

Adsorption of Congored dye onto activated carbon produced from Tectonagrandis bark powder – A study of kinetic and equilibrium adsorption isotherm

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Abstract: The adsorption behavior of congored dye from aqueous solution on to activated carbon prepared from TGBP was investigated under various experimental conditions. Such as contact time, temperature, initial pH, initial dye concentration, at initial pH of 7 and initial dye concentration were carried out by 5 to 50 ppm and adsorbent dosages were investigated. The adsorption data were found to follow the Langmuir and Freundlich model and the adsorbent equilibrium data's fit with first order and second order.

Key word: adsorption kinetic, congored (CR), equilibrium studies and Tectonagrandis Bark Powder (TGBP).

I. Introduction

Dyes are large and important group of chemical present in industrial waste, Dyes in water affect the nature of water, and waste water from textile mill contains dyes in dissolved and suspended form and poses a serious health problem because it has a high concentration of both colors and organic matter. This color of the effluent discharged into various water bodies affects the aquatic flora and fauna and causes many water diseases [1].

The degradation yield compounds such as aromatic amines, which may be carcinogenic or otherwise toxic, most of Azo dyes, are carcinogenic in nature and pose a specific threat to the environment [1].

The majority of dyes used today are Azo compounds. Which are bright in color due to the presence of one or several Azo (-N=N-) groups, which are associated with substituted aromatic structures. Synthetic dyes are extensively used for dyeing and printing in variety of industries [2]. This dye can be investigated as mutagen and reproductive effector. It is a skin, eye and gastrointestinal irritant. It may affect blood clotting and respiratory problems [3].

The adsorption process provides an attractive and alternative treatment especially the adsorbent is inexpensive and readily available such as a study of Rise husk carbon activated by steam [4] adsorption of acid orange – 7 dye [5], dye removal from Bombax cieba tree [6], removal of methyl red dye [7], removal of methyl red dye by sugarcane Bagasse [8], kinetic study on annana squmosa seed [9], cocoa shell adsorbent for the removal of methyl blue [10], removal of anicidine dye by using beakers yeast [11].

In the present work activated carbon from adsorbent as Tectonagrandis bark powder for the removal of congored dye from aqueous solution, various parameter studies conducted initial pH, initial dye concentration and were kinetic data's and equilibrium data's on both adsorption studies were carried out understand to adsorption studies

II. Material and methods

2.1 Preparation of adsorbent

The present study was activated carbon from the Tectonagrandis bark powder (TGBP) by acid treatment to carbonization. This step carried out at 500 °C at 2 hours in muffler furnace. After that it has removed and washed in double distilled water and washed repeatedly, because external of acid can be removed and the carbon is dried in 200°C in oven at 2 hours. After that carbon is grained then the powdered at 75 µm size of Tectonagrandis bark powder stored in a plastic container for further study of experiment.

2.2 Adsorbate (dye)

The congo dye was first synthesized in 1883 by Paul Bottiger, who was working then for the Friedrich Bayer Company in Elberfeld, Germany. Due to the color change from blue to red at PH is 3.0-5.2, Congo red can be blue to red can be used as a pH indicator. It is Sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid (formula; $C_{12}H_{22}N_6Na_2O_6S_2$; molecular weight: 695.66(g/mol). It is a secondary diazo dye. $\lambda_{max}=497nm$.



Structure of Congored

III. Batch adsorption experiment

These experiments were conducted at different adsorbent dosages 2 to 12 mg/L with 50 ml/L dye solution with the initial concentration 5 to 50 ppm. The mixture was agitated at 750 rpm at 30°C. initial equilibrium reached to the concentrated congored dye(CR).The dye solution determined using a colorimeter, The maximum wavelength 500nm, The concentration attained in the adsorbent phase(q_e .mg/g) was calculated by using Equation (1):

$$\% \text{Removal} = (C_o - C_e) / C_o \times 100 \quad (1)$$

Where C_o and C_e are the initial and equilibrium concentration of the dye (mg/L) respectively.

