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## Adsorption Of Fast Green Using Base Treated Carbonized Rice Husk-Kinetics And Thermodynamic Parameters.

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### ABSTRACT

The aim of the study is the utilization of base treated carbonized rice husk in the adsorption of aqueous effluent 'fast green' present in waste waters. The batch adsorption experiment was carried out to understand the parameters like concentration of adsorbent, concentration of dye, pH and contact time for the removal of dye from the aqueous media. The adsorption observations were verified by adsorption isotherm models like Langmuir and Freundlich. With the help of calculated Langmuir constants the thermodynamic parameters like free energy, entropy and enthalpy have been studied. BET, FTIR and TGA techniques were used to understand the surface morphology of the adsorbent, where as the temperature programmed desorption was to understand the nature of the surface functional groups formed. Typical observations proved that the dye removal followed the pseudo second order kinetics.

**Keywords:** Adsorption, low-cost materials, fast green dye, adsorption isotherms, thermodynamics of adsorption.

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## INTRODUCTION

Major alarming global problem is the presence of carcinogenic and mutagenic effluents in the waste waters of industries [1]. The presence of various types of effluents as dye pigments are reported to be carcinogenic and highly toxic to living beings and aquatic life [2]. This necessitates the removal of dyes from waste water. Adsorption is a standard and promising method to adsorb effluents, and further to reduce the biochemical oxygen demand [3]. Recently alkali treated activated carbons and derived adsorbents are frequently utilized for the adsorption of several kinds of effluents from waste water due to the better adsorption efficiencies and could remove effluents to the maximum extent [4 to 7]. Agricultural waste which have lingo-cellulosic materials are extensively used for the removal of effluents [8 to 15]. Conventionally, to remove volatile organic constituents, these wastes are carbonized in an inert atmosphere such that only porous carbonaceous residue is left behind which on further activated, by treating to either chemical, steam or gas [16]. Especially due to the wide surface area and pore structure, base treated carbon has high adsorption efficiency towards organic effluents. Till today so many reports, to explain the adsorption feasibility using paralyzed rice husk [17 to 23], however the genesis behind choosing a particular treatment remains is still not clear.

The occurrence of agricultural waste at an affordable price is an advantage to use as a starting material for the adsorption studies. The investigations reported here deal with the preparation of ACs by using NaOH/HNO<sub>3</sub> activation followed by quantification of functional groups to understand the surface chemistry. The adsorption capacity of AC was tested during the adsorption studies. The present work demonstrates the influence of various effects like variation of dye concentration (fast green), amount of BCRH, contact time, effect of P<sup>H</sup> and the calculation of thermodynamic parameters.

## MATERIALS AND METHODS

### Preparation of adsorbent

Rice husk was locally procured from rice mill. It is washed thoroughly with double distilled water and dried up to 380K. It is further treated with 5M HNO<sub>3</sub> at 333K for 24 hours. It is washed completely for the removal of any additional acid and dry it at 373K in an oven. Then it is treated in nitrogen atmosphere for 1 hour at 973K in a muffle furnace. This is called carbonized rice husk contains 22% silica on washing it raises to 95%. This further treatment with 5M NaOH and repeated washings with distilled water is known as base treated carbonized rice husk.

### Adsorbate

The chemicals used were from Merck Company. The adsorbate is the commercial fast green dye (FG) (C<sub>37</sub>H<sub>37</sub>N<sub>2</sub>O<sub>10</sub>S<sub>3</sub><sup>+</sup>) whose structure is presented in figure 1. 500ppm stock solution of dye (mol.wt:808.86 g) was prepared using distilled water. The maximum absorbance was observed at 624 nm by using Perkin Elmer UV visible spectrophotometer.

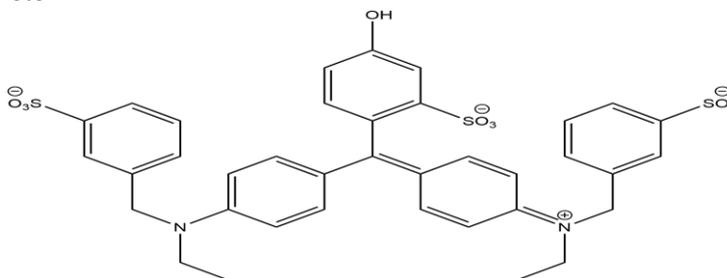


Figure 1: Chemical structure of fast green dye

### Characterization of adsorbent

The adsorbent, BCRH (Base treated carbonized rice husk) was characterized with FTIR (Perkin Elmer, Spectrum 100). The FTIR spectrum of the BCRH (Figure 2) has shown the various functional groups with respect

to their peak value. The stretching vibrations of carboxyl groups or conjugated carbonyl groups (COO in carboxylic acid and lactones groups) are confirmed by the peak range 1680-1800  $\text{cm}^{-1}$  [24,25] respectively.

