

Adsorption of Congo Red Dye from Aqueous Solution Using Agricultural Waste

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ABSTRACT: The potential of Breadfruit seed shell powder, for the removal of congo red (CR) dye from aqueous solution was investigated. The adsorbent was characterized by FTIR and SEM analysis. Batch adsorption studies were conducted and various parameters such as contact time, adsorbent dosage, initial dye concentration, pH and temperature were studied to observe their effects in the dye adsorption process. The optimum conditions for the adsorption of CR onto the adsorbent (BFSSP) was found to be: contact time (60mins), pH (2.0) and temperature (303K) for an initial CR dye concentration of 500mg/L and adsorbent dose 1.0g. The experimental equilibrium adsorption data fitted best and well to the Freundlich isotherm model. The maximum adsorption capacity was found to be 16.00mg/g. The kinetic data conformed to the pseudo-second-order kinetic model, suggesting that the rate limiting step may be chemisorptions. Thermodynamic quantities such as Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were evaluated. The negative values of ΔG^0 and the negative value of ΔH^0 obtained indicated the spontaneous and exothermic nature of the adsorption process while the negative ΔS^0 value obtained indicated decreased randomness during the adsorption process.

Keywords: Adsorption, Breadfruit seed shell powder, Congo red, Isotherms, Kinetics, Thermodynamics.

I. Introduction

The pollution of water resources due to the disposal of dye based effluents has been an increasing worldwide concern for the last few decades. Dyes are natural or synthetic coloured organic compounds having the property of imparting their colours to other substances. Although there are many natural dyes available, the ingrain coloured by these are neither bright nor durable. Hence synthetic dyes are generally used which are cheap and readily available [1]. They also produce brighter colours and are resistant to light, heat and biological degradation [2]. Approximately 10,000 commercially available dyes with over 7×10^5 tonnes of dyestuff are being produced annually across the world today [3]. Synthetic dyes are used widely by various industries such as paper, textile, plastics, paints, food, printing, pharmaceuticals, etc. to colour their products which generate large volumes of coloured wastewater yearly [4, 5]. The discharge of these coloured effluents in the environment has become a worldwide concern due to the toxic nature of these effluents.

Congo red (CR) is a benzidine-based anionic bisazo dye known to metabolize to benzidine, a known human carcinogen [6]. Congo red (CR) is toxic to animals and plants and thus its introduction to water stream is of potential health, environmental, and ecological concern [7]. Therefore, CR containing effluents have to be efficiently treated before they are discharged into the water bodies or the environment.

Over the past few decades, several processes have been used for the removal of dyes from wastewater such as biological (aerobic and anaerobic), chemical precipitation, coagulation/ flocculation, solvent extraction, membrane filtration, ion exchange, ozonation, electrochemical destruction and adsorption [8, 9]. Adsorption process has simplicity of design, more efficient, easy to operate, insensitivity to toxic substances and cost effective, hence, it has been suggested as a potential alternative to the existing physical / chemical /biological methods for the removal of dyes from industrial effluents or waste water [10]. A number of investigations carried out using agricultural materials or the wastes and by product of industries for the removal of dyes from aqueous solutions have been reviewed [11]. However, research interest into production of more economical, easily available and highly efficient adsorbents are still under development. Hence attempts are made in this study to develop a low-cost adsorbent for wastewater treatment using Breadfruit (*Artocarpus altilis*) seed shell powder.

Breadfruit (*Artocarpus altilis*) is a member of Moraceae (fig) family. It has been an important staple crop in the pacific and the south eastern part of Nigeria and its peels are left in the environment during processing and consumption. The objective of this study was to investigate the potential of Bread fruit seed shell as an alternative adsorbent for the removal of Congo red dye from aqueous solution. Characterization of BFSS powder was carried out before and after adsorption using FTIR and SEM analysis. The effect of contact time,

adsorbent dose, initial dye concentration, pH and temperature were evaluated. Adsorption isotherms, kinetics and thermodynamic parameters were also evaluated and reported.

II. Experimental

2.1. Adsorbent collection and Preparation

The Bread fruit seed shell powder BFSSP was collected from farm fields in Aboh Mbaise local Government Area of Imo state, Nigeria. This agricultural waste was washed thoroughly with running and distilled water to remove sand, dirt and other impurities present in it and dried in an oven (at 50°C) until all moistures were removed. It was then ground in a mill and sieved in a sieve shaker of particle size 300µm. The Breadfruit seed shell powder that passed through the sieve were stored in an air tight container, labelled BFSSP and used as adsorbent without any further pre-treatment.

