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Kinetic and Thermodynamic Studies on the Adsorption Behavior of Crocein Orange G Dye Using Casuarina Equisetifolia Bark Carbon

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Abstract: The adsorption behavior of crocein orange G dye from aqueous solution was investigated using Casuarina equisetifolia bark carbon. The effect of various experimental factors such as pH, adsorbent dose, initial dye concentration, contact time and temperature were studied by using the batch technique. The adsorption capacities were evaluated by using Langmuir and Freunlich adsorption isotherm models. Thermodynamic parameters were calculated and it was found that the adsorption of crocein orange G (COG) dye using Casuarina equisetifolia bark carbon (CEBC) was endothermic and adsorption process. Pseudo first order, Pseudo second order models were also used to describe the kinetic data. The adsorbent surface functional groups identification with Fourier Transform Infrared (FTIR) spectroscopy and the morphology of the surface are identified with Scanning Electron Microscope (SEM).
Keywords : Adsorption, Kinetic, CEBC, COG dye, Thermodynamic

I. INTRODUCTION

The increase in population and rapid industrial growth in India has resulted in high demand for dyes and pigments [1]. Dyes are important pollutants in the effluents of textile, leather, food processing, cosmetics and paper manufacturing industries. The discharge of these dye wastes into receiving streams not only affects the aesthetic nature but also reduces photo-synthetic activity [2]. Waste waters offer considerable resistance for their biodegradation [4] and also several commonly used have been reported to be carcinogenic and mutagenic for aquatic organisms [3]. Pollution caused by industrial waste water has become a common problem for many countries [5]. Therefore, it is necessary to reduce dye concentration in the waste water. Adsorption is an attractive and alternative for the treatment of waste water, especially if the adsorbent is inexpensive and does not require an additional pretreatment step before its application. Currently, the most commonly used adsorbent is activated carbon which will successfully remove the dyes from waste water [6, 7]. However, the activated carbon is considered to be an expensive and problem with regeneration of the spent activated carbon in its large scale application. In order to decrease the cost of water treatment, attempts have been made to find inexpensive low-cost adsorbents [8]. Therefore, new, economical, easily available and highly effective adsorbents still need to be found. The present study is used to find out the suitability of CEBC adsorbent to remove the Crocein Orange G dye from aqueous solution.

II. MATERIALS AND METHODS

A. Adsorbate

Crocein Orange G (COG) dye used in this study is purchased from Kevin Scientific Company. COG has molecular formula $C_{16}H_{11}N_2NaO_4S$ which is shown in Fig.1. The dye stock solution was prepared by dissolving accurate weight of dye in distilled water to the concentration of 1g/L.

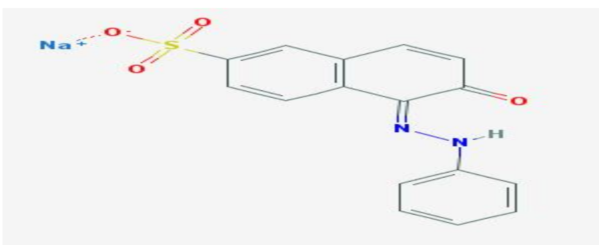

Fig. 1 Structure of Crocein Orange G

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B. Preparation of Casuarina equisetifolia Bark Carbon (CEBC) adsorbent

Casuarina equisetifolia Bark Carbon (CEBC) was collected from local market. The collected CEBC materials were finely powder was treated with con. Sulphuric acid. The carbon was washed until an optimum PH and dried in hot air oven at 110̊C for 24hours, then placed into muffle furnace at 450̊C in 6 hours for complete carbonization of the bark. The resulting powder was used for adsorption experiment.

C. Batch method

Batch adsorption [9] studies were conducted in varying concentration of dye, adsorbent dose, contact time, temperature and pH. The concentration of dye used in the range of 8-40mg/L (8mg/L variation), adsorbent dose varied from 10 to 60 mg (10 mg variation), time varied in the range of 10-60 min (10 min intervals), temperature was varied in 303-333 K (10 K increment) and pH changed in the value of 2-9.The amount of adsorption q_t (mg/g) at time 't' , amount of adsorption at equilibrium q_e (mg/g),and % removal of COG dye were calculated by

$q_t=(C_o-C_t)V/W$ (1)

$q_e=(C_o-C_e)V/W$ (2)

$\% \text{ Removal}=C_o-C_t/C_o \text{ X } 100$ (3)

Where Co (mg/L), C_t (mg/L) and C_e (mg/L) are the liquid phase concentration of NGB dye at initial, at particular time and equilibrium respectively. V (Litre) is the volume of the solution. W (gram) is the mass of dry adsorbent used.