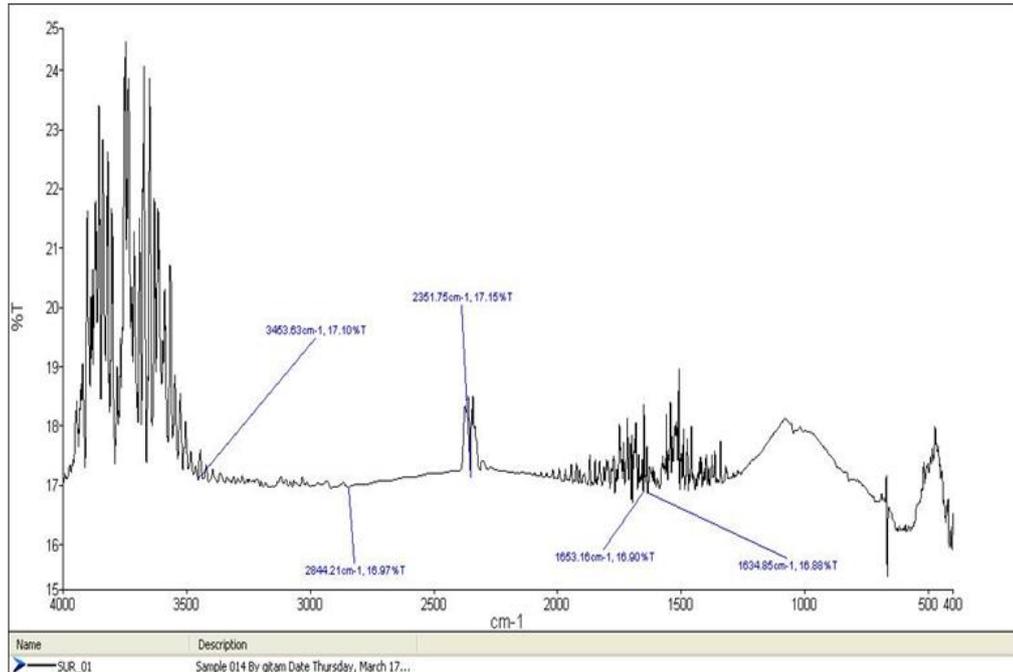


Figure 2: FTIR of base treated carbonized rice husk (BCRH)

The quality of activated carbon is best explained by BET specific surface area. The surface area ( $460\text{m}^2/\text{g}$ ), micropore surface area ( $223\text{m}^2/\text{g}$ ), external surface area ( $147\text{m}^2/\text{g}$ ), and micropore volume ( $0.195\text{cc}/\text{g}$ ) respectively for the base treated rice husk which are calculated using BET method on Nova 2200 (Quantachrome Instruments, USA) adsorption apparatus. The higher surface area is due to the result of higher fixed carbon content.

The moisture content, stability and decomposition of various biomass materials can be well understood by using Thermogravimetry. SDT Q 600 TGA analyser was used for the thermogravimetric analysis (TGA) experiments. Figure 3 shows the percentage weight loss during TGA for BRCH. The temperature range 323 to 383K corresponds to 6.6% weight loss is first stage which is due to the release of moisture during heating. The maximum decomposition observed due to the decomposition of chemically bound water, hemicelluloses, cellulose and lignin to carbon at 383-673 K in the second stage, [26]. In the third stage above 673 K, low weight loss is observed which is due to the formation of volatile products ( $\text{CO}$ ,  $\text{CO}_2$ ) [27].

