

ADSORPTION OF CONGO RED DYE ONTO COCONUT SHELL BASED NaOH ACTIVATED CARBON: KINETICS, THERMODYNAMICS AND OPTIMISATION STUDIES



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ABSTRACT

Coconut Shell (CS) was carbonised, activated with NaOH and used to adsorb Congo Red (CR) dye from its aqueous solution. Proximate and ultimate analyses, Fourier Transform Infra-red (FTIR) and Scanning Electron Microscope (SEM) were used to characterize both the raw and the Coconut Shell Activated Carbon (CSAC) while UV spectrophotometer was used to monitor the CR dye concentration. Batch adsorption experiments were carried out using 100 ml each of 50 mg/l to 250 mg/l CR dye solution at different contact times, and temperature. To establish optimum adsorption conditions, Central Composite Design (CCD) in Response Surface Methodology (RSM) was employed using the initial dye concentration, contact time and temperature as variables at a fixed pH of 3 and 0.2 g/100ml of adsorbent. Adsorption capacity of 122.00 mg/g was obtained with CR concentration, contact time and temperature of 250 mg/l, 180 min and 30°C, respectively. Pseudo first order kinetic model best fitted the experiment. The coefficients of determination of Langmuir, Freundlich and Temkin isotherms were 0.978, 0.974 and 0.863, respectively, with Langmuir isotherm giving a better fit for the adsorption. The maximum monolayer adsorption capacity from Langmuir isotherm was 121.56 mg/g at pH 3 and a temperature of 30°C.

Key Words: Congo red; coconut; optimisation; adsorption isotherm

1. INTRODUCTION

Dyes are among colourants with vast industrial applications whose daily use have resulted in generation of coloured wastewater with attendant pollution effects on the water bodies (Forgacs *et al.*, 2004; Chatterjee *et al.*, 2009; Umar *et al.*, 2015). The coloured effluents mostly are the lost unfixed dye resulting from the competition between the colouring reaction and the hydrolysis of the reactive group. This phenomenon is usually promoted by the dye's formation of covalent bonds with cellulosic fibres because of its molecular structure (Verma, 2011; Umar *et al.*, 2015). Dyes are harmful not only because of their carcinogenic and mutagenic nature but are also stable to biological degradation and these make their removal before discharging the effluents to the environment imperative (Wong and Yu, 1999; Sivaraj *et al.*, 2001; Ojedokun and Bello, 2016). Water bodies as well as the dependent flora and fauna are affected by discharges into the water through disruption of food web, interference with photosynthesis and the colour of the water (Mittal *et al.*, 2009; Ljubas *et al.*, 2015). One prominent example of these dyes is Congo red.

Congo red is a sodium salt of benzidinediazobis-1-naphthylamine-4-sulfonic acid and its molecular formula is $C_{32}H_{22}N_6Na_2O_6S_2$ (Ojedokun and Bello, 2016).

remains persistent once it is discharged into natural environment. It mainly occurs in the effluents discharged from textile, paper, printing, leather industries, *e.t.c.* (Bhattacharya and Sharma, 2004; Ojedokun and Bello, 2016). Its hazardous effects include skin, eye and gastrointestinal irritation, blood clotting and respiratory problems (Mittal *et al.*, 2009). Its removal has been reported to be difficult because of the complex aromatic structure which gives it physico- chemical, thermal and optical stability (Han *et al.*, 2008).

Quite a number of techniques have been employed to remove dyes or reduce their impact on the environment. They include coagulation (Papic *et al.*, 2000), ultra filtration (Purkait *et al.*, 2004; Ahmad *et al.*, 2006), use of oxidizing agents (Alaton and Balcioglu, 2002; Alaton, 2003) and adsorption (Amin, 2008; Han *et al.*, 2008). Adsorption has been reported as been the most versatile and commonly used method for the removal of these pollutants due to its high removal capacity, ease and cost of operation (Ghaedi *et al.*, 2012; Ghaedi *et al.*, 2013). Activated carbon has very high capacity for adsorption due to the structural characteristics and porosity (Adhoum and Monser, 2002). However, commercial activated carbons are very expensive and this has necessitated researches into the production of activated carbon from agricultural wastes (Carvalho *et al.*, 2011) which will in turn mitigate the problem of agricultural waste disposal (Wang and Peng, 2010). These activated carbons from agricultural waste apart from been inexpensive and have been found suitable for the removal of organic and inorganic

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It exists as brownish – red crystals, stable in air with a solubility of 1 g/ 30 ml in water (Mittal *et al.*, 2009) and

contaminants from wastewater (Forgacs *et al.*, 2004; Santhy and Selvapathy, 2006).

