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Biotreatment of a Triphenylmethane dye Solution using Medicinal Plant Rhizome: Acorus Calamus

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Abstract

This article utilizes still popular medicinal herbal plant Acorus calamus rhizome as a decisive substitute for exclusion of Basic Green 4 (BG 4), a cationic dye from its aqueous solutions by making use of batch investigational system. Further plausible mechanisms were achieved by correlating experimental values with the predicted kinetic models thus exploiting high significant rate statistics of the model preferred. Experimental biosorption data were modelled by Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich (D-R) isotherm, Redlich-Peterson (R-P) isotherm, Harkins- Jura (H-J) isotherm and Generalised isotherms. The biosorption route followed the Langmuir isotherm model with high coefficients of correlation ($R^2 > 0.99$).Thermodynamic parameters suggest that the biosorption process is spontaneous and endothermic in nature. Overall, this article summarizes the efficacy of herbal biosorbent for the elimination of BG 4.

Keywords*:* Adsorption, cationic dye, BG 4, kinetic studies, isotherm, thermodynamics.

Introduction

The escalating world population substantially boosts the industrialization and urbanisation sectors. Especially synthetic dyestuffs engrossed much more console when compared to natural dye because of its ease to use, inexpensive cost of synthesis and wide array of colours. This flourishing advancement of dyes widens aquatic contamination by the discharge of industrial effluents containing pollutants. Hence crucial scheme has to be implemented for leading a standard, clean environment and also we have to ensure a guaranteed environment by solving this crisis in a holistic manner. Several ways are offered to resolve this environmental disquiets long time ago, but still assemblage of any one appropriate scheme to sustainability till cessation is a huge challenge[1]. Removing dyes by chemical precipitation and on biological treatment is a tricky procedure. However, it can be stalwartly adsorbed into solids such as adsorbents. That's why adsorption techniques have gained rapid prominence and avails an endeavour among all the conventional physicochemical procedures. The effectiveness of this process lies on its ease with which it can apply to the treatment of wastewater[2, 3]. In this scenario, herbal materials were chosen, because of its diverse compositions, properties and functionalities as carbonaceous precursors for the removal of dye.

Basic Green 4 (BG 4), popularly known as Malachite green, has been meticulously used as an antifungal agent in the fish husbandry globally. Further it finds resourceful applications as a biocide in parasitic healing and also used in fungal and bacterial contagion in fish and fish eggs. It has placed its footpath in textile industries for dyeing nylon, wool, silk, leather, and cotton. The release of BG 4 into the aquatic ecosystem has breed to a large extent and created much concern because of its reported genotoxic, mutagenic, teratogenic and carcinogenic effects[4]. Furthermore its high solubility nature may have the chances to enter into the food chain and cause severe effects on nervous system, reproductive system, liver, brain and kidney.

This article reports the biosorption properties of acorus calamus for MG removal from aqueous solution by focusing on the usage of herbal powder as biosorbent. In the recent years, utilization of herbal medicines has been gaining unique popularity in the world. In this tie, usage of herbal rhizome acorus calamus as biosorbent finds a novel as well as pioneering option from both economical and environmental viewpoint. Previous studies of this rhizome as herbal biosorbents have reported for the removal of methylene blue and crystal violet from aqueous solution. Thus, this study was conceded out with a motivation via the usage of rhizome for the removal of BG 4, which includes an evaluation of various kinetic models, equilibrium isotherms and thermodynamic parameters.

Material and Methods

Preparation of Biosorbent: Acorus calamus was purchased from the local departmental store. The rhizome was thoroughly rinsed with tap water to confiscate the adhering dirt followed by distilled water. The substances were dried up under sun and subsequently oven dehydrated at 100^0C continuously for about 6

hrs. Then, the dried rhizome was crushed using mortar and pestle and sieved to a desired particle sizes and preferred to use as such.

Preparation of Adsorbate Solutions: Basic Green 4 (BG 4) used in this study was of trade quality (CI 42000, FW: 365, MF: $C_{23}H_{25}N_2Cl$, λ_{max}: 618 nm) and used as such. Dye stock solution (1000mgL^{-1}) was prepared by dissolving precisely weighed mass of the dye in double distilled water. Experimental dye solution of dissimilar concentrations was prepared by diluting the stock solution with suitable volume of double distilled water. The initial solution pH was adjusted using 0.1 (N) HCl and 0.1 (N) NaOH solutions.