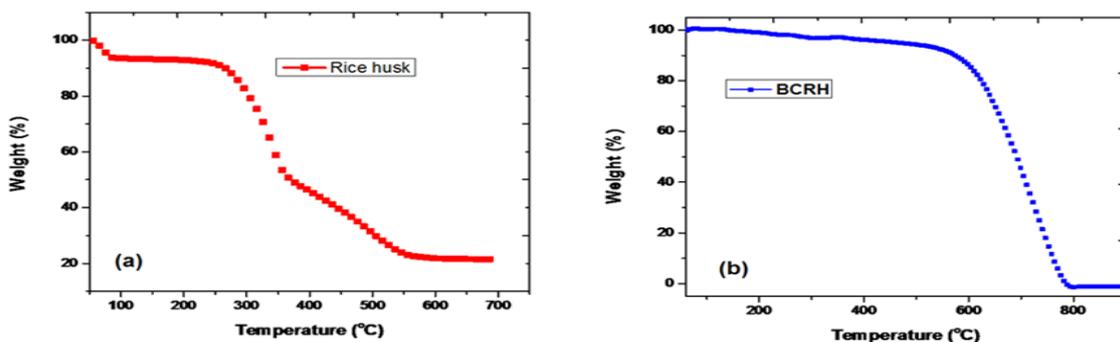


Figure 3: TGA for BCRH

Activation resulted the formation of oxygen containing functional groups, which can be characterized by TPD in the helium atmosphere ( $50\text{mLmin}^{-1}$ , ramp  $10\text{Kmin}^{-1}$ ) using a Quantachrome gas sorption analyzer in the range from 300 to 1,173 K. The amounts of desorbed  $\text{CO}_2$  ( $3.59\text{mmolg}^{-1}$ ) and CO ( $2.78\text{mmolg}^{-1}$ ) of the sample shows that the oxygen presence which influences the adsorption capacity of BCRH. The higher amount of  $\text{CO}_2$  and CO groups are mainly carboxylic groups (that releases  $\text{CO}_2$  below 673 K), carboxylic anhydride groups (that release both  $\text{CO}_2$  and CO above 873 K), lactone groups (that release CO around 923 K), phenol groups (that release CO around 973 K), and carbonyl groups (that release CO around 1,123 K) [28]. In order to assess the quality of coal proximate analysis of BCRH is conducted and the Moisture content (7.6%), Volatile content (36.5%), Ash content (22.3%), Fixed carbon content (26.3%) are calculated and the same data was also obtained using TGA.

## EXPERIMENTAL

### Batch adsorption experiment

The experiment was carried out by the batch adsorption method for a predetermined period with isothermal orbital shaker where the effect of adsorbent, pH, time and temperature were studied. Isothermal study was carried out with different initial concentrations of FG from 25 to 100mg/L, by keeping temperature constant and at 150rpm agitation speed for 2h. The adsorbent dosage was checked from 0.025 to 0.1g/L for better adsorption. The kinetic study was done by varying time from 0 to 120 min. For the thermodynamic study temperature was varied from 300 to 333 K. The measurement of absorbance of colour was done spectrophotometrically at  $\lambda_{\text{max}} = 624\text{nm}$  respectively. The quantity of dye adsorbed at equilibrium,  $q_e$  (in mg/g). The percentage of removal is calculated from the following equation.

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

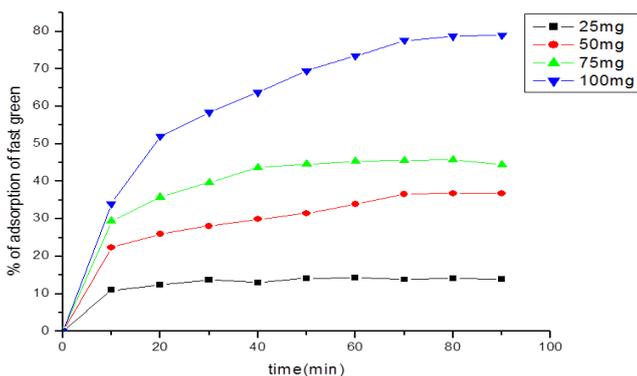
$$\text{Percentage of removal} = \frac{(C_0 - C)}{C_0} \times 100 \dots\dots(2)$$

Where  $C_0$  and  $C_e$  explains the concentration of adsorbate at initial and equilibrium positions, V the volume of solution in liters, W represents the weight of adsorbent in kg, and C is the dye concentration at the completion of adsorption.