Coconut being one of the agricultural products widely applied for this purpose is a fruit whose oil is used for cosmetics, food and pharmaceuticals; the flesh is consumed either raw or in processed form; and the shell is an agricultural waste that has found application as renewable energy source and adsorbent. Studies on coconut shell based adsorbents include the adsorption of methylene blue (Kannan and Sundaram, 2001), heavy metals (Amuda *et al.*, 2007), 2,4,6 – trichlorophenol (Hameed *et al.*, 2008), basic dye (Tan *et al.*, 2008), methylene Blue (Cazetta *et al.*, 2011), ammonium ion (Boopathy *et al.*, 2013), reactive blue 19 dye (Umar *et al.*, 2015), benzene and toluene (Mohammed *et al.*, 2015), phenol and cyanide (Singh. and Balomajumder, 2016). Quite a number of adsorption studies on the CR dye have been reported using various adsorbents. For example, when guava leaf based carbon was activated with 0.3 mol/dm³ of H₃PO₄, a maximum adsorption capacity ($q_{\max}$) of 47.62 mg/g was recorded (Ojedokun and Bello, 2016). Others include TiO₂ nanoparticles with 60% CR removal (Ljubas *et al.*, 2015); marine algae with 97.77% CR removal (Jayaraj *et al.*, 2011); for a silver modified calcium hydroxyapatite, $q_{\max}$ was 267.81 mg/g (Srilakshmi and Saraf, 2016); carbon nanotube, $q_{\max}$ was 1250 mg/g (Yang *et al.*, 2015); Ferrocene based surfactant, $q_{\max}$ was 312.5 mg/g (Kaur *et al.*, 2015); orange peel with 90% CR removal (Namasivayam *et al.*, 1996); raw pine and acid treated pine cone powder, $q_{\max}$ was 40.19 mg/g (Dawood and Sen, 2012); Chitosan hydrogel beads impregnated with cetyl trimethyl ammonium bromide, $q_{\max}$ was 94.39 mg/g (Shadeera *et al.*, 2015).

This present study investigated the adsorption of Congo Red dye from synthesized wastewater using base activated coconut shell carbon and optimized using Central Composite Design (CCD) in Response Surface Methodology (RSM).

2. MATERIALS AND METHODS

2.1 Adsorbent preparation and characterization

Coconuts used for the preparation of adsorbent were obtained from Oja -Titun Market in Ogbomoso, Nigeria. The shells were removed from the fruits, washed with water to remove the debris and then drained overnight. The drained coconut shell was crushed and dried in an oven at a temperature of 105°C until constant weight was attained. The dried coconut shell was carbonized under inert condition in a furnace (Vecstar XF model) at temperature of 700°C for 90 minutes. The carbonized coconut shell was crushed and sieved with a mesh size of 60BSS (0.250 mm). The sieved char was mixed with NaOH pellet and 10 ml of water at a ratio of 3:1

(NaOH: char) (Cazetta *et al.*, 2011). This was transferred into a continuously agitated vertical stainless reactor placed in a furnace operating at a temperature of 800°C for 2 h. The sample was then cooled to room temperature, washed with 0.1 M HCl and then deionized water until the pH of the washing solution reached approximately 6.5 to eliminate activating agent residue and other inorganic species formed during the process (Bello and Ahmad, 2012). The sample was dried at 110°C for 24 h and then stored as CSAC in a tightly closed bottle for this study. Proximate and ultimate analysis were carried out on the dried CS and CSAC using ASTM methods. Scan Electron Microscopic (SEM) analysis was carried out to establish the morphology of the CSAC. Fourier Transform Infrared (FTIR) spectroscopic analysis was also employed to establish phase conversions in the CS and CSAC as well as the surface functional groups.

The pH at point of zero charge (pH_{PZC}) of the CSAC was also determined according to Bello and Ahmad (2012). In order to determine the pH of point zero charge, 0.2 g of the CSAC was transferred into a 100 ml conical flask containing 50 ml of 0.01 M NaCl. The pH_{initial} was adjusted to between 2 and 10 by the addition of 0.1 M HCl or 0.1 M NaOH for the CSAC. The conical flask was sealed and placed in a shaker for 48 h under atmospheric condition. The content of the flask was filtered and the final pH was then measured using a pH meter. pH_{PZC} is the point where the curve of ($pH_{\text{initial}} - pH_{\text{final}}$) against pH_{initial} intersect the abscissa and then $pH_{\text{initial}} = pH_{\text{final}}$ (Bello and Ahmad, 2012).

2.2 Preparation of Congo red dye solution

Congo Red (CR) dye has a chemical formula C₃₂H₂₂N₆Na₂O₆S₂ and has a molecular weight of 696.66 g/mol. CR of 500 mg/L concentration was prepared by dissolving 0.5 g CR in 600 mL of distilled water and then, distilled water was added with constant stirring to make it up to 1000 mL mark. The other solutions used for the experiment were prepared from the stock solution using serial dilution.