Equilibrium Adsorption Studies: To analyse the adsorption isotherm, 0.150g of prepared adsorbent was added with 100 mL of dye solution of dissimilar concentrations in the range of 20–100 mg/L at pH 8.0 for 120min with constant shaking at ambient temperature of 26±2 °C. Replica testing was conceded for all the functioning variables considered and only the average values were chosen Linear regression analyses were used to determine slopes and intercepts of the linear plots and for statistical analyses of the data.

Calculation of Dye Concentration for Isotherm Studies: The amount of dye adsorbed, q_e(mg/g) and percentage of removal were calculated by using the following equation.

$$q_e = \frac{(C_0 - C_e)}{W} V \quad (1)$$

Where: q_e = the dye concentration on the adsorbent at equilibrium (mmol of dye/g of acorus calamus), C_o = the initial dye concentration in the liquid phase (mmol of dye/l), Ce = the liquid-phase dye concentration at equilibrium (mmol of dye/l), V = the total volume of dye-acorus calamus mixture, and m = mass of adsorbent used (g).

Results and Discussion

Characterization of Biosorbent: SEM analysis is an added constructive instrument for scrutinising the surface morphology of a prepared biosorbent. The porous and irregular surface structure of the biosorbent can be clearly observed in the SEM image and EDX spectra as shown in figure-1.

Biosorption Kinetics: Exploring adsorption kinetics is gaining utmost importance, since it easily forecast the competence power of adsorbent. To achieve this various kinetic models, namely, pseudofirst-order, pseudosecond-order and Weber's intraparticle diffusion were applied to categorize the mechanism of the adsorption process.

The pseudofirst-order kinetic model believes uptake of dye by adsorbent is time dependent and this range is directly relative to divergence of saturation concentration of dye and the biosorbent amount , which is the common phenomenon occurring in the initial stage of biosrption route [5].

A linear form of the Lagergren's pseudofirst-order equation can be expressed as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

Where k_1 is the pseudofirst-order rate constant and q_e and q_t are the adsorption ability at equilibrium and at time t, respectively. The factors k_1 and q_e were calculated from the plots of log (q_e-q_t) versus t as shown in figure-2 and are summarized in table-1. The values of the correlation coefficients (R^2) were very low. Moreover, massive disparity among experimental (q_e,exp) and calculated (q_e,cal) values of the adsorption were also observed, which indicates that the adsorption of BG 4 onto the acorus calamus did not comply with the pseudofirst-order model.

The pseudosecond-order kinetic model is based on the postulation that adsorption involved will be chemical sorption or chemisorption [6].

Pseudo-second-order kinetic model is given as:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

The linear form of pseudosecond-order kinetic model is expressed as

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

Where: k_2 is the pseudosecond-order adsorption rate constant. The values of K_2 and q_e can be calculated from the slope and intercept of plots of t/q_t versus t as shown in figure-3.

The coefficient of determination, R^2, of the kinetic models are shown in table-1, is highest for the pseudo 2nd order model, with $R^2 > 0.99$ while lagergren 1st order showed much lower values at higher concentration. The predicted value of q_e for the pseudo 2nd order is very close to the experimental q_e, whereas the Lagergren 1st order predicted a value much lower than experimental q_e. Hence, by taking consideration of the R^2, error analysis functions and the value of the predicted q_e, it can be concluded that the pseudo 2nd order model is the finest fit model to predict the behaviour of the adsorption process The best fit to the pseudo-second-order kinetics also implies that the sorption process may be chemisorptions involving mutual sharing or exchange of electrons. Previous literature also reports that the kinetics of the sorption of BG 4 onto saraca asoca leaf powder and luffa cylindrica follows pseudo 2nd order reaction rate[7,8].

The kinetic data were further analyzed by Weber's intraparticle diffusion model, which is mainly analysed to study the diffusion mechanisms. According to this model, the adsorption route on a permeable adsorbent proceeds in multi-step way such as transport of the adsorbate out of the solution, film diffusion, intraparticle diffusion in the pores and in the solid phase[9].

$$q_t = K_{int} t^{0.5} + C \quad (5)$$

Where k_i is the intraparticle diffusion rate constant and C_i is the intercept. The value of C relates to the thickness of the boundary layer. The larger C implies the greater effect of the boundary layer.