## RESULTS AND DISCUSSION

### Effect of variation of adsorbent:

The removal of dye (FG) using BCRH was reported by varying the amount of adsorbent (25,50,75 and 100mg/100mL) while maintaining the other parameters like dye (FG) concentration (100 mg/L), temperature (298 K), and time (100 min) constant. Effluent removal increases with increasing adsorbent (BCRH) amount. (Fig.4). Maximum dye (FG) adsorption was obtained within 60 min after which dye (FG) concentration in the solution remains fixed. As shown in Fig 4. At optimum concentration, the unit adsorption capacity of fast green decreases with increasing BCRH (adsorbent) dose. The adsorption increases with adsorbent concentration is due to availability of number of adsorption sites; however, the unit adsorption capacity decreases with increasing adsorbent dose. This decrease is because of unsaturation of adsorption sites [29].

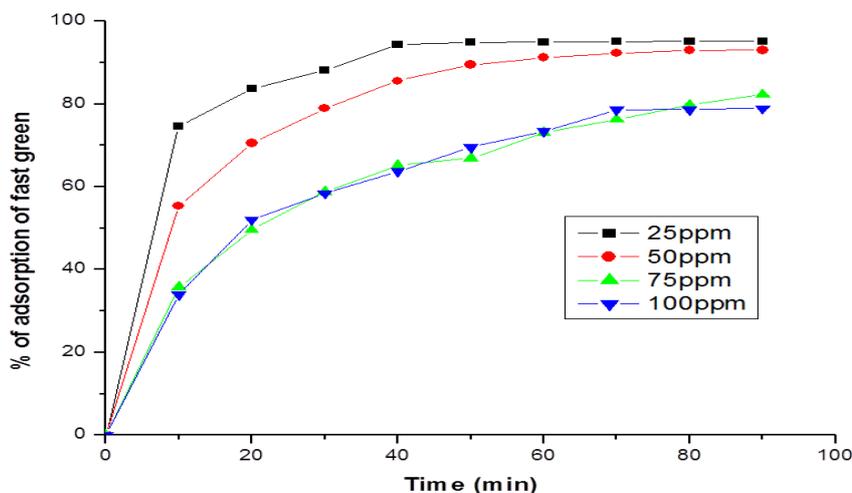


**Figure 4: Effect of adsorbent on adsorption of 100ppm of fast green at 298K**

Figure 5 explains the adsorption capacity is increased with increment of adsorbent dosage. The removal percentage of dye raised to 80% as the adsorbent varied from 0.025g to 0.1g for 100 ml of solution. These reports explained that more surface area was made due to increased mass of adsorbent. Hence, total number of sites increases. In addition the Figure.5 explains that, 0.1g of adsorbent is the optimum amount for the fast green removal. The adsorption of dye on the base treated activated rice husk can be explained by surface acidic groups present on the activated carbon surface. The dispersive interactions, hydrogen bonding, and donor-acceptor interactions [30] that may take place on the surface.

**Effects of dye and contact time**

The effects of variation of dye and contact time for the adsorption of dye were observed and results are shown in Figure.5. The concentration of dyes ranges from 25ppm, 50ppm, 75ppm and 100ppm per 100ml containing 100mg of BCRH. The concentration at which fast green dye shows maximum adsorption is at 25 ppm for a contact period of 1 hour (Table 1). Figure 5 demonstrates that, adsorption capacity enhances with increment in contact time between adsorbate and adsorbent. It demonstrates that more time is required for the dye to make an attraction complex with BCRH. From the graph it is understood that, initial adsorption takes place very rapidly as soon as the dye and BCRH in contact. Soon after that when some of the easily available active sites engaged, dye has to search more active sites for adsorption which requires some extra time. So, removal percentage is increased steadily over the period of experiment. It is observed that fast green and BCRH should be in contact for minimum of 80 minutes in order to obtain the maximum adsorption percentage.