D. Characterization of the adsorbent

The purpose of using activated carbon is to enhance the efficiency of adsorption without the evolution of huge amounts of fumes while carbonization the bark material. Excess moisture can removed inside the pores of the adsorbent material then the carbonized material kept in an oven for 24 h at temperature 110^0C. Morphology of the adsorbent material performed using Scanning electron micrograph (SEM) analysis. The surface functional groups of the activated carbon studied by Fourier transform infrared (FTIR) spectroscopy in before and after adsorption.

III. RESULTS AND DISCUSSION

A. Characteristic studies of activated carbon

1) *FTIR study:* Fourier transform infrared (FTIR) spectroscopy provides evidence for the presence of functional groups on the surface of Casuarina equsetifolia bark carbon material before activation. The broad band around 3263.51 cm^{-1} was observed in the sample which was attributed to the O-H stretching vibration of hydrogen bonded hydroxyl groups in carboxylic, phenolic, or alcoholic functional groups and adsorbed water over the raw material. The band at 2923cm^{-1} was ascribed to asymmetric C-H stretching vibrations of aliphatic carbon of the raw material. After carbonization, these vibrations decreased greatly for the CEBC, indicating that the hydrogen was removed to a large extent. The appearance of the band at 1728.42 cm^{-1} is due to the C=O stretching in aliphatic ketone. An intense band was centered at 1604 cm^{-1} which corresponded to the carbonyl (C=O) stretching vibration of quinine. The band at 1383.86 cm^{-1} indicates the symmetric stretching vibrations of COO- as shown in the Fig. 2(a). After the carbonization, all these peaks disappeared, indicating that much of the organic matter was eliminated The bands around 1000-1300 cm^{-1} are usually found in oxidized carbons and are assigned to C-O stretching in acids, alcohols, phenols, ethers, and /or ester groups as shown in Fig 2(b).