According to this model, the plots of q_t versus $t^{1/2}$ must be linear and should pass through the origin. Or else, if it exhibit multilinear plots, then obviously more steps are occuring. Here in this study, none of the lines passing through the origin reveal that this model never be an operating phenomenon.

Additionally, the rate constant k_i,1 and k_i,2 at different initial concentrations are also listed in Table 1. It is clear that when dye concentration increases rate constant values also increases. It can be explained by the growing effect of driving force that led to reducing the diffusion of dye molecules in the boundary layer and enhancing the diffusion in the solid. The k_i,1 values greater than k_i,2 values suggested that the film diffusion step was an important step for the adsorption of BG 4 onto the acorus calamus.

Adsorption Isotherms: Adsorption isotherm depicts the significant aspects of sorbate molecules or ions interaction with the active sites of sorbent surface and also predicts the skill of an adsorbent to confiscate effluent. In this study, equilibrium data were modulated at different concentrations of MG to afford appropriate justification for the models chosen. Further all the categories of models disclose the mutual rapport existing between adsorbed dye ions on the biomass (q_e) and dye ions in residual solutions (C_e) at a constant temperature[10].

The Langmuir isotherm always verdict on the solid assumption that each adsorption spot is alike and predominately assumes monolayer sorption onto outer surface of the biosorbent.

The linearized equation of Langmuir is represented as follows:

$$\frac{1}{q_e} = \frac{1}{Q_0 K_L C_e} + \frac{1}{Q_0} \quad (6)$$

Where q_e is the equilibrium dye concentration (mol g^{-1}); C_e is the equilibrium dye concentration in solution (mol l^{-1}); Q_O is the monolayer capacity of the adsorbent (mol g^{-1}); K_L is the adsorption equilibrium constant.

The parameters obtained from the plot as shown in figure-5 are listed in table-2. For revealing superior truth of the design chosen, correlation coefficients were calculated. Exploration values projected that Langmuir isotherm endow well with the equilibrium data[11]. The crucial mechanistic pathways of the Langmuir isotherm can be uttered by usage of factor called equilibrium parameter R_L, which is a dimensionless constant mainly resolved to forecast the high affinity of adsorption route. In the present investigation, the R_L value less than one tentatively reveals the feasibility of biosorbent towards dye.

The Freundlich equation is an empirical model and at all times it conveys heterogeneous system. Its equation is given by

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (7)$$

Where q_e is the equilibrium dye concentration on the adsorbent (mol g^{-1}); C_e is the equilibrium dye concentration in solution (mol l^{-1}); K_F, is the Freundlich constant; n is the heterogeneity factor. The linear plot of $\log q_e$ versus $\log C_e$ was shown in figure-6 and the values of n and K_f calculated from the slope and intercept are given in table-2. For this isotherm determining the magnitude of Freundlich constant n is considered as utmost essential since its values characterize favourable biosorption process[12]. For the present study the value of n comes around 4 enlightening beneficial usage of AC on MG biosorption.

Temkin isotherm always quotes out indirect relations of dye with adsorbent and put forward the message that the heat of adsorption relay on the dye molecules. Further adsorption of dye molecules decrease linearly upon saturation[13]. It is expressed as given below

$$q_e = BT \ln A + B \ln C_e \quad (8)$$

Where, B is the constant related to heat of sorption (J/mol), A is the isotherm constant (L/g), R is the gas constant T is the absolute temperature (K). Therefore, by plotting q_e versus ln C_e facilitates values for constants A and B as shown in figure-7. From the Temkin plot, the following values were estimated: A = 6 L/g, B=415.47 J/mol indicating a physical adsorption process and the R^2=0.96 as shown in table 2.

Dubinin-Radushkecivh (D-R) isotherm was applied to make a distinction relating physical and chemical adsorption. It is given by[14]:

$$\ln q_t = \ln q_m - K \varepsilon^2 \quad (9)$$

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e}\right] \quad (10)$$

Where: R is the gas constant (8.314 J/mol K), and T (K) is the temperature, q_m (mg/g) is the maximum adsorption capacity

based on D-R isotherm and K is related to mean adsorption energy (E in kJ/mol) given by:

$$E = \frac{1}{\sqrt{2K}} \quad (11)$$

A plot of $\ln q_e$ versus ε^2 shown in figure-8 confer the value of maximum adsorption capacity q_m (mg/g) from the intercept and the value of K from the slope. This isotherm estimates mean adsorption energy (E) and depending upon the value we can able to prove the way in which the reaction proceeds. The determined value for the adsorption of BG 4 on AC is 35.35 kJ/mol and summarized in table-2.