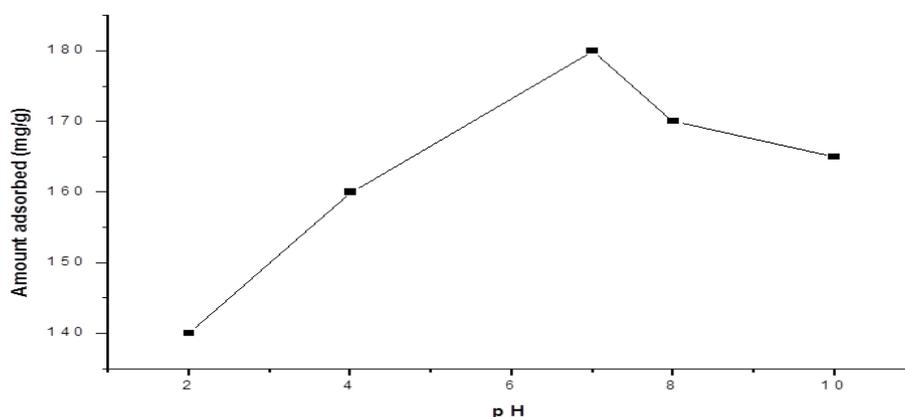
**Figure 5: Effect of adsorbate concentration (dye) and contact time on adsorption of fast green at 100mg of BCRH in 100ml**

**Table 1: Equilibrium parameters  $q_e$  and % of adsorption: (0.1 gm of BCRH)/100ml**

FG dye	25ppm	50ppm	75ppm	100ppm
$q_e$ (mg/g)	23.73	46.15	57.50	78.60
% adsorption	94.92	92.3	76.66	78.6

**Variation of pH**

Effect of pH is another significant parameter in the adsorption phenomenon, as varying pH may vary the surface properties of the adsorbent. The effect of pH in the removal of effluent is best explained in the pH range of 2 to 10. The standard buffers are used to maintain the required pH of the media. Figure 6 represents the variation of pH during adsorption of dye (FG) on BCRH at equilibrium conditions. At pH=7 the adsorbent surface is negatively charged that facilitates more electrostatic attraction between positive adsorbate species (FG) and adsorbent (BCRH) that leads to sharp increment in adsorption capacity of dye.



**Figure 6: Effect of pH on adsorption of fast green (25ppm) on BCRH (0.1g) at298K**

**Adsorption isotherms**

In general, for the demonstration of adsorption capacity and the feasibility of the process for a given application, the selection of most appropriate adsorbent and for preliminary determination of adsorbent dose requirements the adsorption isotherms are more appropriate. Langmuir isotherm is frequently used to represent the data of adsorption. It explains that the adsorption takes place at homogeneous sites, where all sites are equivalent and there are no interactions between adsorbate molecule and adjacent sides. The data can be studied from the linear form of the Langmuir isotherm equation. To calculate the maximum adsorption efficiency, the Langmuir isotherm equation of the following linearized form was used to the sorption equilibrium at different adsorbents doses. The isotherm is explained by following equation.

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \dots\dots(3)$$

Where  $C_e$  represents the equilibrium concentration of dye in aqueous phase (mg/L),  $q_e$  (mg/g) is quantity of dye absorbed at equilibrium,  $Q_m$  (mg/g) is the maximum monolayer adsorption capacity of adsorbent and  $K_L$  (L/mg) is the energy of adsorption. A plot of  $q_e$  versus time explains the adsorption of FG on BCRH at different concentrations of Fast green (Figure7). A linear plot of  $C_e/q_e$  versus  $C_e$  shows the validity of Langmuir model (Table2).  $Q_m$  and  $K_L$  are the Langmuir constants obtained from slope and intercept respectively (Figure 8).

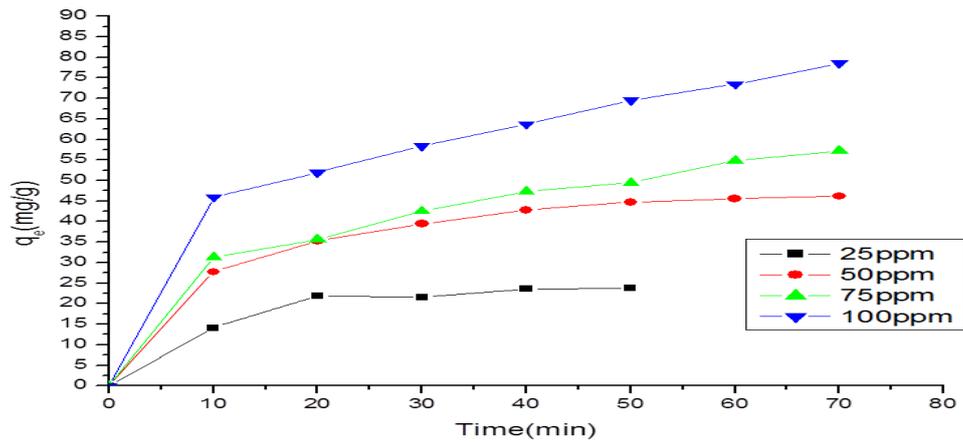


Figure 7: Plot of  $q_e$  versus time for the adsorption of fast green on BCRH (0.1g) at 298K