2.3 Batch equilibrium experiment

Batch equilibrium tests were carried out on the adsorption of CR onto CSAC. The adsorption experiments were carried out in 250 ml conical flasks with stopper on a mechanical shaker equipped with a thermostatic water bath operating at 120 rpm. The effect of CR initial concentration, contact time and temperature were investigated. For the equilibrium studies, the experiments were carried out for 3 h to ensure that equilibrium was reached at three different temperatures (30, 40 and 50°C) and five initial CR concentrations (50, 100, 150, 200 and 250 mg/L). During the experiment, 0.2 g of CSAC was

measured into the 250 ml flask and 100 ml of CR solution was added, the parameter considered was varied while the others were kept constant. The pH of the solution was adjusted to 3 by addition of 0.1M HCl based on previous experiments (Cazetta *et al.*, 2011; Bello and Ahmad, 2012) and pH_{PZC} (5.09). Sample solutions were withdrawn at predetermined time intervals to determine the quantity of the dye removed from the solution. Concentrations of dye solutions were calculated by determining absorbance at a wavelength of 497 nm using UV-Vis spectrophotometer. The adsorbed phase concentration (q_t , in mg/g) at time (t) was calculated using equation (1)

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

Where, C_0 and C_t are the initial and the final CR concentration (mg/L), respectively; V is the adsorbate volume (L) and m is the mass of adsorbent used (g). The adsorption at equilibrium, q_e (mg/g), was calculated according to Equation (2)

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

Where, C_0 and C_e are the initial and the final (equilibrium) CR concentration (mg/L) respectively; V is the adsorbate volume (L); and m is the mass of adsorbent used (g).

2.4 Adsorption isotherm and kinetic studies

The parameters estimated from different adsorption isotherm models give insight on the sorption mechanisms of the adsorbent. In this study the suitability of Langmuir isotherm models (Langmuir, 1918) as presented in equations (3) and (4), Freundlich isotherm model (Freundlich, 1906) (equation 5) and Temkin isotherm models (Temkin and Pyzhev, 1939) (equations 6 and 7) to fit the equilibrium data were evaluated. While the kinetic models such as pseudo- first order (Lagergren, 1898) (equations 8 and 9) and pseudo-second order (Ho and McKay, 1999) (equations 10 and 11) were used to understand the adsorption dynamics in relation to time. The isotherm and kinetic models were fitted using the non-linear fitting method in Origin 6.0 software.

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

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

$$q_e = K_F C_e^{1/n} \quad (5)$$

$$q_e = B \ln(K_T C_e) \quad (6)$$

$$B = \frac{RT}{b} \quad (7)$$

$$q_t = q_e (1 - e^{-K_1 t}) \quad (8)$$

$$h_o = K_1 q_e \quad (9)$$

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad (10)$$

$$h_o = K_2 q_e^2 \quad (11)$$

where q_m = maximum adsorption capacity; K_L = Langmuir constant; R_L = separation factor; K_F and n = Freundlich constants; B = Temkin isotherm constant; K_T = the equilibrium binding constant corresponding to the maximum energy; K_1 and K_2 = rates constants for pseudo-first and pseudo - second order adsorption, respectively; h_o = initial adsorption rate.

2.5 Thermodynamic study

The thermodynamic parameters, which characterize the equilibrium state of a system, are the standard Gibbs free energy change (ΔG°). The standard enthalpy change (ΔH°) and the standard entropy change (ΔS°). These parameters were determined to investigate the feasibility, spontaneity and the nature of the interaction of the adsorption process. This was achieved by using equation (12) to (14) (Faust and Aly, 1987; Ojedokun and Bello, 2016):

$$\ln K_o = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

$$\Delta G^\circ = -RT \ln K_o \quad (13)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

Where K_o is q_e/C_e . ΔG° , ΔH° and ΔS° are change in Gibbs, free energy, (kJ/mol), enthalpy (kJ/mol) and entropy (kJ/mol. K) of adsorption, respectively. R is the universal gas constant (8.314 J/K/ mol) and T is the temperature (K). Batch adsorption studies were carried out with CR solution at varying temperature (30, 40 and 50°C). A Von't Hoff graph was plotted, taking $\ln(K_o)$ against $1/T$ for initial concentration. Values of ΔH° and ΔS° were calculated from the slope and intercept of Hoff plots,

2.6 Optimization study

Central Composite Design (CCD) of Response Surface Methodology (RSM) in Design Expert 6.8.0 was used to design three factors (initial concentration, temperature and time) at three levels to estimate the

optimum adsorption conditions. The RSM was used to estimate the regression model of the adsorption capacity of CSAC in terms of the three factors after which the optimization routine was used to estimate the optimum value of the adsorption. The terms of the model generated was evaluated using ANOVA and F- statistics at $p < 0.05$. The design points for the experiment is as shown on Table 1