Harkins-Jura adsorption isotherm accounts for multilayer adsorption and can be explained with the existence of heterogenous pore distribution[15]. It can be expressed as

$$\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A}\log C_e \quad (12)$$

Where: B and A are the isotherm constants.

H-J plot for the adsorption of CV onto AC is shown in figure-9. The constants A and B values were determined from the slope and intercept of the plots, respectively. The R^2 value for this isotherm is 0.73 as shown in Table 2, proving that there is no option for multilayer adsorption on the sorbent sites. A list of the obtained parameters together with r^2 values is provided in Table 2.

Redlich–Peterson isotherm is a compilation of both Langmuir and the Freundlich isotherms[16]. It can be described as follows:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \quad (13)$$

Equation-13 can be converted to a linear form by taking logarithms:

$$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \ln a_R + \beta \ln C_e \quad (14)$$

Examination of the plot shows the effectiveness behaviour of dyes under examination studied and shown in figure-10.

Activation energy and biosorption thermodynamics: Calculating thermodynamics parameters has immense significance to assess spontaneity, heat change and the degree of freedom. It is mainly conducted to identify the outcome of temperature removal for the BG 4 by AC, at temperatures 300-320K, concentration ranging from of 20-100 mg L^{-1} and adsorbent dosage 0.15g L^{-1}. The dye adsorption seems to be greater at higher temperature than at lower. This sort of differences may due the relations existing between the functional group of the sorbent with sorbate.

Thermodynamic parameters can be calculated from the following equation.

$$\Delta G^o = -RT \ln K_d \quad (15)$$

Where R is the universal gas constant (8.314 $Jmol^{-1}$ K^{-1}), T the temperature (K) and K_d is the distribution coefficient. If the value of ΔG^o is negative, the chemical reaction can occur spontaneously at a given temperature.
The K_d value was calculated using the following equation.

$$K_d = \frac{q_e}{C_e} \quad (16)$$

Where: q_e and C_e are the equilibrium concentrations of BG 4 (mg L^{-1}) on the adsorbent and in the solution respectively. The enthalpy change (ΔH^o) and entropy change (ΔS^o) can be calculated from the following equation.

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (17)$$

This equation can be written as

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (18)$$

The Gibbs free energy changes (ΔG^0) were calculated from equation-17, and the values of ΔG^o, ΔH^o, and ΔS^o for the adsorption of CV onto AC were given in table-3. The negative values of ΔG^o indicated the feasibility and spontaneous nature of the adsorption process. The positive value of enthalpy change shows that the adsorption process is endothermic. In addition, the positive value of ΔS^o suggested an increase in randomness during the adsorption of BG 4 on the adsorbent. Analogous results were observed as a proof on bentonite[17] activated carbon prepared from de-oiled soya[18] and hen feathers[19].

Conclusion

The current study reveals the usage of acorus calamus as one of the innovative carbon precursor materials. Out of the different isotherm analysed, the best fit of Langmuir model has been the evidence for the formation of monolayer coverage of the dye at the periphery of the adsorbent. The separation factor (R_L) value portrays the feasibility of the reaction process being evaluated for the present study. The Adsorption progression tag on pseudo second-order kinetics. Evaluation of thermodynamic parameters indicated that the adsorption process was endothermic and there occurs increased disorder. The various results obtained indicated that the adsorbent chosen for the study was efficient and could be used for the removal of industrial dye effluents.

Table-1
Isotherm constants for biosorption of BG 4 by AC

Langmuir Isotherm		**Freundlich Isotherm**		**Tempkin Isotherm**		**D-R Isotherm**		**Harkin-Jura isotherm**	
Q_0 (mg g^{-1})	50	k_f (mg g^{-1})	16.94	A_T(L/mg)	19.89	q_m(mg/g)	3.64	A	0.0027
R_L	0.06	n	4.01	b_T	6.00	K_{ad}(mol^2/kJ^2)	$4.40x10^{-4}$	B	0.0038
b(L mg^{-1})	0.87	R^2	0.90	B	415.47	E(KJ/mol)	35.35	R^2	0.73
R^2	0.99			R^2	0.96	R^2	0.99		

Table-2
Kinetics parameters for biosorption of BG 4 by AC at different concentrations