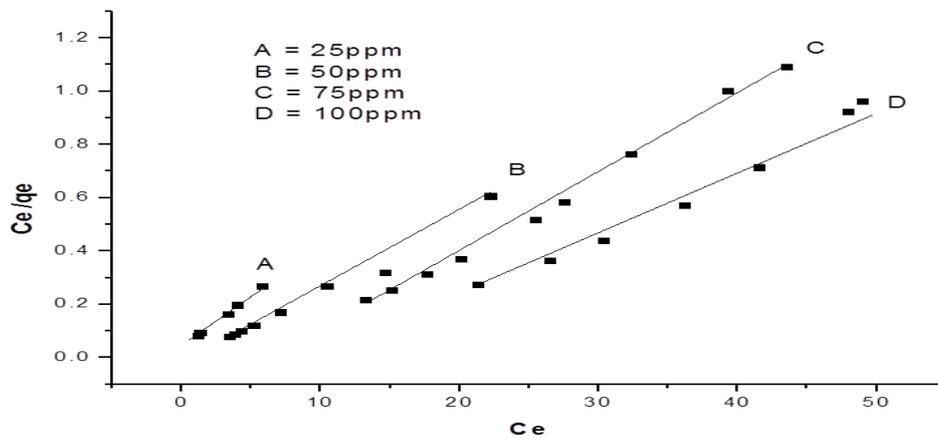


Figure 8: Langmuir adsorption isotherms on adsorption of fast green on BCRH (0.1g) at 298K

Table 2: Estimated parameters of Langmuir isotherms:

FG dye	25ppm	50ppm	75ppm	100ppm
$Q_m$ (mg/g)	23.80	55.55	50.0	66.66
$K_L$ (L/mg)	2.47	0.6666	0.8333	0.3409
$R^2$	0.987	0.959	0.847	0.968
$R_L$	0.01593	0.0291	0.01575	0.0285

An important characteristics of the Langmuir isotherms is represented by a dimensionless constant called “equilibrium parameter,  $R_L$ ”.

$$R_L = \frac{1}{1 + bC_0} \dots\dots\dots(4)$$

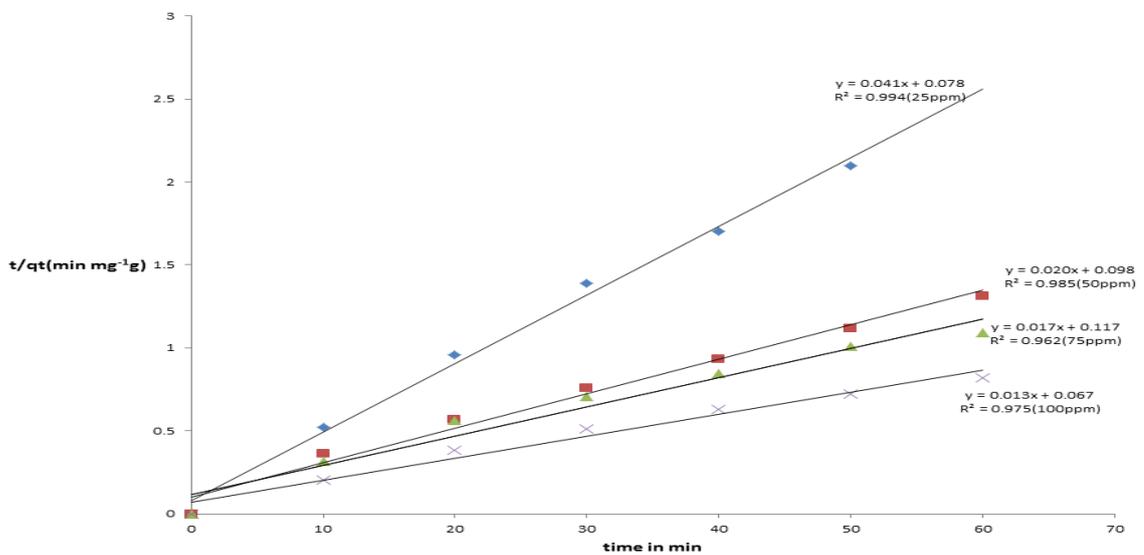
In (4)  $b$  ( $K_L$ ) is the Langmuir constant,  $C_0$  is the initial concentration of dye (in milligrams per liter), and  $R_L$  values indicate the type of the isotherm. Favorable adsorption as  $R_L$  value between 0 and 1. [31]. In the present study The values of  $R_L$  were observed from 0 to 1 for dye variations of 25, 50, 75 and 100 mg/L.