2.2. Preparation of adsorbate Solutions

Analytical grade CR dye (C₃₂H₂₂N₆O₆S₂Na₂; molecular weight 696.68; λ_{max}= 500nm) was obtained from the laboratory. A stock solution of CR dye of concentration 1000mg/L was prepared by dissolving 1g of powder CR dye in 1L of distilled water. Experimental dye solutions of desired concentration were obtained by appropriate dilution of the stock solution.

2.3. Adsorbent characterization

Fourier transform infra-red (FTIR) spectrophotometer was used to identify the different functional groups available on the adsorbent sites and their effect on dye adsorption. The FTIR of the adsorbent was taken before adsorption using FTIR spectrophotometer (Shimadzu-8400S). 0.1g of the adsorbent was encapsulated with 1g of KBr spectroscopy grade (merk, Darmstadt, Germany) and by introducing the mix in a piston's cell of a hydraulic pump with compression pressure 15KPa/cm², the solid translucent disk was obtained which was introduced in an oven for 4hrs at 105°C to ensure the non interference of any existing water vapour or CO₂ molecules. The FTIR spectrum was then recorded within the wave number range 4000 – 500cm⁻¹. In addition, surface morphology and texture of the adsorbent was analyzed using scanning electron microscope (SEM) (Model-PHENOM ProX). Prior to scanning, some quantity of the adsorbent was placed on a double adhesive sticker placed in a sputter machine for 5 sec; this gave the adsorbent a conductive property. Sample (adsorbent) stud was fixed on a charge reduction sample holder, and then was charged in the SEM machine.

2.4. Batch Adsorption Experiments

Batch adsorption of CR dye onto the adsorbent (BFSSP) was conducted in a 250ml airtight Erlenmeyer flask containing 100ml of known concentration of the CR dye solution and an accurately weighed amount of the adsorbent. The mixtures in the flasks were agitated on a mechanical shaker operating at a constant speed of 100 rpm. The effect of contact time (10, 20, 40, 60, 80, 100 & 120 min), adsorbent dosage (0.5, 1, 2, 3 & 4 g), initial CR dye concentration (25, 50, 75, 100 & 125 mg/L), pH (2, 4, 6, 8 & 10) and temperature (303, 313, 323, 333 & 343 K) were evaluated. The flask containing the samples were withdrawn from the shaker at predetermined time intervals, filtered and the final concentrations of CR dye in the supernatant solutions were analyzed using the UV-visible spectrophotometer (Model Hitachi – 2800). The pH of the solution was adjusted using 1M HCl or NaOH. The amount of equilibrium uptake of CR dye was determined using

$$q_e = \frac{(C_o - C_e)V}{M} \quad (1)$$

$$\% \text{ Dye Removal} = \frac{(C_o - C_e)V}{C_o} \times 100 \quad (2)$$

Where q_e is the amount of dye taken up by the adsorbent at equilibrium (mg/g), C_o is the initial dye concentration (mg/L), C_e is the dye concentration at equilibrium (mg/L), M is the mass of the adsorbent (g), and V is the volume of the solution, (L).

III. Adsorption isotherms

Two adsorption isotherm models were applied to describe the sorption equilibrium in the present study such as Langmuir and Freundlich isotherm models.

3.1.1. Langmuir isotherm

The Langmuir model describes the monolayer adsorption. It assumes a uniform energy of adsorption, a single (homogenous) layer of adsorbed solute at a constant temperature [12, 13].

The linear form of Langmuir equation is given as

$$\frac{C_e}{q_e} = \frac{1}{q_m K_1} + \frac{C_e}{q_m} \quad (3)$$

Where q_e (mg/g) is the amount of dye adsorbed at equilibrium, q_m (mg/g), the amount of dye adsorbed when saturation is attained, C_e is the equilibrium dye concentration (mg/L) and K_1 is Langmuir constant related to the binding strength of dye onto the adsorbent.

3.1.2. Freundlich isotherm

The Freundlich model is an empirical equation that is very useful in describing the distribution of solute between solid and aqueous phases at a point of saturation. The basic assumption of this model is that there is an exponential variation in site energies of adsorbent and also the fall in heat of adsorption is logarithmic [14].

The linearized form of Freundlich equation is expressed as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

Where K_f and n are the Freundlich constants that represent adsorption capacity and intensity (strength) of adsorption respectively. The significance of n is as follows: $n = 1$ (linear); $n < 1$ (chemical process); $n > 1$ (physical process) [15].