3. RESULTS AND DISCUSSION

3.1 CSAC characterization

The proximate and ultimate analysis of CS and CSAC are as shown on Table 2. The initial moisture content of CS (8.50 %) was reduced to 2.21 % for the CSAC. Activated carbon is generally priced on a moisture free basis and hence the moisture content should be as low as possible. The volatile content (66.90 %) is high compared with fixed carbon content of 23.20 % in the CS which later increased to 88.14 % in CSAC after activation. The ash content for the CSAC was 3.98 %. The inorganic material contained in activated carbon is measured as ash content and should generally be in the range between 2 and 10% (Marsh and Rodriguez-Reinoso, 2006). The high (89.56 %) carbon content of the CSAC is an indication of its fitness for the adsorption purposes which is in

agreement with the findings of Mohd Iqbalidin *et al.* (2013). The textural structure of the of CSAC as obtained from the SEM at a magnification of 1000 is shown in Figure 1. It is characterised by irregular and porous surface morphology. The pores were prominent on the CSAC surface. The pores observed have been attributed to the loss of volatile matter and the effect of the activating agent on the CS (Bello and Ahamad, 2012; Mohd Iqbalidin *et al.*, 2013).

The FTIR spectra for the CS and CSAC are as shown in Figure 2a and 2b, respectively to evaluate the chemical structure of the two materials. The prominent broad bands on Figure 2a for CS are around 3404 cm^{-1} (hydroxyl group), 2900 cm^{-1} (C-H stretching vibration), 1612 cm^{-1} (C=O carbonyl group); 1465 cm^{-1} (C=C bond of aromatic ring), 1300 cm^{-1} (axial deformation of ketone), 1100 cm^{-1} (angular deformation of ketone), 1058 cm^{-1} (angular deformation of ether) and 580 cm^{-1} (O-H bending vibration). These groups are evidence of the lignocellulosic structure of the CS (Cazetta *et al.*, 2011). As shown on Figure 2b, there were decrease in the functionality of CS after activation as many bands disappeared. The symmetrical stretching of C=C were at 1700 cm^{-1} and C=O of carboxyl groups at 1500 cm^{-1} .

Table1: Range of levels for parameters used in the adsorption capacity test

Parameters	Range of levels		
	-1	0	+1
A: Initial lead ions concentration (mg/l)	50	150	250
B: Contact time (minutes)	15	97.5	180
C: Temperature ($^{\circ}\text{C}$)	30	40	50

Table 2: Proximate and ultimate analysis of CS and CSAC

Samples	Proximate Analysis				Ultimate Analysis			
	Moisture Content	Volatiles	Fixed carbon	Ash	C	H	S	(N+O)*
CS (%)	8.50	66.90	23.20	1.40	54.20	5.60	0.08	40.12
CSAC (%)	2.21	5.67	88.14	3.98	89.56	1.48	0.05	8.91

* Calculated by difference

The pH_{PZC} of CSAC was determined to be 5.09. This implies that CSAC surface is positively charged in solution up to this pH and becomes negatively charged in solution above the pH. Higher CR dye adsorption onto CSAC is expected at low pH due to the more positive charge on the adsorbent surface. As observed by Bello and Semire (2012), the carboxyl group has a pK_a value between 3.0

and 5.0 and at pH lower than these, carboxylate groups carried positive charge resulting in an electrostatic attraction between negatively charged SO_3^- groups on the dye molecule and the positively charged adsorbent surface while electrostatic repulsion between anionic CR dye and anionic CSAC surface is expected at basic pH medium. Hence the choice of pH of 3 for this study.

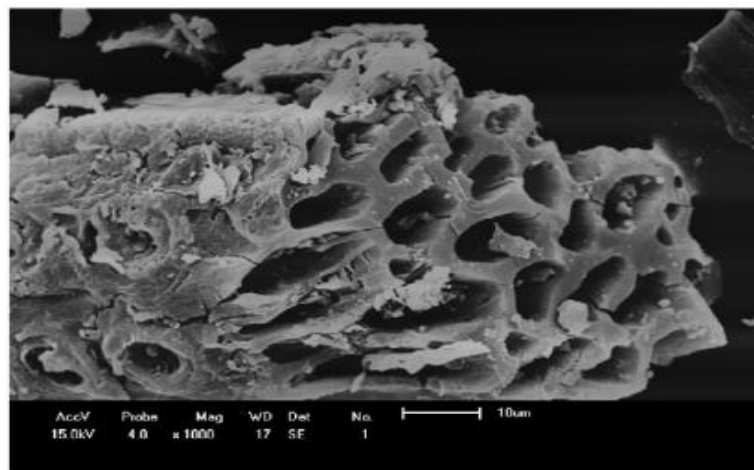


Figure 1: SEM micrograph of CSAC (magnification 1000x)