Kinetic Models	**Model Coefficients**	**Initial Concentration**	
		10 mg/l	**20 mg/l**
Pseudo first order	q_e(mg g-1)	6.33	12.55
	q_{calc}(mg g-1)	$1.00x10^2$	$1.00x10^2$
	$k_1 min^{-1}$	0.769	0.866
	R^2	0.97	0.96
Pseudo-second order	q_{calc}(mg g-1)	7.83	13.58
	k_2(g $mg^{-1}min^{-1}$)	4.327	1.088
	R^2	0.99	0.99
Intraparticle diffusion	k_{int}(mg $g^{-1}min^{-0.5}$)	0.26	3.42
	C	1.75	1.13
	R^2	0.98	0.85

Table-3
Thermodynamic parameters for biosorption of BG 4 by AC

Conc. (mg/l)	**T (K)**	**K_P**	**ΔG^o (KJ mol^{-1})**	**ΔS^o (J mol^{-1} K^{-1})**	**ΔH^o (KJ mol^{-1})**
20mg/l	300	1.3600	-1501.7	74.425	23.8
	310	1.4800	-1999.4		
	320	1.5800	-2805.8		
40mg/l	300	1.2800	-1062.5	52.084	16.7
	310	1.4100	-1393.2		
	320	1.5200	-1813.3		
60mg/l	300	0.8754	-820.7	40.571	13.0
	310	0.9932	-1128.1		
	320	1.1310	-1501.7		
80mg/l	300	0.2623	-452.5	22.827	7.3
	310	0.4050	-694.4		
	320	0.5877	-965.6		
100mg/l	300	0.0953	-311.6	16.239	5.2
	310	0.1823	-0.5		
	320	0.4054	-1.1		