3.2. Adsorption kinetics

The pseudo-first-order and pseudo-second-order kinetic models were applied to study the adsorption kinetics of CR dye to compute the extent of uptake in the adsorption process.

3.2.1. Pseudo-first-order kinetic model

The linear form of the pseudo-first-order kinetic mode is represented by

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

Where q_e and q_t are the values of amount of the dye adsorbed per unit mass on the adsorbents at equilibrium and at various time t , respectively, k_1 is the Pseudo-first-order adsorption rate constant (min^{-1}). The values of k_1 and calculated q_e can be determined from the slope and intercept respectively, of the linear plot of $\ln(q_e - q_t)$ versus t .

3.2.2. Pseudo-second-order kinetic model

The pseudo-second-order kinetic model is expressed by

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

Where K_2 is the pseudo-second-order adsorption rate constant (g/mg/min) and q_e is the amount of dye adsorbed (mg/g) on the adsorbent at equilibrium. The initial adsorption rate, h ($\text{mg.g}^{-1}.\text{min}^{-1}$) is expressed as:

$$h = k_2 q_e^2 \quad (7)$$

The plot of t/q_t versus t gives a linear relationship which allows computation of k_2 , h and calculated q_e .

Among these models, the criterion for their applicability is based on judgment on the respective correlation coefficient (R^2) and agreement between experimental and calculated value of q_e [15- 17].

3.3. Thermodynamic parameters

The thermodynamic parameters such as change in Gibb's free energy change (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were determined using the following equations:

The Gibb's free energy, ΔG , equation is expressed as follows [18, 19]:

$$\Delta G = -RT \ln K_{ads} \quad (8)$$

The equilibrium constants (K_{ads}) were calculated according to the following equation:

$$K_{ads} = \frac{(q_e^m)}{(C_e)} \quad (9)$$

Where: R is gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is absolute temperature in Kelvin, q_e^m is dye concentration on the solid at equilibrium and C_e is dye concentration in solution at equilibrium.

The Van't Hoff equation is expressed as follows [18- 20]:

$$\ln K_{ads} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (10)$$

Where R is gas constant, T is absolute temperature in Kelvin, ΔS^0 and ΔH^0 are entropy and enthalpy respectively. The plot of $\ln K_{ads}$ versus $1/T$ gives a linear relationship, which allows the computation of ΔH and ΔS values from the slope and intercept respectively.

IV. RESULTS AND DISCUSSION

4.1. Adsorbent characterization

The FTIR spectra of BFSSP before and after adsorption (Fig. 1 & 2) of CR dye were analyzed to determine the vibration frequency changes in their functional groups. For BFSSP before adsorption, various peaks are at 3629.37 cm^{-1} (O-H stretch, free hydroxyl from alcohols and phenols), 3421.10 cm^{-1} (O-H stretch, H-bonded from alcohols and phenols), 2923.31 cm^{-1} (C-H stretch, from alkanes), 1733.85 cm^{-1} (C=O stretch from aldehydes), 1716.63 cm^{-1} (C=O stretch from ketones), 1697.42 cm^{-1} (C=O stretch from carboxylic acid), 1647.38 cm^{-1} (C=C stretch), 1541.49 cm^{-1} (N-O asymmetrical stretch in nitro compounds) 1457.59 cm^{-1} (C-C stretch in rings), 1244.14 cm^{-1} (C-N stretch in aliphatic amines), 1155.46 cm^{-1} (C-H wag in alkyl halides) 1078.74 & 1029.51 cm^{-1} (C-O stretch) and 526.76 cm^{-1} (C-X stretch alkyl halides) [21].

After adsorption of CR dye it was found out that most of the functional groups on the adsorbent were affected after the dye uptake process. This is judged from shifts in the position of some of the functional groups to lower frequency or band intensity before and after CR adsorption. The functional groups that moved to lower frequency or band intensity after CR adsorption includes: C-H, N-O, C-C (in rings), and C-O from 2923.31 cm^{-1} , 1541.49 cm^{-1} , 1457.59 cm^{-1} and 1029.51 cm^{-1} respectively to 2921.34 cm^{-1} , 1541.24 cm^{-1} , 1457.35 cm^{-1} and 1027.04 cm^{-1} respectively. The functional groups that moved to higher frequency or band intensity includes: O-H (free hydroxyl), O-H (H-bonded) and C=C from 3629.37 cm^{-1} , 3421.10 cm^{-1} and 1647.38 cm^{-1} to 3629.40 cm^{-1} , 3421.18 cm^{-1} and 1647.42 cm^{-1} respectively. This indicates involvement of these groups for CR binding to BFSSP [22].