3.1 Effect of the Initial dye concentration

Fig. (1) shows that the effect of initial congored dye concentration on the adsorption of *Tectonagrandis* bark powder at 5 ppm to 50 ppm and 7pH, where adsorbent dosage fixed with 15mg/L at 30°C, An increasing initial dye concentration leads to a decreased adsorption capacity Fig. (1) shows the dye adsorbed to achieve equilibrium adsorption within 60 min the graph is plotted at % removal Vs initial dye concentration.

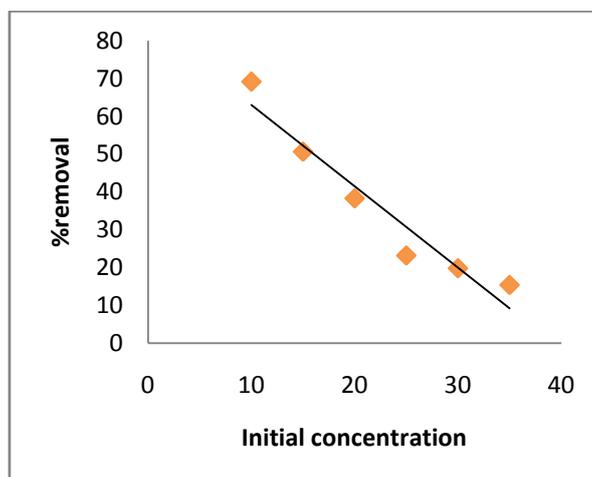


Fig. (1) effect of initial dye concentration of CR dye adsorption dose 15mg/50ml; 7pH at 1hours

3.2 Effect of adsorbent dose

The effect of adsorbent dose was studied by agitating of different adsorbent dosages (20mg to 12mg/L), and the particle size 75µm of *Tectonagrandis* bark powder and 50ml (congored dye) 20ppm dye concentration using water bath shaker at 30°C . This experiment conducted with 7PH, agitating was provided for 60min contact time at a constants agitating speed of 120rpm.it shows at Fig. (2).

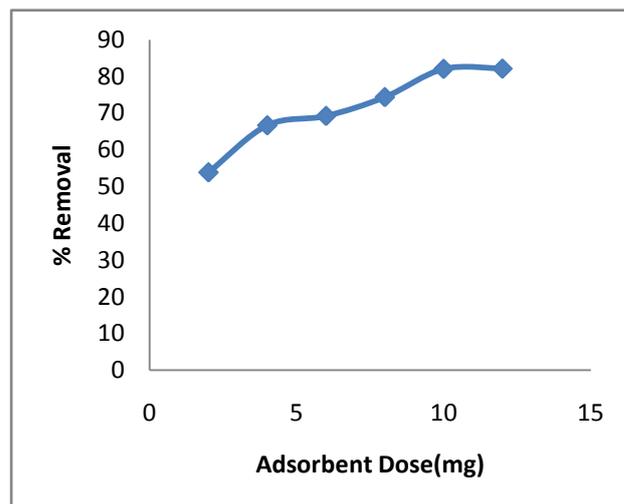


Fig. (2) effect of adsorbent dose on the adsorption of congored dye 20ppm, contact time-60min, pH=7; Tem30°C using Tectonagrandis bark powder.

3.3 Effect of Temperature

The effect Temperature was conducted at the range of 20°C to 60°C. The adsorbent dosage 15mg/50ml of TGBP AND 50ml of congored dye solution (5 to 50ppm) using water bath shaker to 20°C to 60°C the experiment conducted with 7 pH, agitating was provided at 1 hours.

3.4 Effect of pH

These experiments were conducted at various pH 3, 5, 7, 9, 11, 13. This range can be maintained from acetic and alkaline medium by using the amount of 0.01 HCl and NaOH is added. The initial pH of stock solution 7.37 in 1000ppm dye solution from the present work the adsorption of congored at low pH range 3 to 7, the % removal was increased (86.66) and the higher pH 7 to 13 the % removal decreased, because of deprotonation of surface of electron diffusion. The resulting the adsorption shows Fig(3). The graph is plotted initial pH Vs after pH.