**Adsorption kinetics**

The rate constant and the order of the FG adsorption on BCRH were observed by varying the initial concentration of the FG (25-100mg/L) and the adsorbent (BCRH) dose (0.025-0.1g/100mL). From Eq.5, the results were established based on a pseudo second order kinetic model and the corresponding plots are shown in Figure 9.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots\dots\dots(5)$$

Where  $q_e$  (in mg per gram) is the equilibrium adsorbate quantity,  $q_t$  (in mg per gram) is the adsorbate quantity any time  $t$ ,  $k_2$  (in grams per milligram minute) is the rate constant for pseudo second order adsorption behavior [32,33].  $t/q$  against  $t$  determines the slope and intercept,  $q_e$  and second order rate constant  $k_2$  (Figure 9). As seen in Table 3,  $q_t$  increases while enhancing the initial concentration. The values of the coefficients determination ( $R^2$ ) = 0.99 represents a good fit.



**Figure 9: Pseudo second order kinetic model for the adsorption of fast green on BCRH (0.1g) at 298K**

**Table 3: Calculated parameters for pseudo second order kinetics from Figure 12**

FG	25ppm	50ppm	75ppm	100ppm
$Q_e$ (mg/g)	25.6	50.0	58.82	76.92
$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	0.009274	0.0040	0.0024	0.0025
$R^2$	0.994	0.962	0.985	0.975

The isotherm of Freundlich adsorption is as in equation (6).

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \dots\dots\dots(6)$$

Adsorption capacity is  $K_f$  represents the Freundlich constant and  $1/n$  represents the adsorption intensity or surface heterogeneity. Linear form of Freundlich (Fig 10) adsorption isotherm was fitted to the adsorption data for FG adsorption by the base treated carbonized rice husk. Freundlich isotherm model fitted better at 25ppm of fast green dye. The values of Freundlich constants  $K_f$  (15.31mg/g) and  $1/n$  (0.2147) for FG adsorption by BCRH are calculated from Fig.10.