Furthermore, Fig. 3 shows the SEM image of BFSS powder. It can be observed from Fig. 3 that the external surface of BFSS powder is very irregular with heterogeneous ridges and pores.

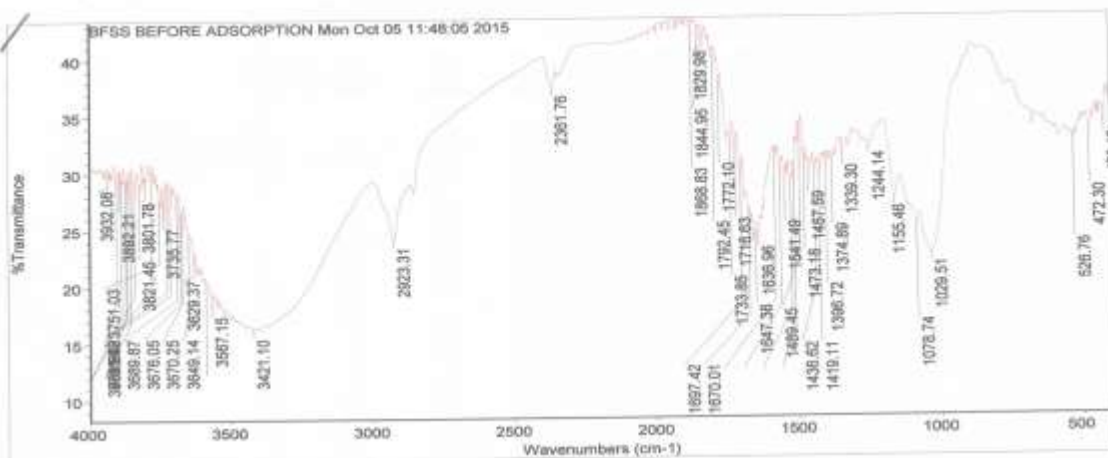


Fig. 1: FTIR Spectra of BFSSP before adsorption

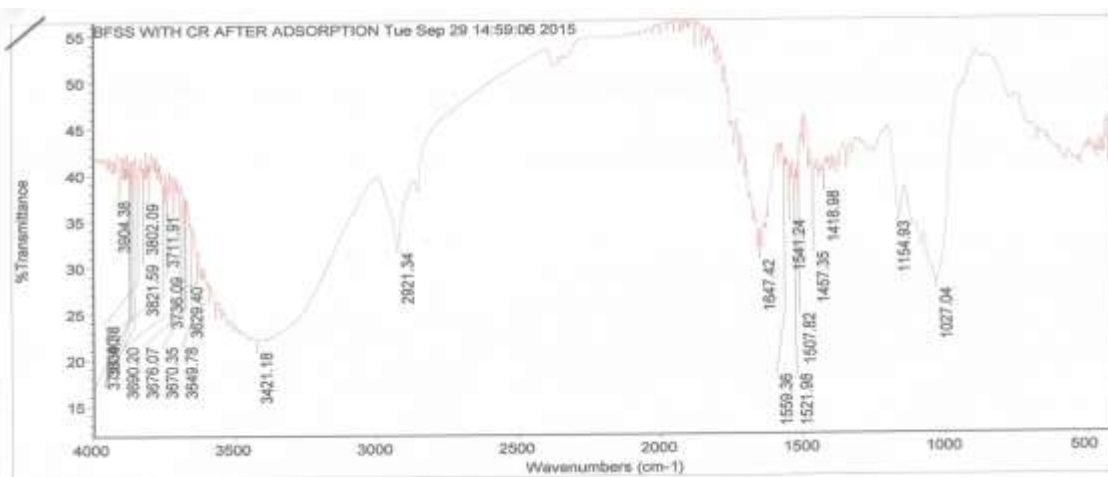


Fig. 2: FTIR Spectra of BFSSP after adsorption

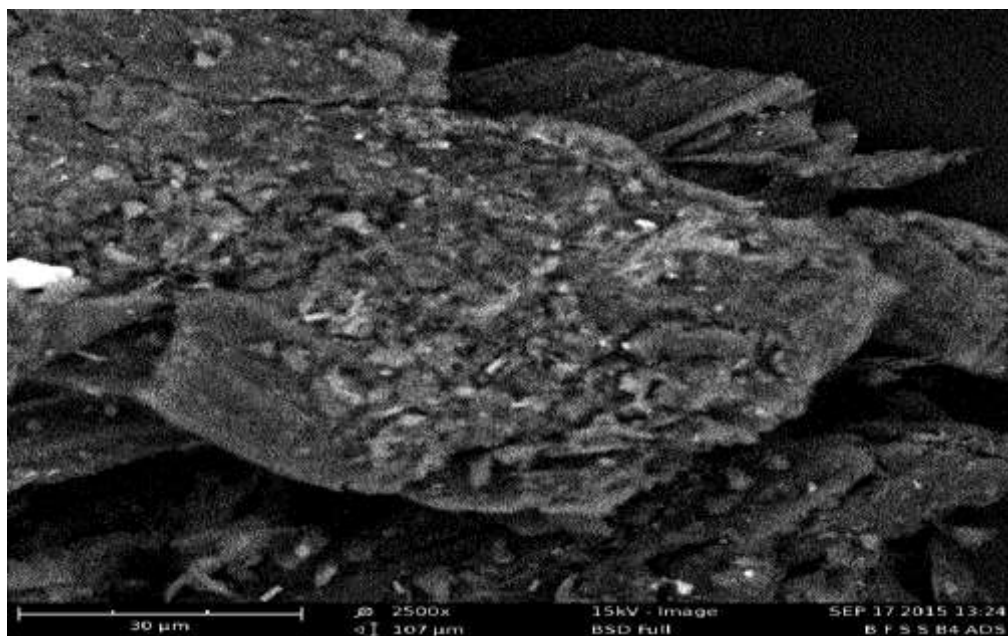


Fig. 3: SEM micrograph of BFSSP surface at magnification 2500×

4.2. Effect of Contact Time

The effect of contact time on the removal of CR dye is depicted in Fig. 4. It can be observed that there was a rapid removal in the first 10 minutes and it proceeds slowly until equilibrium time at 60 minutes. Later it decreases. Similar result has been reported for the adsorption of MB onto raw corn cobs powder [1]. It can be inferred from the rapid sorption rate at the initial stages that there were great quantity of active sites on the external surface of BFSSP which resulted in the swift CR dye removal. The slower rate of removal at the later stages can be accredited to the diffusion of the dyes into the inner part of the adsorbent since the external