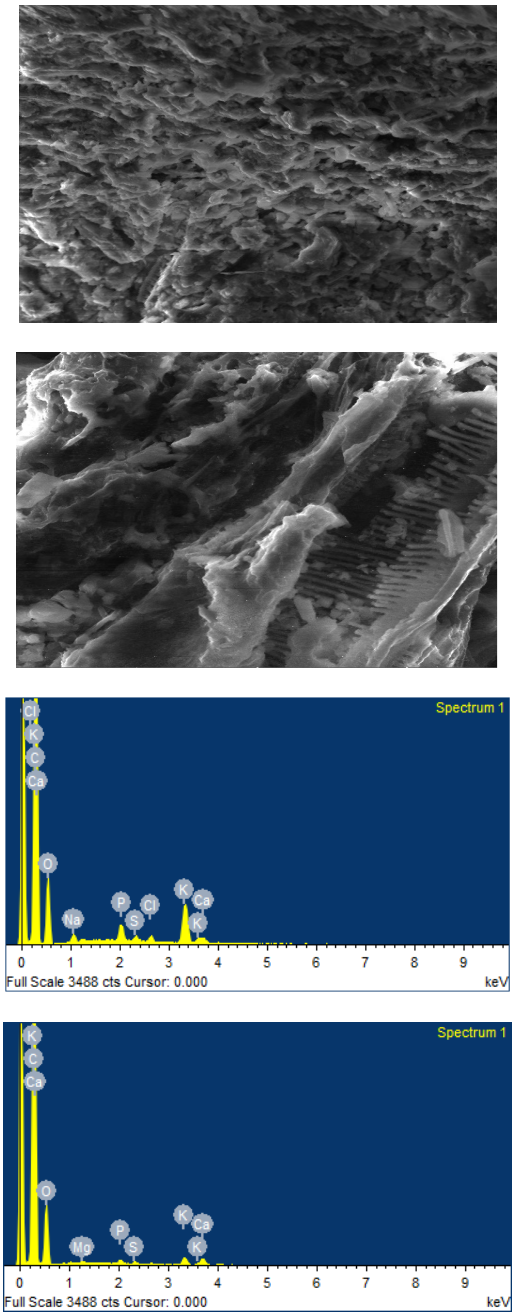

Figure-1
SEM and EDX images of AC before and after MG adsorption

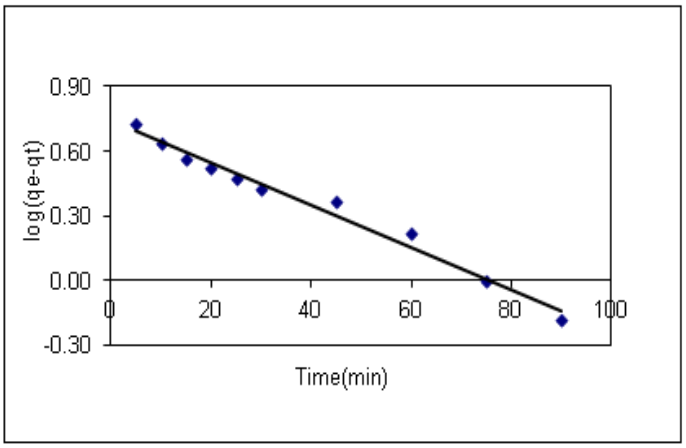

Figure-2
Pseudo first order kinetics for the adsorption of BG 4 dye onto AC

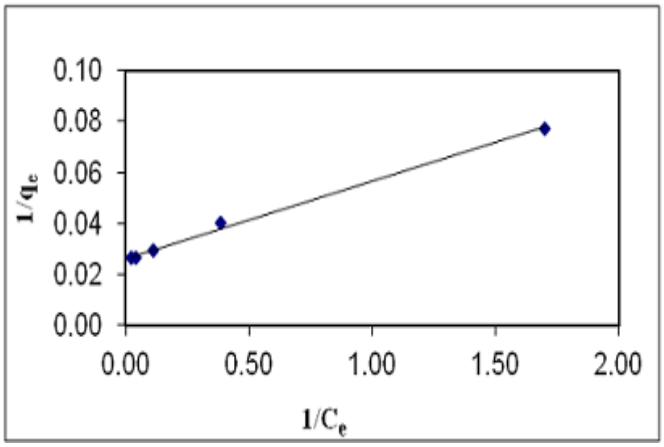

Figure-5
Linearlised Langmuir isotherm plot for the adsorption of BG 4 dye onto AC

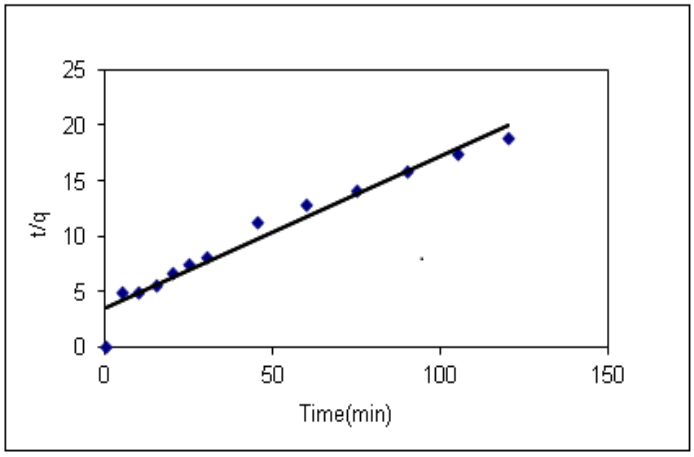

Figure-3
Pseudo second order kinetics for the adsorption of BG 4 dye onto AC

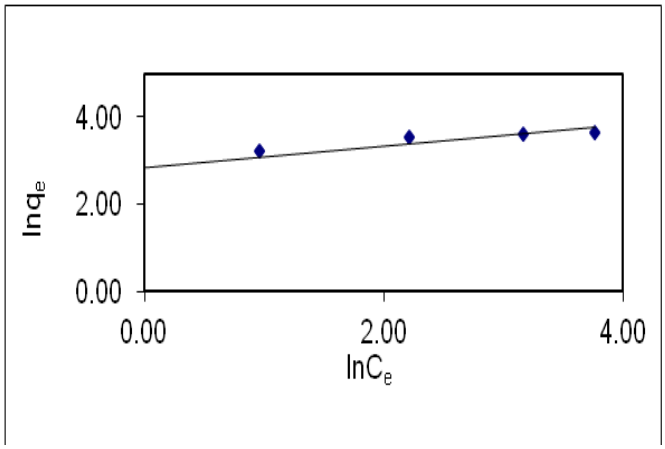

Figure-6
Linearlised Freundlich isotherm plot for the adsorption of BG 4 dye onto AC.