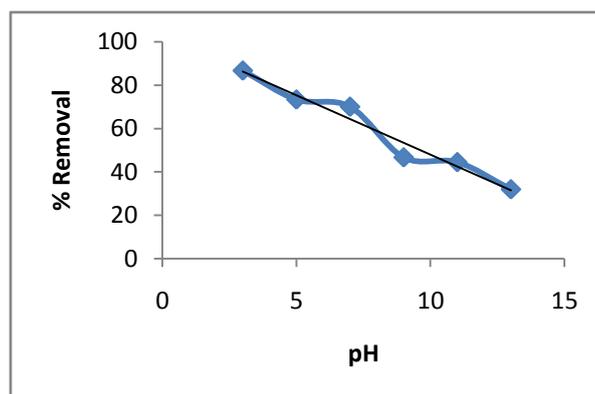
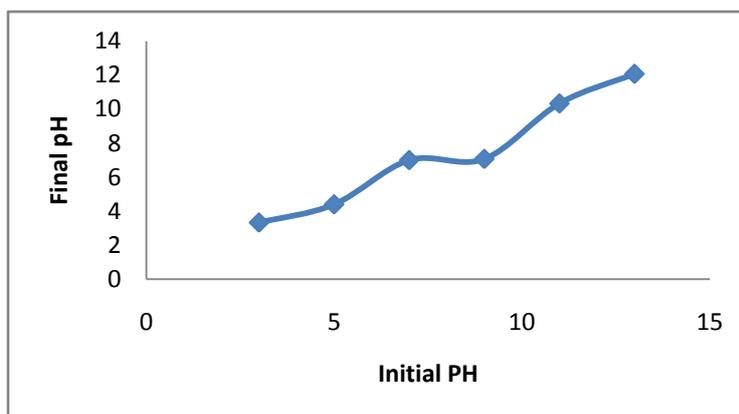


Fig (3) effect of pH on Removal of CR=15mg/50ml; Time-1hours.

3.5 Effect of ZPC

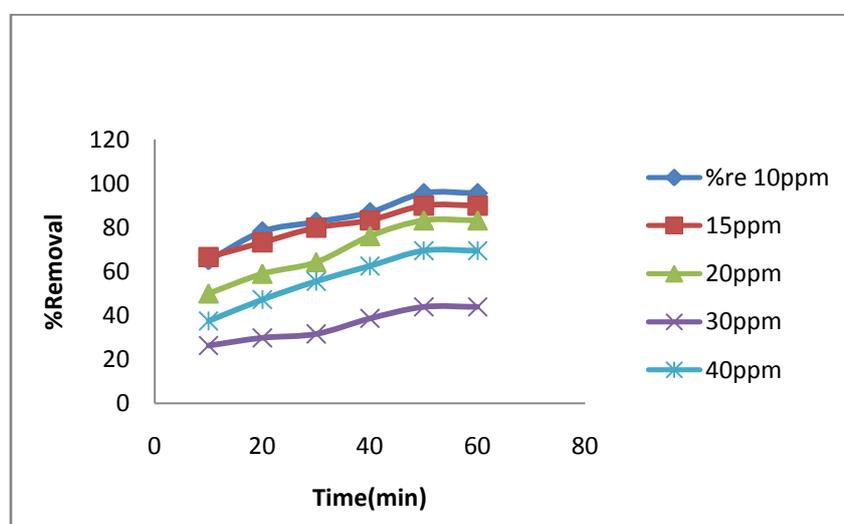
In this present study a very important method is used to determine Zpc of adsorbent. The point of Zero charge (ZPC) is defined as the pH at which the surface of adsorbent has neutral charge. The pH zpc adsorbent depends on several factor such as the nature of crystallinity impurity constant Temperature degree of adsorption of H⁺ and OH⁻, and therefore it must vary adsorbent, These study the adjusting the pH can using 0.01mol/L Hcl and NaOH. The 15mg of adsorbent dose was added 15ppm of CR dye solution (50ml), after the pH stabilized (at 24 hours). The final pH is noted, the graph is plotted initial pH and after pH was used to studied to determined Zpc of activated carbon. The initial and final pH values were equal as shown Fig (4). This point taken as pHzpc. In this study pHzpc was found to be 7.00.