surface has been occupied by the molecules of the dye [2]. Once equilibrium is attained, there was no further increase since the remaining vacant sites are difficult to occupy probably due to the repulsive forces between the molecules on the adsorbents and the bulk phase [23, 24]

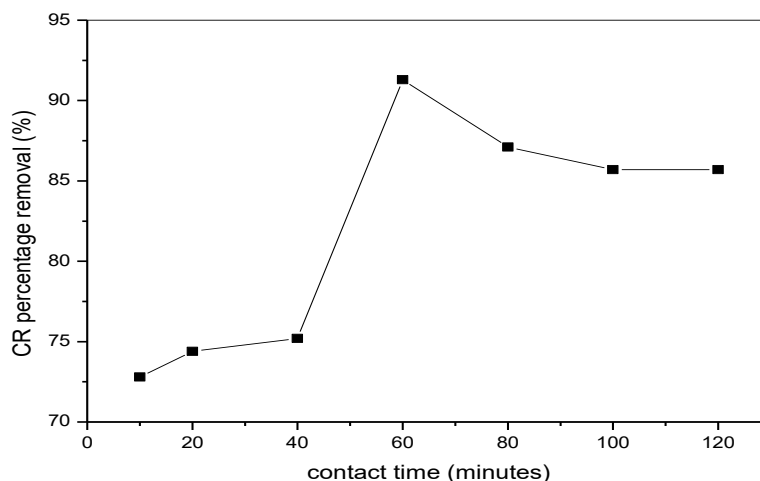


Fig. 4: Effect of contact time on percentage removal of CR dye

4.3 Effect of Adsorbent Dosage

The effect of adsorbent dosage on the percentage removal of CR dye is shown in Fig. 5. It can be observed that the percentage removal of CR dye increased with increase in adsorbent dosage. This is as a result of increase in the number of active sites on BFSSP surface with the increase in the adsorbent dosage [25]. Although the percentage removal of CR dye increased with increase of adsorbent dosage, the equilibrium adsorption capacity decreased with increase of adsorbent dosage (figure not shown). This may be due to aggregation of the adsorption sites which limits the availability of all the active sites during adsorption process [17, 26]. Similar trend has been reported for the adsorption of CR dye by Roots of *Eichhornia crassipe* [27].