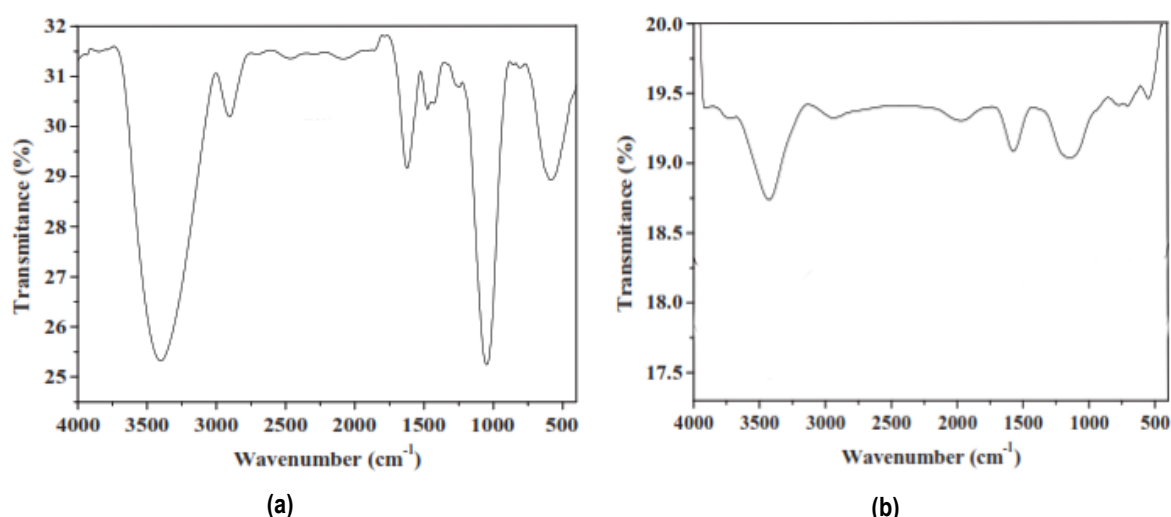


Figure 2: FTIR spectra of CS(a) and CSAC (b)

3.2 Batch Adsorption Studies

3.2.1 Effects of contact time and initial CR dye concentration

The effects of the initial concentration (50 - 250 mg/L) and contact time on the adsorption capacity of CSAC in removing CR dye from its solution at a pH of 3, 30°C and adsorbent dose of 0.2 g/100 ml of CR dye solution is shown on Figure 3. The CR dye uptake was rapid at the initial stage and later became constant on reaching its equilibrium stage. The reduction in adsorption uptake was due to the decrease in concentration gradient between the adsorbate in solution and adsorbate on adsorbent surface due to accumulation of CR dye on the vacant sites thereby producing electrostatic hindrance or repulsive forces between the dye molecules and the surface of adsorbent. Figure 3 can be divided into fast, slow and equilibrium portion corresponding to first 30 minutes, the portion between 30 and 90 minutes; and the portion between 90 and 180 minutes, respectively. The equilibrium portion is characterized by practical non-sorption where rate of sorption may be equal to rate of desorption. The equilibrium stage shows the maximum

adsorption capacity of each adsorbent under the operating conditions (Ojedokun and Bello, 2016). In addition, as the initial CR dye concentration increased from 50 to 250 mg/L, the loading capacity of the CSAC increased from 24.38 to 121.56 mg/g. Thus, the adsorption capacity was enhanced with increased initial concentration. As a result of increased diffusion process, the equilibrium adsorption uptake increased (Ojedokun and Bello, 2016).

Effect of Temperature

The effects of the initial concentration (50 - 250 mg/L) and temperature (30°C, 40°C and 50°C) on the adsorption capacity of CSAC in removing CR dye from its solution at a pH of 3, 30°C, 180 min. and adsorbent dose of 0.2g/100 ml of CR dye solution is shown on Figure 5. Adsorption uptake increased with increasing initial concentration for the various temperatures but however decrease with increasing temperature at various initial concentrations of CR dye.