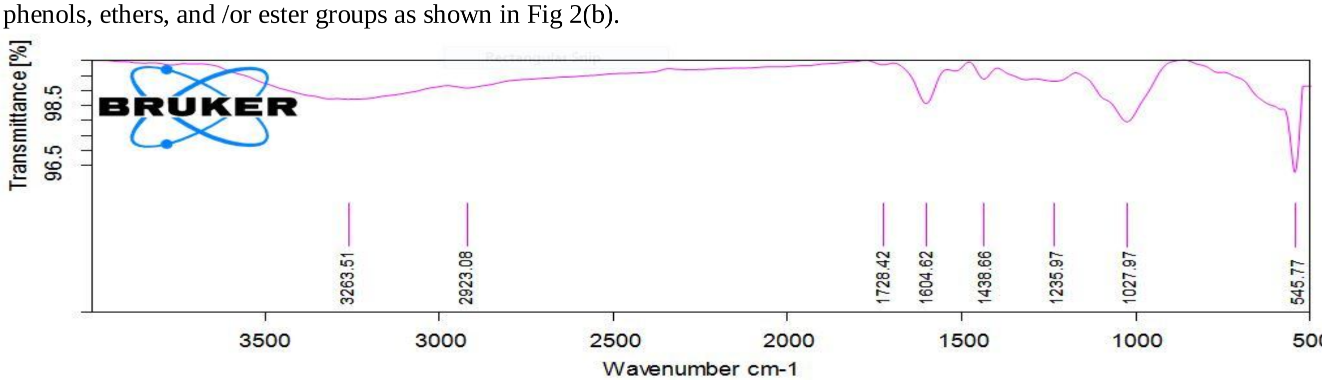

Fig. 2(a) FTIR analysis of CEBC before activation

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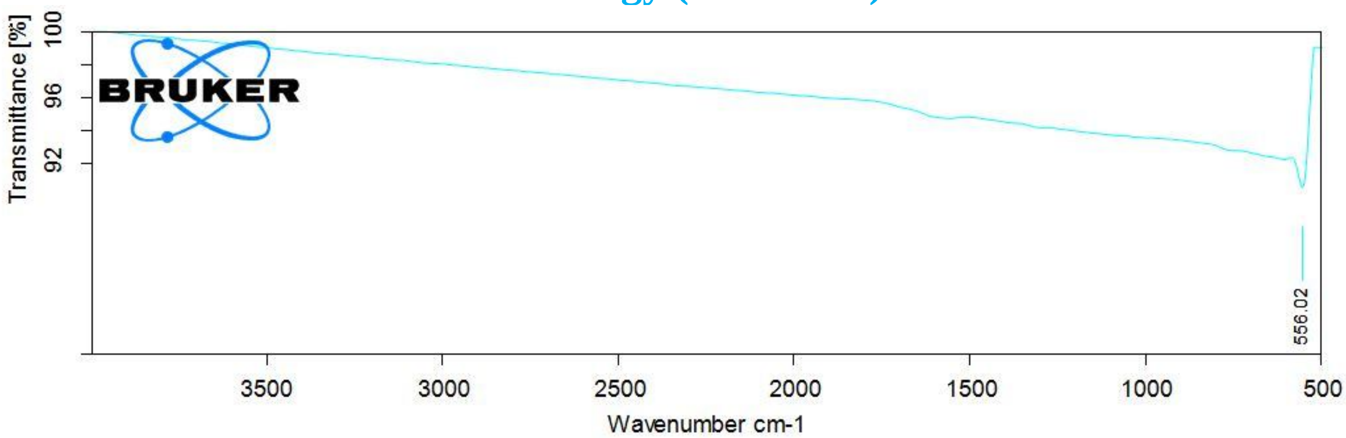

Fig. 2(b) FTIR analysis of CEBC after activation

2) *SEM Study:* The Scanning Electron Microscope (SEM) provides the information about the surface morphology of the adsorbent material. The SEM image of adsorption is shown in Fig 3. The Figure shows that there was porous structure in the surface. The porous structure was wholly occupied with the COG dye molecules. Hence, there was a complete occupied site of the surface of the adsorbent material which shows almost flatten surface image. This image structure concluded that the COG dye is strongly adsorbed on the surface of the activated carbon.

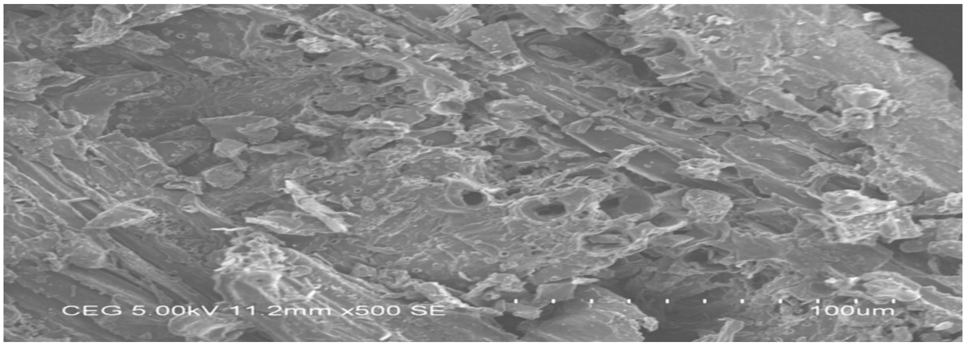

Fig. 3 SEM image of activated carbon

B. *Parameters Study*

1) *Effect of pH:* The solution pH tremendously affected the nature and progression of the adsorption process. So it is essential to check the solution pH before proceeding to the adsorption process. In this study the solution pH was varied in the range of 2-10 and the effect of pH was presented in Fig.4. From the investigation of various pH values, the pH value of 2 shows the higher percentage removal compared to other pH values. Therefore the pH value of 2 was chosen as optimum pH for the removal of Crocein Orange G on the Casuarina equisetifolia bark activated carbon.

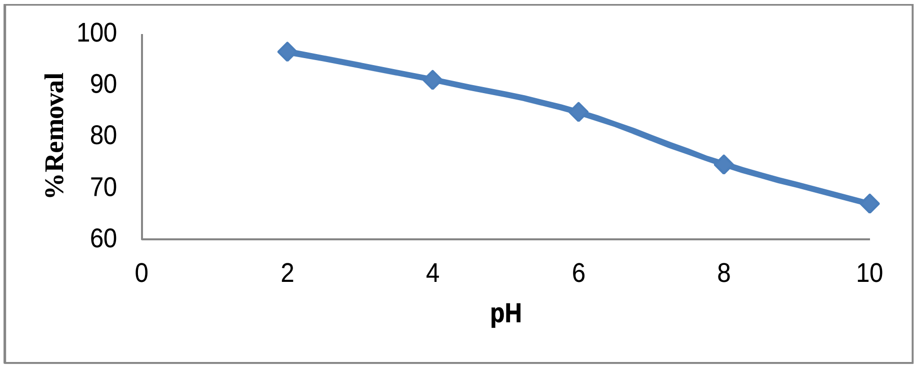

Fig.4 Effect of initial pH for the removal of COG dye

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Volume 5 Issue V, May 2017
ISSN: 2321-9653

2) *Effect of CEBC adsorbent dose:* To study the effect of CEBC dose on the COG adsorption, different amounts of CEBC powder (10-60mg) were added into a 250ml conical flask containing a definite volume (25ml in the each flask)of fixed initial concentration (8mg/L) of dye solution without changing the PH of solution at 30°C as shown in Fig .5. The flasks were placed in thermostatic orbital shaker for 60 minutes and the COG dye concentrations were measured at equilibrium.