Fig(4) Effect of pH of CR=15ppm/L ; 1 hourse ; dose 15mg/50ml

3.6 Effect of contact Time

The effect of contact time was studied to determine the time taken by adsorbent to reach equilibrium. The experiment taken from various concentrations of 5 to 50ppm/L at 7pH adsorbent dosages fixed with 15mg/L. The adsorbent gradually increased to 10 to 40 minutes in all condition then equilibrium data are collected in 50 to 60 minutes was efficient to achieve equilibrium and adsorption did not change with further increasing the contact time therefore uptake the adsorbed dye concentration. The end of 50 minutes the equilibrium values are given, This values are respectively show in the figer. (5).



Fig(5) Effect of contact Time CR Dose15mg/50ml; pH=7

IV. Adsorption Kinetics

The adsorption kinetics data were processed to study the dynamics of the adsorption process in expression of the order of rate constant kinetic data were analyses with the pseudo first order and pseudo order kinetic model to CR dye adsorbed on to TGBP.

4.1 pseudo first order modal

Lagergren proposed a pseudo first order kinetic model from the equation(2):

$$\log(q_e - qt) = \log q_e - \frac{k}{2.303}t \quad (2)$$

Where q_e is the amount of dye adsorbed (mg/l) at equilibrium time, qt is the amount of dye adsorbed (mg/L) at Time (min). K is the equilibrium constant of first order adsorption (1/min).

Pseudo first order adsorption process (min⁻¹). Figures (6,7, 8) show the plot of linearized from of pseudo first order at all concentration study. The slopes were taken from the intercept of plot $\log(q_e - qt)$ and time. It is used to determined the first order rate constant K and equilibrium adsorption density q_e noted table: 1 for different concentration of CR dye (10, 15, 20,) ppm on TGBP.

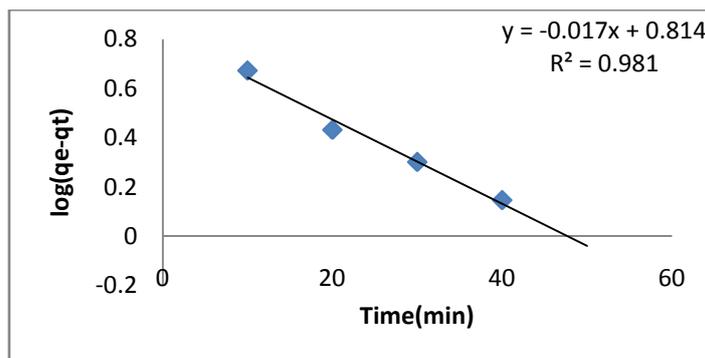


Figure. (6)

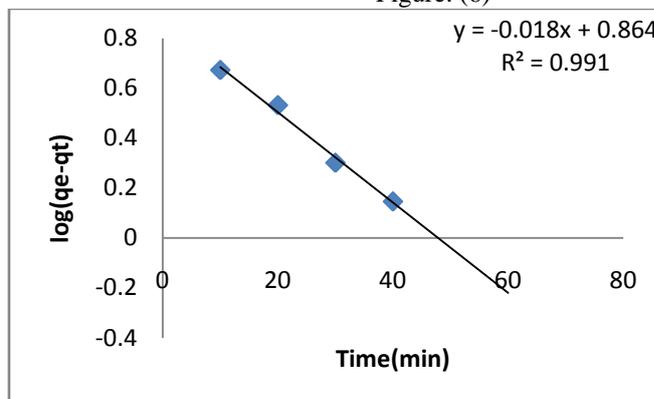


Figure. (7)

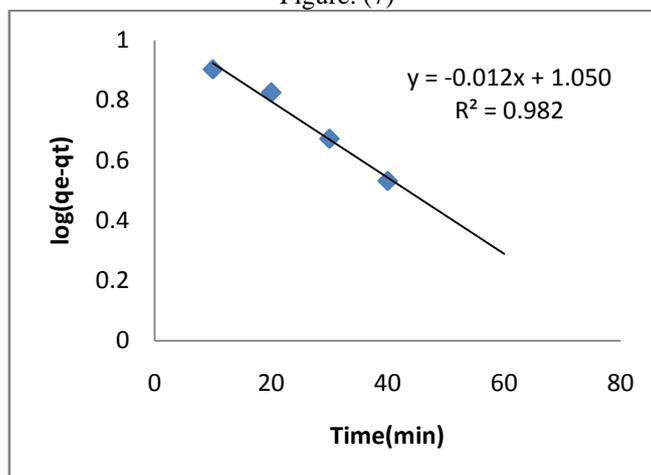


Figure. (8)