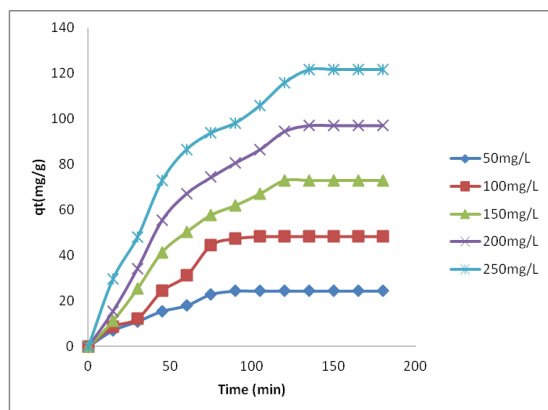


Figure 3: Effect of initial dye concentration on the adsorption of CR dye by CSAC

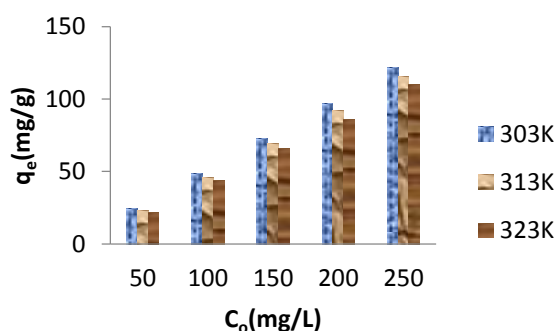


Figure 5: Effect of initial dye concentration and temperature on the adsorption of CR dyes onto CSAC.

The decrease in adsorption uptake as temperature increased from 30°C to 50°C may be due to increase in the solubility of the dyes that resulted in a stronger

interaction forces between CR dyes and solvent than those between dyes and CSAC (Shadeera *et al.*, 2015). High temperature is related to the increasing Brownian movement of molecules in solution might also lead to the breaking of existing intermolecular bonds between CSAC and CR dye (Bello and Ahamad, 2012).

3.3 Adsorption Isotherm

The parameters of isotherm models employed in this study at 30°C and 250 mg/L CR concentration shown on Table 3. The Langmuir adsorption isotherm assumes that the maximum monolayer adsorption occurs when the surface is covered by a monolayer of adsorbates and the mean q_m of CSAC are 121.56, 115.59 and 109.71 mg/g at 30, 40 and 50°C, respectively. The value of R_L indicate whether the isotherm is irreversible if ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$), unfavorable ($R_L > 1$). The value of R_L obtained for initial concentration of 250mg/L in this study as reported in Table 3 at various temperatures indicating that the adsorption of CR dye on to CSAC is favorable as the values lies between 0 and 1. Freundlich isotherm is used to illustrate the non-ideal heterogeneous behaviour of adsorption process. The extent of adsorption was described by the value of K_F . It was found that the extent of adsorption was 18.436, 6.223 and 3.655 for 30, 40 and 50°C, respectively. The value of n calculated from the Freundlich model was greater than 1 indicating that the adsorption was favourable. The equilibrium binding constant, B which is the Temkin isotherm constant were 54.029, 53.23 and 52.19 for 30, 40 and 50°C, respectively. The three models had very high R^2 but Langmuir model best describe the isotherm as can be seen on Table 3.

Table 3: Isotherm constant and correlation coefficient for the adsorption of CR onto CSAC at different temperatures

Temp. (°C)	Langmuir isotherm				Freundlich isotherm				Temkin isotherm		
	q_{max} (mg/g)	k_L (L/mg)	R_L	R^2	k_F	$1/n$	n	R^2	K_T	B	R^2
30	121.56	0.060	0.063	0.978	18.436	0.903	1.107	0.974	1.049	54.029	0.863
40	115.59	0.007	0.363	0.996	6.223	0.981	1.019	0.996	0.355	53.23	0.920
50	109.71	0.003	0.607	0.998	3.655	0.989	1.011	0.998	0.219	52.19	0.931

3.4 Adsorption kinetics

The estimated kinetic parameters for the pseudo-first and pseudo-second order kinetics for the adsorption of CR dye onto CSAC is shown on Table 4. The values of K_1 and K_2 reduced as the values of the initial CR dye concentrations increased from 50 to 250 mg/L for pseudo-first and pseudo-second order, respectively. This is due to

increase in mass transfer resistance between the aqueous and solid phases as initial concentration increases (Ojedokun and Bello, 2016). The correlation coefficients (R^2) ranged between 0.922 and 0.988 for pseudo-first order and 0.785 and 0.891 for pseudo-second order. In terms of R^2 , pseudo-first kinetic model best describes the system.