From the Figure, it was observed that the % removal increase initially up to 30mg/25ml and reaches limiting value with fractional difference. Thus, adsorption increases with an increase in the dose of adsorbent due to availability of more active sites for adsorption. However, a further increase in the dose of adsorbent did not affect the % removal of dye because of the unavailability of adsorbate due to saturation. So the experiments were carried out by using 30mg/25ml of adsorbent dose.

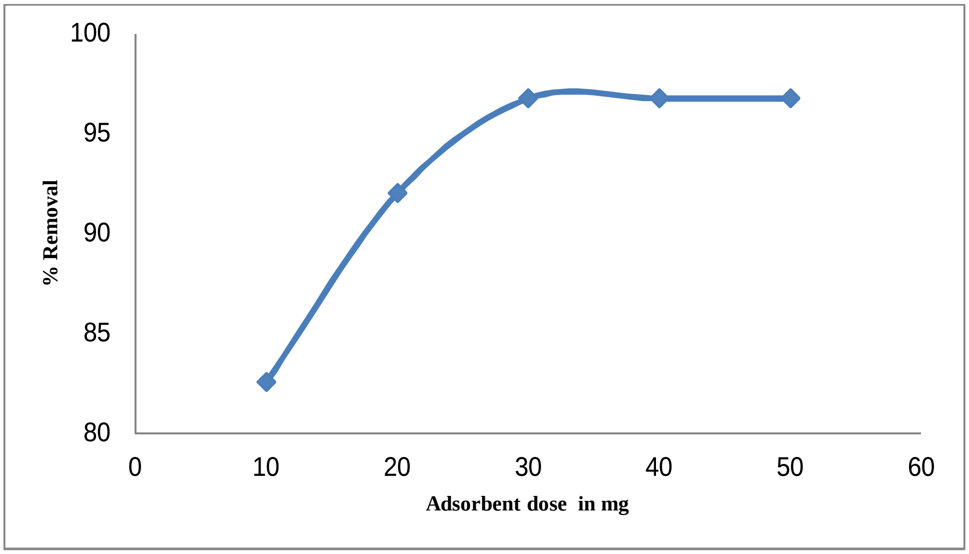

Fig. 5 Effect of adsorbent dose for the removal of COG dye

3) *Effect of contact time:* The effect of contact time between adsorbent CEBC and adsorbate (COG) were determined by keeping COG dye concentration, adsorbent dosage, pH and temperature were constant. In the present study, the adsorption process of COG using CEBC was studied for various time intervals such as 10, 20,30,40,50 and 60 minutes. The results were presented in Fig .6.It was observed that initially increase in time enhances the rate of adsorption and its equilibrium was almost attained and 96.32% dye removal takes place within 50minutes. Hereafter there were no appreciable changes in adsorption. So, 50 minutes was the sufficient time for the maximum adsorption of dye.