Figure. (7,8,9) -pseudo –first-order Kinetic for CR on Tectonagrandis bark powder

The comparison of results with correlation-co- efficient is shown Table (1). The R2 is approximately (0.981, 0.991, 0.982).The theoretical q_e values obtained from pseudo first order kinetic model to give reasonable values. It suggests that this range adsorption system found in first order reactions.

Table (1) K values of CR dye from pseudo first order kinetic for 15,20,25ppm using Tectonagrandis bark

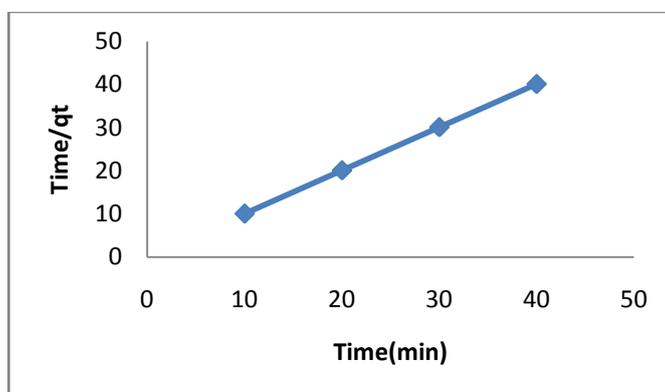
Initialdye concentration(ppm)	K value $\text{min}^{-1}(\times 10^{-3})$	R ² value
10	0.32	0.981
15	0.13	0.991
20	0.18	0.982

4.2 The pseudo sound-order Kinetic model

The pseudo second order kinetic model which is based on the assumption that chemisorptions is the rate- determining step can be expressed as equation(3):

$$t/q_t = 1/K q_e^2 + t/q_e \quad (3)$$

Where K_2 is pseudo second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). The straight line for pseudo second order model was obtained and it indicates the applicability of this Kinetic model. The second order rate constant K_2 values were calculated from the slop of the line in Figure (9). The pseudo second order reaction rate model adequately described the kinetics of dye adsorption with high correlation coefficient for all range of dye concentration. The best result obtained from the second order kinetic model. The correlation coefficient for second order kinetic model obtained in 1. The q_e values is also very well with the experimental data's. These results indicate that the adsorption of system studied belongs to the pseudo second order kinetic model. The respective values are given in the Table2. The similar phenomena are also observed in adsorption of CR dye on Tectonagrandis bark powder.



Figure(9) effect of pseudo second order Kinetic for CR on to TGBP : pH=7; Doss=15mg/50ml; Using 15ppm

Table 2 Kinetic constant for CR on TGBP

Initial concentration (ppm)	15PPM
$Q_{eq}(\text{exp})$ (mg/g)	0.998
K (min^{-1}) $\times 10^{-3}$	5.84
R^2	1

V. Equilibrium study

Adsorption isotherm can amount of solute adsorbed per unit of adsorbent as a function of equilibrium concentration in bulk solution of constant time. It can be applied to Langmuir and Freundlich as follows. Langmuir isotherm

This type of adsorption isotherm based on monolayer of adsorption surface of carbon adsorbed on congored dye and can be explained in linear form of equation(4):

$$C_e q_e = 1/Q_0 + b C_e / Q_0 \quad (4)$$

Where C_e is equilibrium concentration of dye solution, q_e is amount of adsorbed at equilibrium(mg/g), Q_0 (mg/g) and b is Langmuir constant. It represents the monolayer adsorption capacity. The plot of C_e/q_e Vs C_e gives straight line of slope $1/Q_0$ and intercept $1/Q_0 b$. show fig. (10).