Table 4: Pseudo first order and Pseudo second order Kinetic Parameter and Correlation coefficient obtained for adsorption of CR onto CSAC at different concentration

Model	CR Concentrations (mg/L)				
	50	100	150	200	250
Pseudo first order					
q_{exp} (mg/g)	24.38	48.32	72.78	97.07	121.56
k_1 (min ⁻¹)	0.026	0.021	0.020	0.019	0.018
q_{cal} (mg/g)	24.14	47.16	70.77	94.15	118.37
R^2	0.971	0.922	0.971	0.977	0.988
h (mg/g.min)	0.6276	0.9904	1.4154	1.7889	2.3678
Pseudo second order					
k_2 (g.mg ⁻¹ min ⁻¹)	0.002	0.001	0.001	0.0008	0.0006
q_{cal} (mg/g)	22.17	42.68	64.00	85.09	107.47
h (mg. g ⁻¹ min ⁻¹)	0.983	1.821	4.096	5.792	6.930
R^2	0.854	0.785	0.849	0.861	0.891

3.5 Adsorption Thermodynamics

The effect of temperature on the adsorption process are better understood from thermodynamic parameters as shown on Table 5. The negative values of ΔH° obtained in the adsorption of CR dye onto CSAC signify the exothermic nature of the adsorption process. The negative value of ΔS° indicate that decrease in randomness occurred at solid–solution interface during the adsorption

process which is a low affinity of adsorbent towards dye molecules at high temperature (Ojedokun and Bello,2016). The values of ΔG° were negative at all studied temperatures, inferring that the adsorption was spontaneous in nature. Since the absolute value of ΔG° decreased with increasing temperature, it suggests that the sorption process is more favourable at low temperature.

Table 5. Thermodynamic parameter for the adsorption of CR onto CSAC at different temperature

Temperature (K)	Equilibrium Constant (Kc)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol. K)
303	2.872	-7.23	-66.25	-0.20
313	1.803	-4.69		
323	1.278	-3.43		

3.6 Optimization study

The adsorption capacity of CSAC obtained from experiments conducted as a result of various combination of factors (concentration, time and temperatures) using the CCD is as shown on Table 6 as well as the predicted values from the model developed from the RSM analysis. The estimated coefficients of the terms of the model of CR uptake in terms of the factors using RSM and its functional significance are as presented in Table 7 while Analysis of Variance (ANOVA) of the model is as presented in Table 8. As indicated on Table 7, the model's F- value of 159.73 implies that the model term was significant. Value of Prob > F less than 0.05 indicated that the model is statistically significant. The R^2 -value of 0.9938 and adjusted R^2 of 0.9876 show a high correlation between actual and predicted value. Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 44.19 in this research indicates an adequate signal. This model can be used to navigate the design space. The coefficient of variation (CV) as the ratio of the standard

error of estimate to the mean value of the observed response is a measure of reproducibility of the model. Generally, a model can be considered reasonably reproducible if its CV is not greater than 10 per cent (Reed *et al.*, 2002; Agarry and Ogunleye,2012). Hence, the low variation coefficient value (CV = 7.47 %) obtained indicates a high precision and reliability of the experiments. Given all these indices, the errors between the predicted value and actual CR dye uptake (Table 5) were very small indicating that model developed was successful in capturing the correlation between the process variables and adsorption capacity. The lack of fit is designed to determine whether the selected model is adequate to describe the observed data, or whether a more complicated model should be used. As shown on Table 8, the p-value of the lack of fit of the model is 0.2284 which is not significant and this indicates a significant correlation between the independent variables and the adsorption capacity.

Table 6: CCD Matrix for CR dye Adsorption on to CSAC

Factors			Response	
CR initial Concentration (mg/L) :A	Contact Time (min):B	Temperature (°C) : C	Experimental Adsorption Capacity (mg/g)	Predicted Adsorption Capacity (mg/g)
50	15	30	7.00	6.54
250	15	30	29.64	31.00
50	180	30	24.38	25.74
250	180	30	121.56	121.10
50	15	50	6.32	7.19
250	15	50	26.75	25.80
50	180	50	22.00	21.05
250	180	50	109.71	110.58
50	97.5	40	23.16	22.35
250	97.5	40	95.20	94.39
150	15	40	10.58	9.77
150	180	40	69.14	68.33
150	97.5	30	63.10	61.31
150	97.5	50	56.20	56.37
150	97.5	40	55.80	56.31
150	97.5	40	55.60	56.31
150	97.5	40	55.20	56.31
150	97.5	40	56.10	56.31
150	97.5	40	55.60	56.31
50	15	30	7.00	6.54

Table 7: Statistical parameters for the adsorption capacity of CSAC on CR

Source	Coefficients	F- Value	p-value
Intercept	56.31	159.73	0.0001*
A	30.00	654.55	0.0001*
B	26.65	516.53	0.0001*
C	-2.47	4.44	0.0444*
A ²	2.05	0.84	0.3837
B ²	-17.27	59.24	0.0001*
C ²	2.52	1.27	0.2896
AB	17.73	182.85	0.0001*
AC	-1.46	1.24	0.2943
BC	-1.33	1.03	0.3360