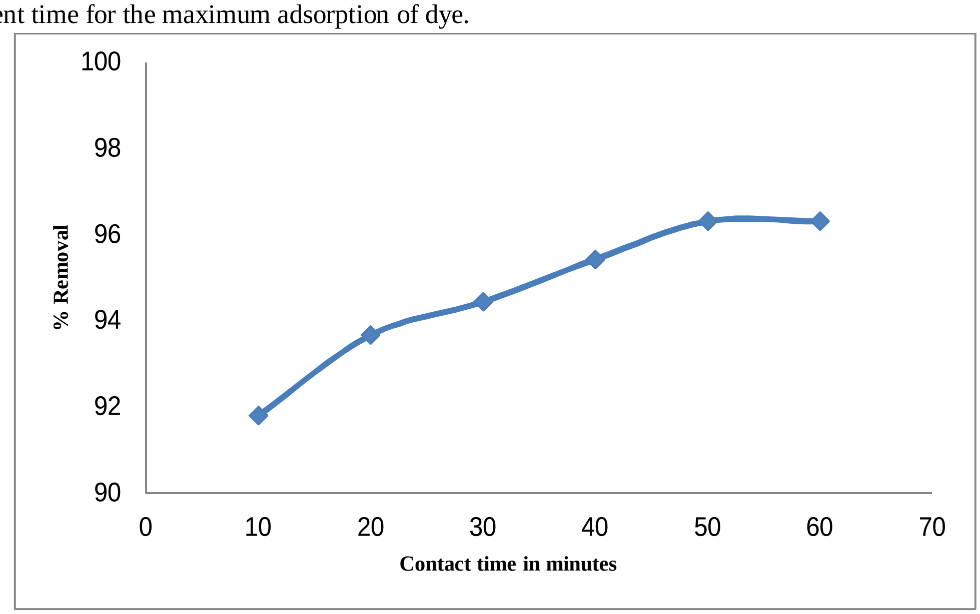

Fig. 6 Effect of contact time for the removal of COG dye

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4) *Effect of temperature :*The effect of temperature was carried out at four different temperatures such as 30̊C, 40̊C, 50̊C and 60̊C in a thermostatic orbital shaker for 50 minutes. Samples were withdrawn at suitable time interval; filtrate was analyzed for the remaining dye concentration. Temperature has significant effects on the adsorption capacity, thermodynamic parameter and kinetic process depending on the structure and surface functional groups of an adsorbent.

C. Adsorption Isotherms

The adsorption isotherm shows how the adsorbate molecules are distributed between the adsorbent and solution. The Langmuir and Freundlich isotherm were used to measure the adsorption capacity of the CEBC adsorbent for the removal of COG dye.

1) *Langmuir Isotherm :*The Langmuir [10] isotherm equation can be described by

$1/q_e=1/q_mK_LC_e+1/q_m$ (4)

Where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate per unit mass of adsorbent, q_m and K_L are Langmuir constants related to adsorption capacity and rate of adsorption respectively. q_m is the amount of adsorbate a complete monolayer coverage (mg/g) which gives the maximum adsorption capacity of the adsorbent and KL (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption. The linear plot of specific adsorption capacity $1/q_e$ against the equilibrium concentration ($1/C_e$) shows that the adsorption obeys the Langmuir model which is shown in Fig .7. The Langmuir constant q_m and K_L were determined from the slop and intercept of the plot. The equilibrium parameter RL [11] is used to find out the feasibility of the Langmuir isotherm

$R_L=1/1+K_LCo$ (5)

Where Co (mg/L) is the initial concentration of adsorbate and KL (L/mg) is Langmuir isotherm constant. The RL value between 0<RL<1 is favorable for adsorption.

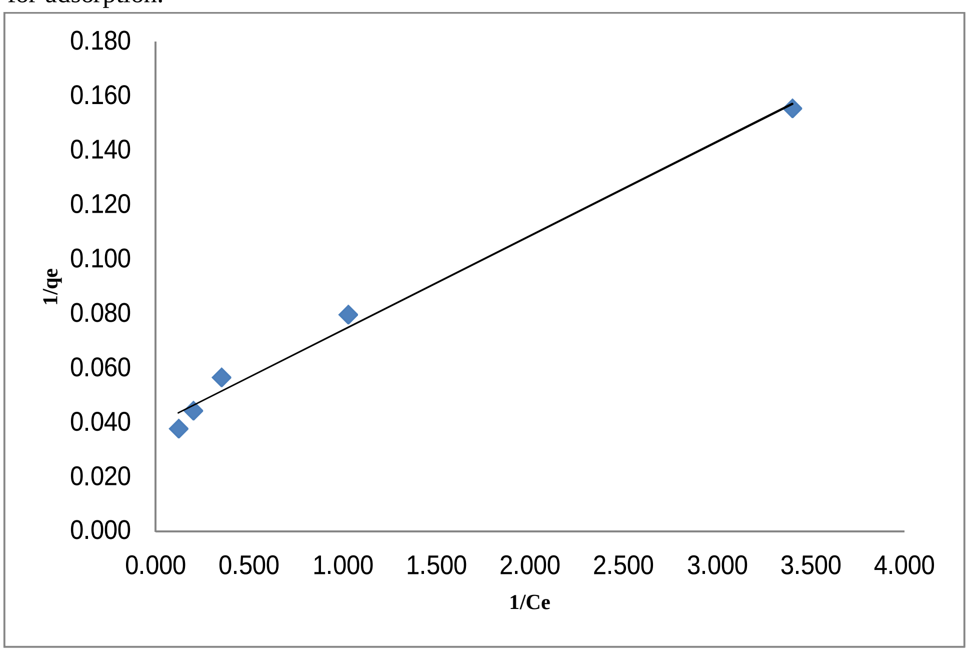

Fig. 7 Langmuir isotherms for the adsorption of COG dye

2) *Freundlich Isotherm :* Freundlich isotherm [12] is represented by the equation