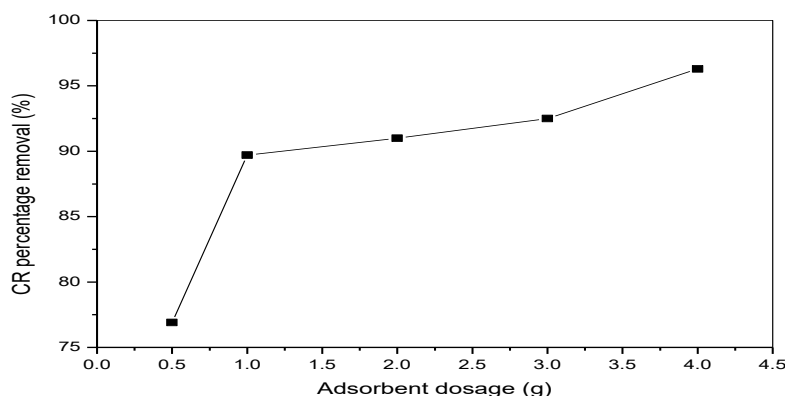


Fig.5: Effect of adsorbent dosage on percentage removal of CR dye

4.4. Effect of Initial Dye Concentration

The effect of initial CR dye concentration is depicted in Fig. 6. It can be observed that the percentage removal of CR dye increased with increase in initial concentration. This is due to the fact that with increase in dye concentration, more dye molecules are available for adsorption by the adsorbent. This is attributed to the effect of concentration gradient which is the main driving force for the adsorption process (28). Similar trend has been reported by Enenebeaku *et al.* (1). Moreover, the equilibrium adsorption capacity also increased with increase in initial dye concentration (figure not shown). This is credited to the fact that increasing dye concentration increases the driving force to overcome all mass transfer resistances of the CR between the aqueous and solid phase, leading to an increase in equilibrium adsorption capacity [15, 29].

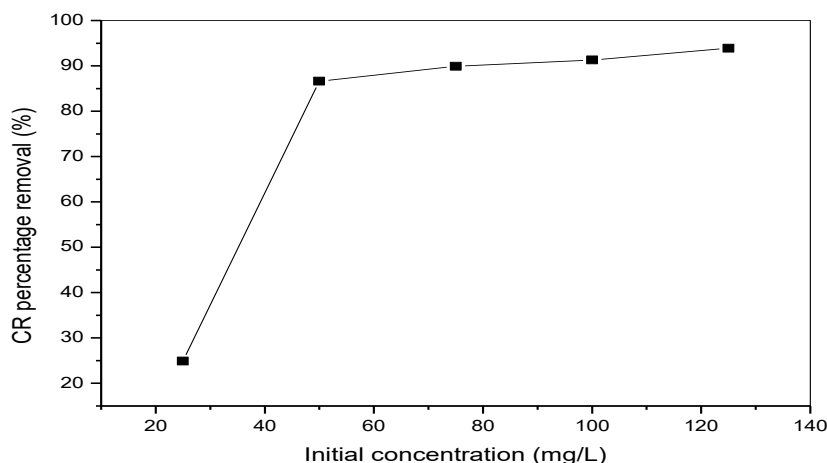


Fig. 6: Effect of initial concentration on percentage removal of CR

4.5. Effect of pH

The influence of pH on the adsorption of CR onto BFSSP is illustrated in Fig. 7. It was observed that the percentage removal and adsorption capacity of CR by BFSSP decreased as pH increased from 2 to 10. Optimum sorption was obtained at pH of 2. The decrease in percentage removal and adsorption capacity with increase in pH can be attributed to the fact that at high pH values of the solution, the presence of excess hydroxyl ion in the solution competes with the anionic groups of the CR dye for the adsorption sites on the adsorbent surface. While at low pH values, the negative charges (OH⁻) in the solution decreases and the adsorbent surface is more positively charged, thus enhancing attraction of more amounts of the anions of the CR dye [30].