R² = 0.9938; Adj. R² = 0.9876; Pred R² = 0.9473

CV= 7.47, Adeq Precision= 44.19

*Significant at p<0.05

Table 8: Analysis of variance for the adsorption capacity of CSAC on CR

Source	DF	Sum of Square	Mean Square	F- Ratio	p-Value
Model	9	19766.6	2196.29	159.73	0.0001*
Linear	3	16163.23	16163.23	1175.52	0.0001*
Square	3	843.50	843.50	61.35	0.0001*

Interaction	3	2545.37	2545.37	185.12	0.0003*
Residual	9	123.75	13.75		
Lack of Fit	5	123.32	24.66	2.26	0.2284
Pure Error	4	0.43	0.11		
Cor Total	18	19890.35			

The resulting model of the CR uptake from the RSM analysis is the equation (15):

$$\text{CR dye uptake (mg/g)} = 56.31 + 30A + 26.65B - 2.47C - 17.27B^2 + 17.73AB \quad (15)$$

Where A = Initial concentration of CR dye, B = Contact Time, C = Temperature.

The 3D plot along with the contour to estimate optimum value for the three factors considered are shown in Figure 6. Figure 6 a shows the combined effect of initial concentration and contact time on adsorption uptake of CR dye. Figure 6 b represents the effects of initial concentration and temperature and- Figure 6c depicted combined effect of contact time and temperature. The RSM gave an optimum point of 122.00 mg/g of CR dye uptake attainable with 250 mg /L, 180 minutes and temperature of 30°C.

coconut shell exhibited significant adsorption capacity for Congo red. Variables such as initial CR dye concentration, contact time and temperature had a strong influence on the CR dye uptake. The adsorption capacity was influenced positively by contact time and initial concentration and negatively by temperature. The kinetic and isotherm parameters of the process were also determined. The obtained second-order polynomial quadratic regression model for the responses of adsorption uptake was significant. Finally, the mathematical model obtained was also employed to establish the optimum process conditions.

4. CONCLUSION

This study demonstrated the adsorption capacity of coconut shell activated carbon. The activated

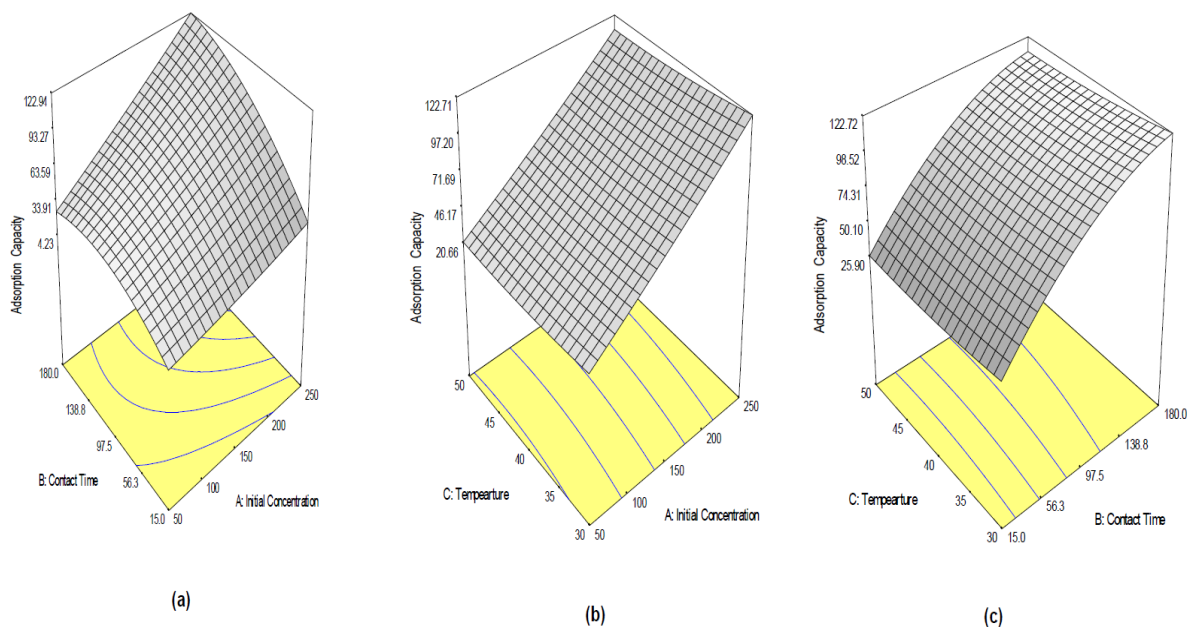


Figure 6: Effects of combination of factors on the adsorption capacity of CSAC on CR (a) Concentration vs Contact Time (b) Concentration vs Temperature (c) Time vs Temperature at 0.3 g adsorbent dose and pH (3).

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