$\log q_e = \log K_f + 1/n \log C_e$ (6)

Where q_e is the amount of dye adsorbed per unit weight of the adsorbent (mg/L), K_f is $[mg/g(mg/L)^{-1/n}]$ measure of adsorption capacity and 1/n is the adsorption intensity. In general if K_f value increases then adsorption capacity for a given adsorbate increases. The magnitude of the exponent 1/n gives an indication of the favorability of adsorption. The adsorption is linear; if n<1, it implies that the adsorption process is favored by chemisorption and if n>1, the adsorption process is favored by physisorption. The linear plot of specific adsorption capacity log q_e against the equilibrium concentration log C_e shows that the adsorption doesn't obey the Freunlich model which is shown in Fig .8.

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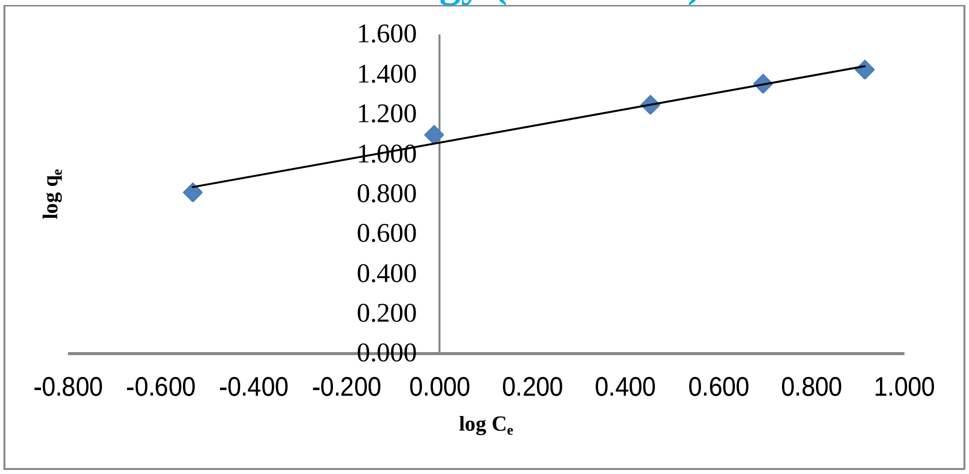

Fig. 8 Freunlich isotherms for the adsorption of COG dye

TABLE I
ADSORPTION ISOTHERM PARAMETER FOR THE ADSORPTION OF COG DYE

Langmuir parameter			Freundlich parameter		
q_m(mg/g)	K_L(L/mg)	R^2	$K_{F(}$(mg/g)(1/mg)$^{(1/n)}$)	n(g/L)	R^2
25.316	75.660	0.9902	2.882	2.416	0.987

D. Adsorption Kinetics

The rate constant for the adsorption of COG was determined using pseudo first order, pseudo second order, and intra particle diffusion models.

1) *Pseudo first order equation:* The adsorption kinetic data were described by the pseudo first order model which is the earliest known equation, described the adsorption rate based on the adsorption capacity. The pseudo second order rate equation can be written as [13].

$\log (q_e\text{-}q_t)=\log qe\text{-}t.k_1/2.303$ (7)

Where q_e is the amount of dye adsorbed at equilibrium (mg/L), q_t is the amount of dye adsorbed (mg/g) at time t, K_1 is the rate constant (min^{-1}) of the pseudo first order.

