.29	-1519.26	-1569.23
120	4.415	35.393	-1280.2	-1302.27	-1346.42	-1390.57
140	3.775	24.202	-1100.62	-1119.49	-1717.45	-1773.09

Regeneration of Spent Carbon

Spent activated carbon (SAC) disposal at a landfill creates soil pollution, so they needed to be regenerated and reused. Repetitive usage of regenerated and reused SAC provides economic profit. Chemical regeneration method was one of the more apt and inexpensive technique. In this study, SAC was regenerated using sodium hydroxide (NaOH) solution. The effectiveness of NaOH in regeneration of SAC was tabulated. The regeneration performance for SAC was calculated via the equation [31]

$$RE\% = \frac{A_r}{A_0} \times 100$$

Where A_0 is original adsorption capacity and A_r is adsorption capacity of the regenerated ECAC

The regeneration efficiency of regenerated SAC was as good as to fresh activated carbon with regeneration efficiency more than 90% in iodine adsorption test and 95% in MB adsorption test.

Reuse of Degraded Spent Carbon

The raw materials used in the production of cement are finite and non-renewable and need to be conserved for future generations. To attain sustainable construction a strong trend favoring the increased use of admixture in concrete is emerging throughout the world. In this study the degraded spent carbon (DSC) is used as admixture. Replacement made for 0%, 1%, 2%, 3% and 4%. High % replacement of 4 % was considered and its economic feasibility was represented in **Tables 10** and **11**. The Physical properties and compression strength test of material were tested and results are given in the Table 12.

Table 10 Regeneration Efficiency Parameters of SAC

Sample	Regeneration methods	Regeneration efficiency (%)	Yield (%)	Particle size degradation (%) after 5 cycles of operation
SAC1	alkali treatment	93.8%	95	0.33

Table 11 Cost Comparison

Materials	Cost of Conventional Concrete			Cost of 4 % Replacement of DSC		
	Quantity	Cost per Kg	Cost in Rs. /m ³	Quantity	Cost per Kg	Cost in Rs. /m ³
Cement	352.0	7 / Kg	2464.0	337.92	7 / Kg	2365.44
DSC	-	-	-	14.08	0.50 / Kg	7.04
Coarse aggregate	1215.0	0.65/ Kg	789.75	1215.0	0.65/ Kg	789.75
Fine aggregate	776.0	0.85/ Kg	659.60	776.0	0.85/ Kg	659.60
Total Cost			3913.35/-			3821.83/-

Table 12 Physical properties and ultimate strength of the Specimen
(Testing material: Bharathi cement – OPC53 Grade + 4% DSC)

S.No.	Test	Results	IS code values as per IS12269:2013
1	Fineness Test	3.2 %	Not more than 10%
2	Soundness	0.5 mm	10 mm
3	Consistency	27 %	----
4	Initial Setting Time	35 mins	30 mins
5	Final Setting Time	630 mins	600 mins
6	Compression Strength Test (Average of 5 Cubes)	24.26 N/mm ² (3 days) 35.81 N/mm ² (7 days) 51.92 N/mm ² (14 days)	27 N/mm ² 37 N/mm ² 53 N/mm ²
The result showed that 4 % replacement of DSC in concrete is economic and safe to use in construction to sustain its better quality.			

Conclusion

- Adsorption of MB and CR dyes increased with contact time, temperature and adsorbent dose. pH_{zpc} of the adsorbent was found to be 6.
- A maximum of 90% colour of MB and CR were removed at pH-12 and pH-2 but pH-7 was optimized, so that discarded colour removed solution can be reused for vehicles cleaning and washing purposes.
- The values of $R^2 < 1$ (Hall constant), obtained in this study was highly favorable to Freundlich adsorption isotherm indicated that the adsorption of CR and MB dyes on ECAC were physisorption at low temperature and chemisorption at high temperature which was further proved in D-R isotherm and thermodynamics studies (more negative ΔG values).
- Adsorption of CR and MB dyes on the adsorbent was fitted more appropriately by pseudo second order kinetic model it was evidenced by q_e and R^2 values.
- Intraparticle diffusion constant (K_{id}), adsorption capacity (K_f) and monolayer concentration (X_m) increase with the increase in temperature revealed that adsorption of CR and MB on ECAC is endothermic and it was further strengthened by the positive values of ΔH .

- The spontaneity and feasibility of the adsorption process are shown by the negative values of ΔG .
- Charcoal prepared from waste materials, *Eichhornia Crassipes* (EC) was found to be cost effective in removing CR and MB dyes from aqueous solutions without leaving any secondary pollutant.
- SAC was effectively regenerated, recovered and reused which renders that this decolourisation method was more economical, valuable and important.
- The aquatic waste weeds were efficiently made into wealth. Hence it is hoped that these studies can be extended further for the removal of colored effluents of dyeing and processing industries.

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Publication History

Received	11 th Dec 2017
Revised	20 th Dec 2017
Accepted	20 th Dec 2017
Online	30 th Dec 2017