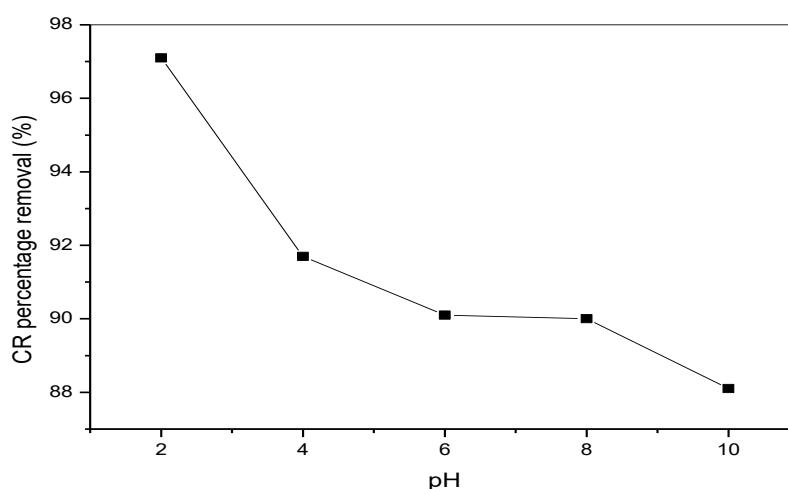


Fig.7: Effect of pH on percentage removal of CR dye

4.6. Effect of Temperature

The influence of temperature on the percentage removal of CR by BFSSP is illustrated in Fig. 8. It can be observed that increase in temperature resulted in decrease in percentage removal of CR by BFSSP. Similar observation has been reported for the adsorption of CR dye onto Ash of Cassia Fistula seeds [31]. This decrease in removal efficiency with increase in temperature can be attributed to the weakening of the physical bonding between the adsorbate (CR dye molecules) and the active sites of the adsorbent (BFSSP). In addition the CR dye solubility also increased with increase in temperature resulting in the interaction between the solute and the solvent to be stronger than that between the solute and the adsorbent. Consequently the solute was more difficult to adsorb [32, 33].

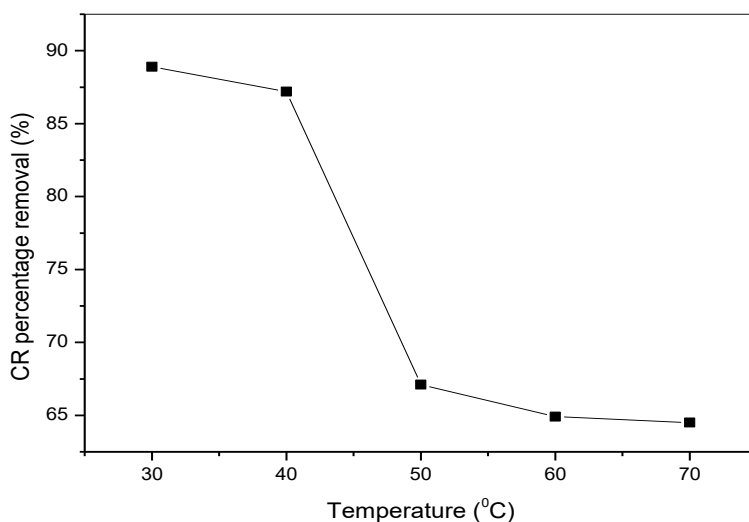


Fig.8: Effect of Temperature on percentage removal of CR dye

4.7. Adsorption Isotherms

Langmuir and Freundlich isotherm models were applied to describe the relationship between the CR dye concentration in the bulk solution and that on the BFSS powder's surface. The results are shown in Table 1.