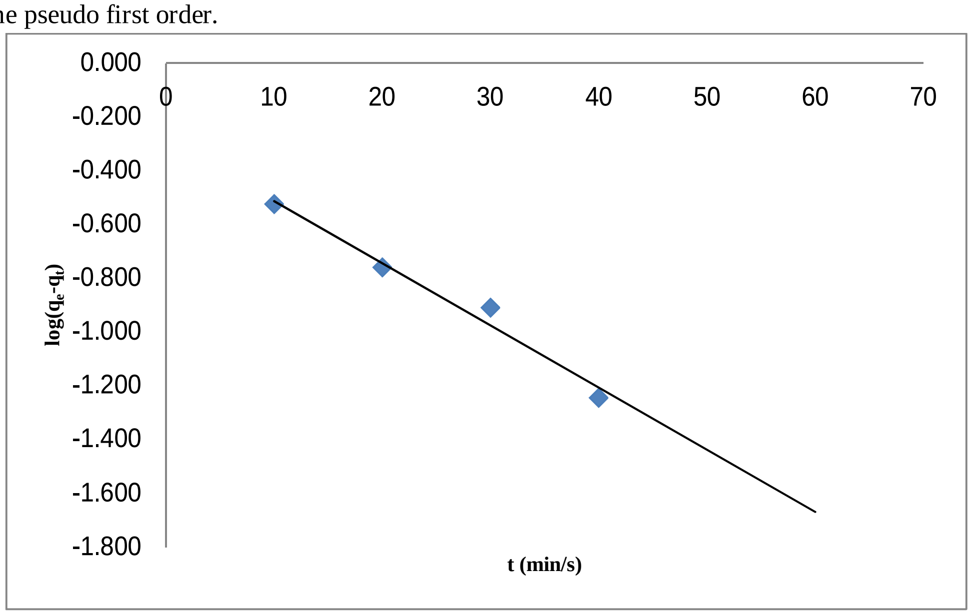

Fig. 9 Pseudo first order kinetic plot for the adsorption of COG on CEBC.

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2) *Pseudo second order equation:* The pseudo second order [14] rate expression is represented as

$t/q_t=1/h+1/q_e \times t$ (8)

Where (mg/g-1min-1) is the initial adsorption rate at t→0 and K is the rate constant of the pseudo second order kinetic equation (gmg-1min-1). The plot of t/q_t versus t is shown in Figure 10. The q_e, k and h can be determined from the slope and intercept of the plot respectively and listed in Table 2.

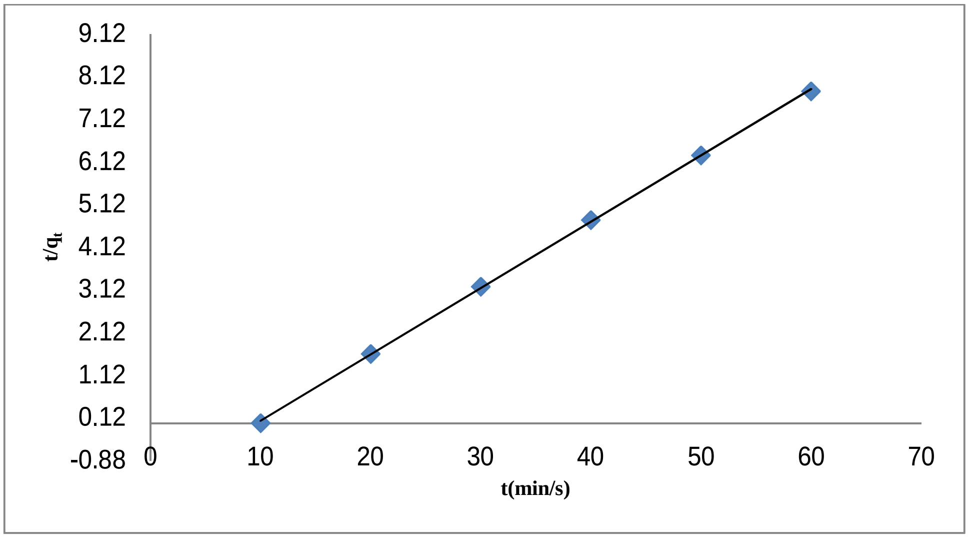

Fig. 10 Pseudo second order kinetic plot for the adsorption of COG on CEBC.

TABLE II

ADSORPTION KINETIC PARAMETER FOR THE ADSORPTION OF COG DYE

Pseudo first order			Pseudo second order		
$K_{ad}(min^{-1})$	q_e(mg/g)	R^2	q_e(mg/g)	$h(mgg^{-1}min^{-1})$	R^2
0.048	0.7546	0.978	6.4267	0.667	0.9998

E. *Thermodynamic studies*

The effect of temperature on the adsorption process was investigated with the thermodynamic parameter like change in Gibbs free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS). The thermodynamic parameter values were presented in Table III. From Table, the Gibbs free energy (ΔG) shows negative sign of an experimental value intimates that the process is spontaneous in nature. The reduction of the negative value at higher temperatures reveals that the equilibrium quantity reduces at higher temperatures. The positive value of change in enthalpy (ΔH) indicates that the endothermic nature of the process involved during the adsorption, moreover an interaction between the solute and the solvent particle involves in complex phenomenon on the solid surface. The change in entropy (ΔS) provides positive value implies that the conscious choice of an adsorbent raises with the increment of an orderliness between the adsorbate and the adsorbent molecules. From the results we may conclude that the adsorption of Crocein orange G on Casuarina equisetifolia bark carbon was feasible.