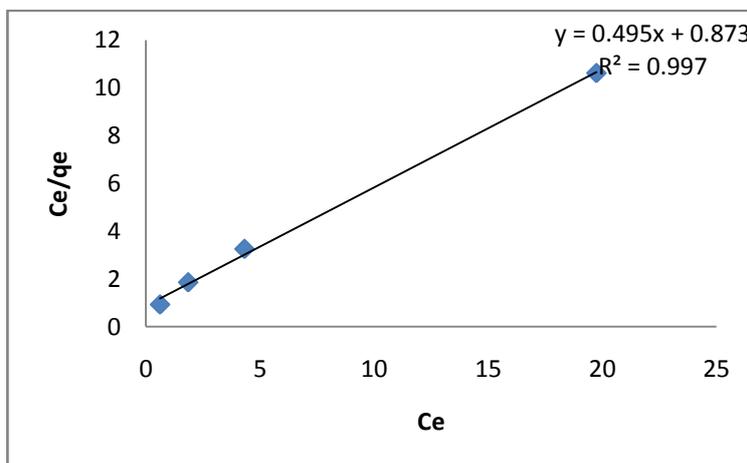


Figure. (10) Langmuir adsorption isotherm for CR dye on TGBP: Doss15mg/50ml; pH=7; Time 60 min

The linear form of correlation coefficient value $R^2(0.997)$. These values can suggest that the Langmuir isotherm provides a good result for the adsorption model.

Freundlich Isotherm

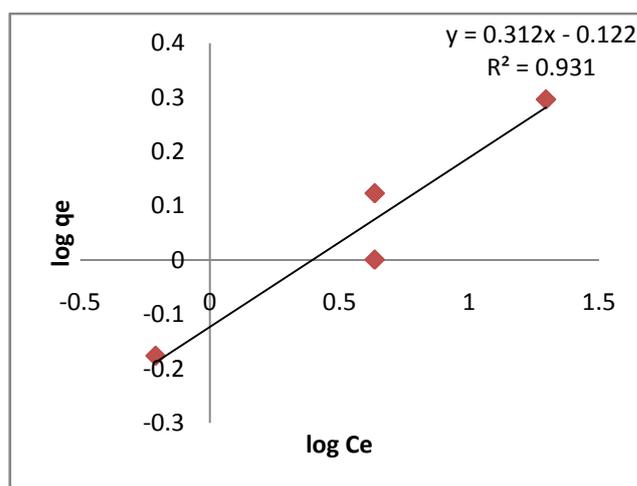
This type of isotherm can be a heterogeneous adsorption process. Adsorption takes place on a heterogeneous surface, and through the multilayer adsorption mechanism. And can be explained by the linear form of the Freundlich equation (5):

$$\log q_e = \log K_f + 1/n \log C_e \quad (5)$$

q_e = amount of adsorbed, C_e = equilibrium concentration, K_f = the constant of the system. (Defined as

unit equilibrium constant), and n . ($1/n$) is ranging between 0 and 1, measuring adsorption intensity.

From this study of Congo red dye conducted for 60 minutes with 15 mg/L in different times, at pH 7, the values of K_f and n determined from the intercept and slopes. The linear plot of $\log q_e$ vs $\log C_e$. This adsorption data are shown in Figure (11).



Freundlich adsorption isotherm for CR at 15mg/50ml of adsorption concentration

Table (3)-Langmuir and Freundlich adsorption isotherm constants for CR on Tectonagrandis bark powder.

Langmuir model	Freundlich model
$Q_0(\text{mg/g})=2.0202$	$n=1.4684$
$b=0.4321$	$K_f=0.7550$
$R^2=0.997$	$R^2=0.931$

VI. Conclusions

The results obtained from the present investigation are helpful for Congo red dye adsorption onto Tectonagrandis bark powder. The studies were followed by adsorbent data, contact time, initial dye concentration, and pH. The amount of dye removal was found to increase with an increase in time and adsorbent dose and increasing pH. The amount of dye removal was found to increase with an increase in time and adsorbent dose and increasing pH, optimum contact time 1 hour (60 minutes). Maximum adsorption occurs at 7 pH. Increasing pH, the percentage removal is decreased because of the protonation of the surface of electron diffusion. The present results show that the Langmuir and Freundlich models showed a good fit with equilibrium data. And it is followed by pseudo first order and pseudo second order kinetic models using a concentration range of 10, 15, 20, 30 mg/L.

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