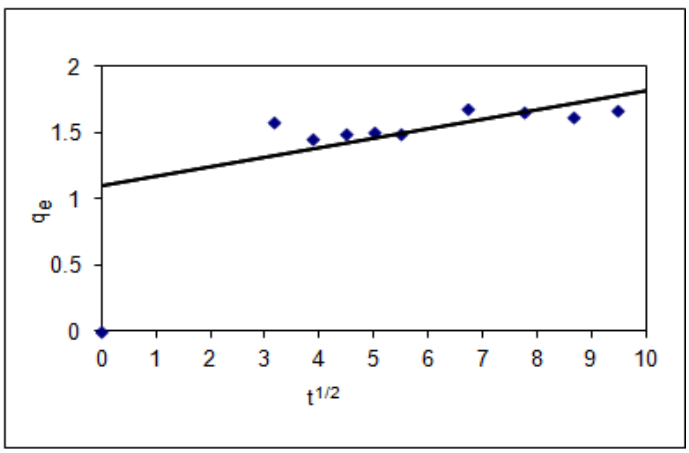

Figure-4
Intra-Particle plot for the adsorption of BG 4 dye onto AC

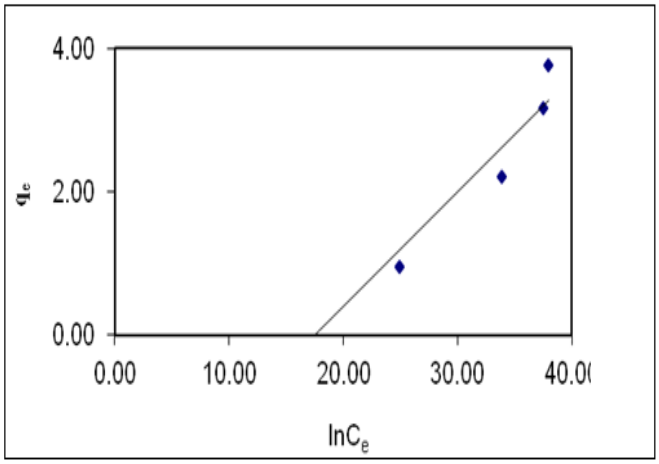

Figure-7
Tempkin isotherm plot for the adsorption of BG 4 dye onto AC

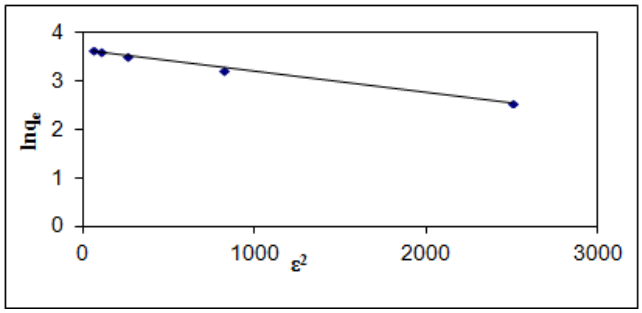

Figure-8
D-R isotherm plot for the adsorption of BG 4 dye onto AC

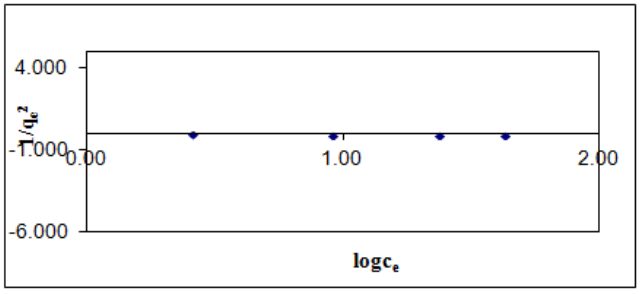

Figure-9
H-J isotherm plot for the adsorption of BG 4 dye onto AC

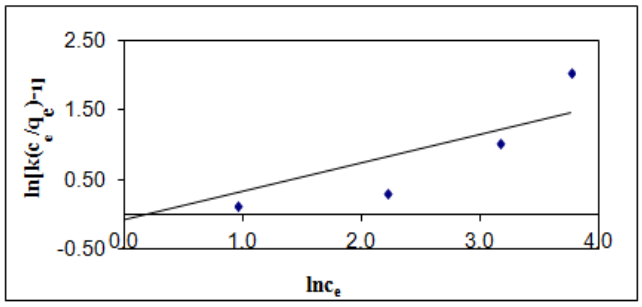

Figure-10
R-P isotherm plot for the adsorption of BG 4 dye onto AC

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