TABLE III

Thermodynamic Parameter For The Adsorption Of Cog Dye

T(K)	ΔG^0 (KJ mol^{-1})	ΔH^0(KJ mol^{-1})	ΔS^0(KJ mol^{-1} k^{-1})
303	-8.013	20.347	128.113
313	-8.559		
323	-9.152		
333	-9.679		

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.IV. CONCLUSION

The results of this study shows that the Casuarina equisetifolia Bark Carbon can be used for the removal of the dyes Crocein orange G from aqueous solution. The equilibrium data were fitted to the Langmuir model. The kinetics of the adsorption process was the best fit with pseudo second order model. This adsorption studies shows that Casuarina equisetifolia Bark Carbon can be used as an efficient adsorbent for the removal of Crocein orange G dyes from aqueous solution. The thermodynamic studies indicate that adsorption process is endothermic and physical adsorption.

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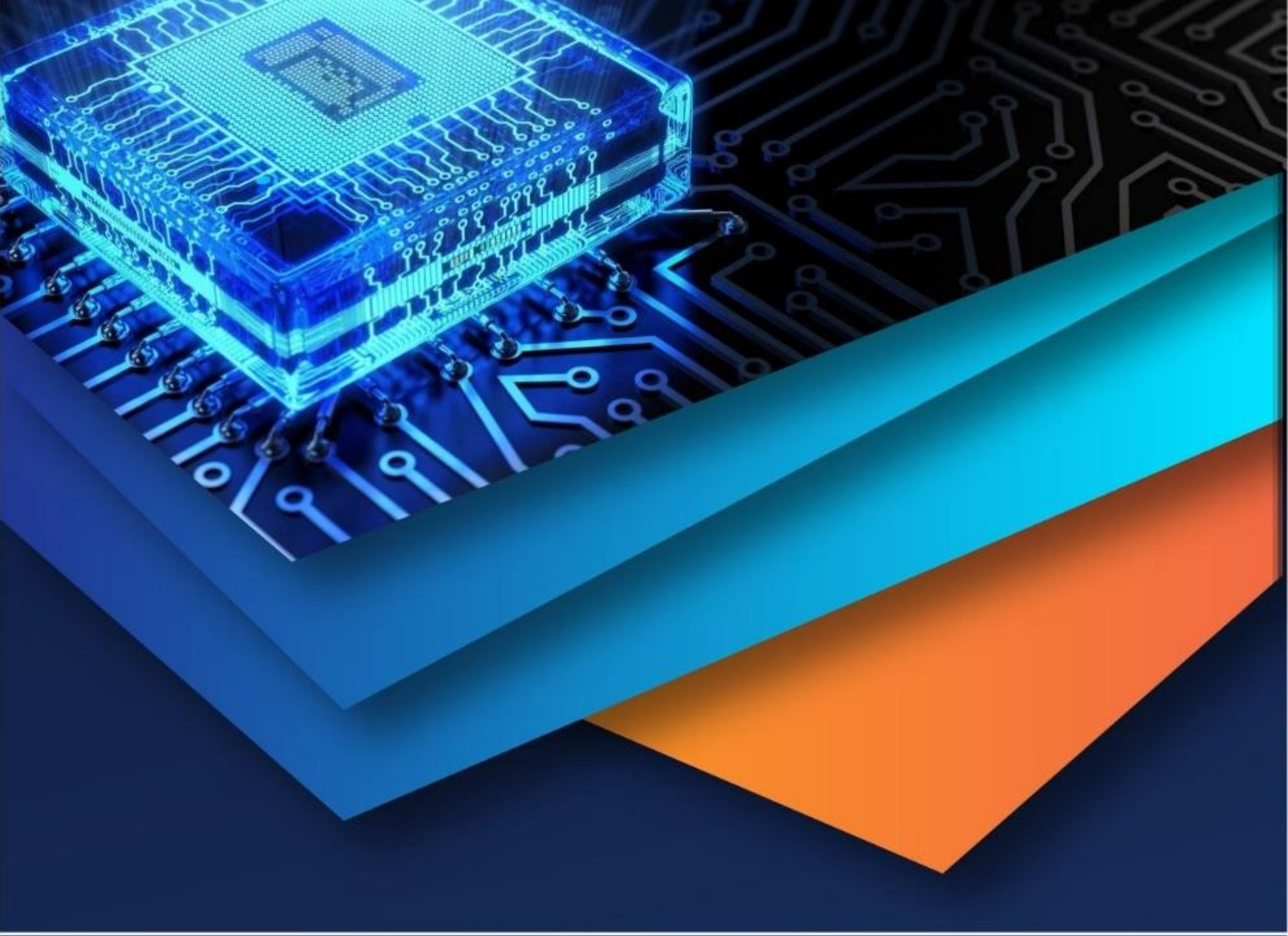

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