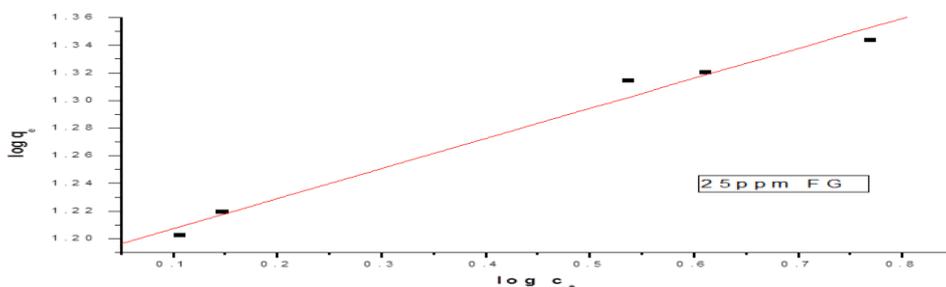


Figure 10: Freundlich isotherm for FG adsorption on BCRH

Calculation of thermodynamic parameters

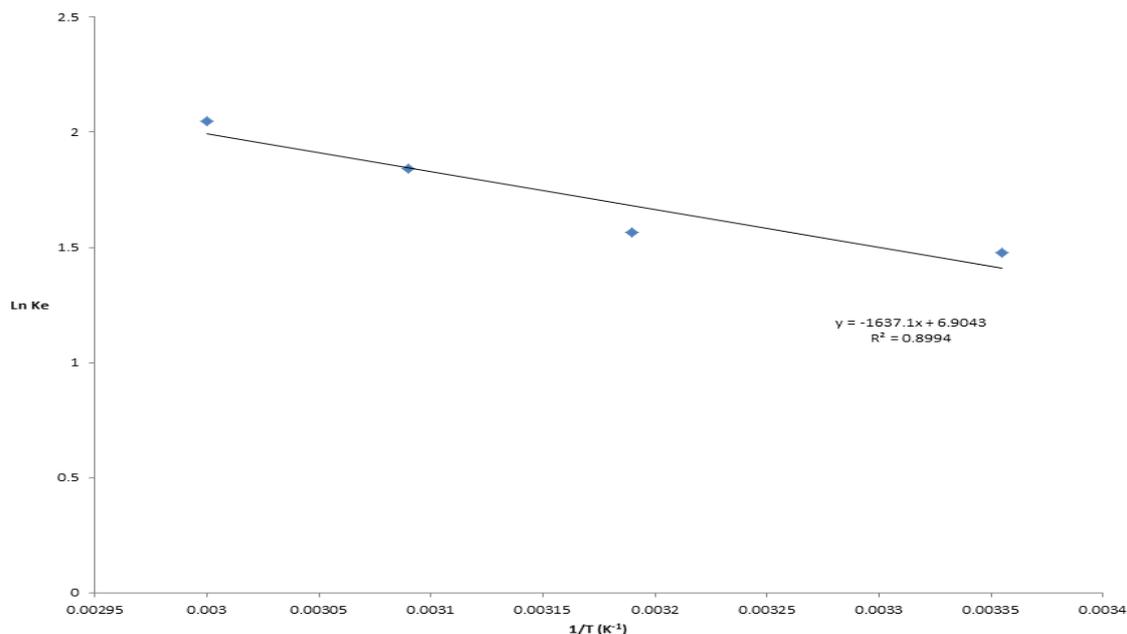
The change in standard free energy ( $\Delta G^\circ$ , in joules per mole) was calculated using Equations 7 and 8, which is a function of concentration and adsorbent dose and the observations are shown in Table 4.

$$K_e = \frac{C_{solid}}{C_{liquid}} \dots\dots\dots(7)$$

$$\Delta G = -RT \ln K_e \dots\dots\dots(8)$$

$$\ln K_e = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \dots\dots\dots(9)$$

Where  $C_{solid}$  (mg/L) is the solid phase concentration of dye, i.e., on the surface of BCRH,  $C_{liquid}$ (mg/L) is the liquid phase concentration of dye. i.e on the surface of BCRH,  $C_{liquid}$  (mg/L) is the liquid phase concentration of dye, i.e., in solution, R (8.314JK<sup>-1</sup>mol<sup>-1</sup>) and T (K) is the absolute scale. The negative sign of Gibb’s free energy change explains the spontaneity of the process. From these observations, it is established that the values of  $\Delta G$  becomes more negative with increase in the adsorbent quantity from 25 to 100mg/100 mL of solution and less negative with increasing dye concentration. From the slope and the intercept of the linear plot (negative slope) of  $\ln K_e$  against  $1/T$ , the values of energy  $\Delta H$  and  $\Delta S$  can be determined in the temperature range of 298K, 313K,323K and 333K. (Figure 11). The spontaneity of the adsorption is due to negative value of  $\Delta G^\circ$ .



**Figure 11: Thermodynamic parameters for the adsorption of fast green (100ppm) on BCRH (0.1g)**

**Table 4: Calculation of thermodynamic parameters:**

$\Delta G = -RT\ln K_d$ (J/mol)	$\Delta S$ (J/mol)	$\Delta H$ (J/mol)
298K= -3654.4	57.39	13610.0
313K= -4072.5		
323K= -4949.23		
333K= -5647.86		

### CONCLUSIONS

From these experiments, it may be understood that the base treated carbonized rice husk (BCRH) has been advised to be useful for reducing water pollution due to dyes, as it is best used as a low cost alternative adsorbent for the removal of toxic dye FG. The figures of percentage (%) removal at various temperatures for Fast green dye, explains the negative value of  $\Delta G^\circ$  which indicates that adsorption was spontaneous. The experimental data are well described by Langmuir and Freundlich isotherm model. It has been studied that FG adsorption on BCRH establishes pseudo-second-order kinetics, which confirms both physisorption as well as chemisorptions. Hence it can be a substitute for other high cost bio adsorbents in the adsorption process.

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