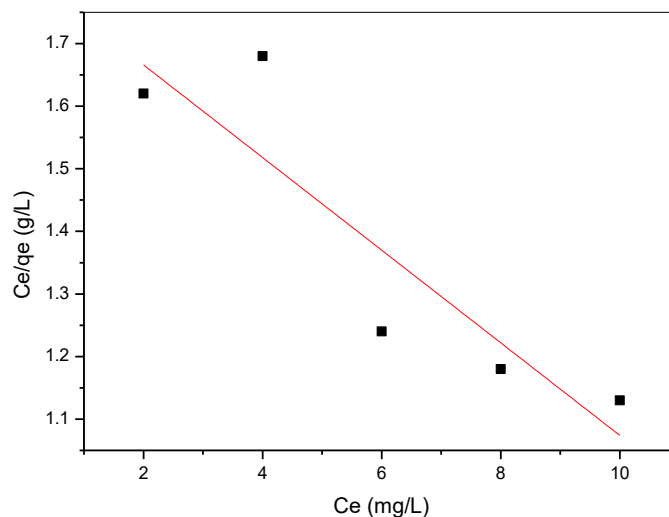


Fig. 9: Langmuir adsorption isotherm plot for CR dye onto BFSSP

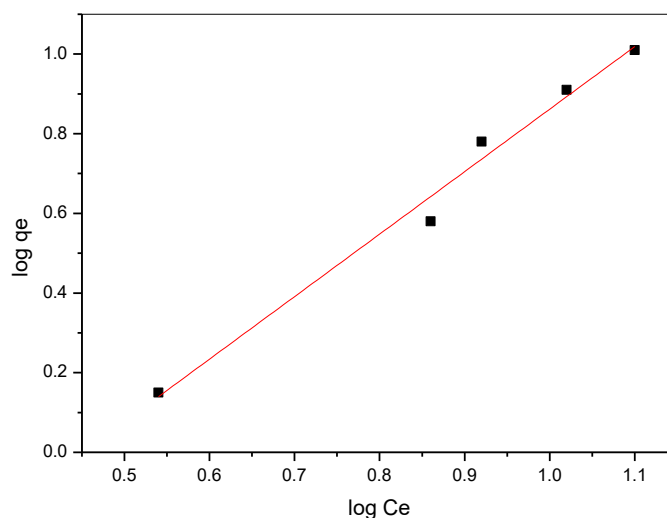


Fig. 10: Freundlich adsorption isotherm plot for CR dye onto BFSSP

Fig. 9 and 10 show the Langmuir and Freundlich model plots for the adsorption of CR onto BFSSP respectively. The isotherm parameters and R^2 values are summarized in Table 1. It is evident from the plots and the values of correlation coefficient (R^2) (Table 1) that the Langmuir isotherms plot was inadequate in describing the adsorption processes. The experimental data fitted well with the Freundlich isotherm model, hence, the Freundlich model is efficient in describing the adsorption of CR onto BFSSP and such adsorptions mainly occurred on the heterogeneous surface of the BFSS powder. In addition, Freundlich isotherm constant, n , (Table 1) was found to be less than 1 indicating that the adsorption of CR by BFSSP is a chemical process (15).

Table 1: The Isotherm Parameters and Values of Correlation Coefficient for the Adsorption of CR onto BFSS Powder

Langmuir	q_m (mg/g)	K_L	R^2
	16.00	0.04	0.600
Freundlich	K_F (mg/g)(L/mg) ^{1/n}	n	R^2
	2.527	0.694	0.958

4.8. Adsorption Kinetics

Two kinetic models i.e., pseudo-first-order and pseudo-second-order kinetic models as mentioned earlier were applied to investigate the reaction pathways and potential rate determining steps of the adsorption of CR dye onto Breadfruit seed shell powder.

The pseudo-first-order model did not provide a good fit to the experimental data as the plot of $\ln(q_e - q_t)$ versus t was non linear with low R^2 value (Fig. 11). Moreover, the theoretical and experimental equilibrium adsorption capacity q_e obtained from the plot varied widely, suggesting the inadequacy of the pseudo-first-order model for describing the adsorption kinetics of CR dye onto BFSS powder. The first-order rate constant, k_1 , the correlation coefficients, R^2 and the theoretical and experimental equilibrium adsorption capacity q_e are given in Table 2.

Furthermore, the kinetic data was best fitted to the pseudo-second-order model. The pseudo-second-order rate constant, k_2 , the initial adsorption rate, h and the theoretical and experimental equilibrium adsorption capacity are given in Table 2. The plot of t/q_t against t is depicted in Fig.12. Contrary to the pseudo-first-order model, the fitting of the kinetic data in the pseudo-second-order model showed excellent linearity with high

correlation coefficients, R^2 . In addition, there was good agreement between the calculated q_e and the experimental q_e values (i.e., the q_e values were close) indicating that the adsorption of CR dye by Bread fruit seed shell powder followed the pseudo-second-order kinetics. Hence the adsorption process is controlled by chemisorptions [16, 34]. This suggests that the forming of interaction between the adsorbate and the adsorbent on the external surface of BFSSP (film diffusion) is the rate determining step [2].

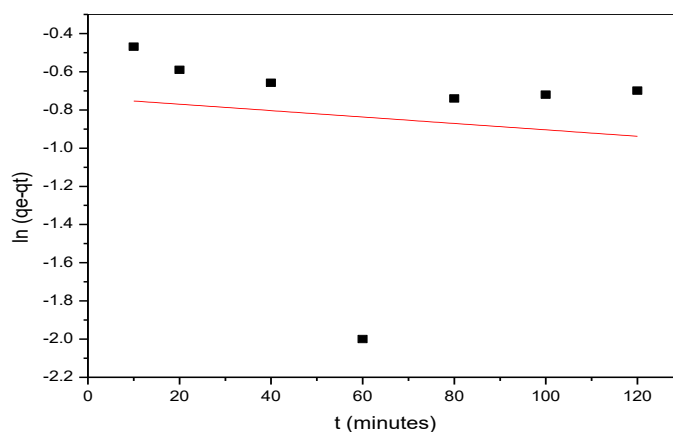


Fig. 11: Pseudo first-order plot for adsorption of CR onto BFSSP.

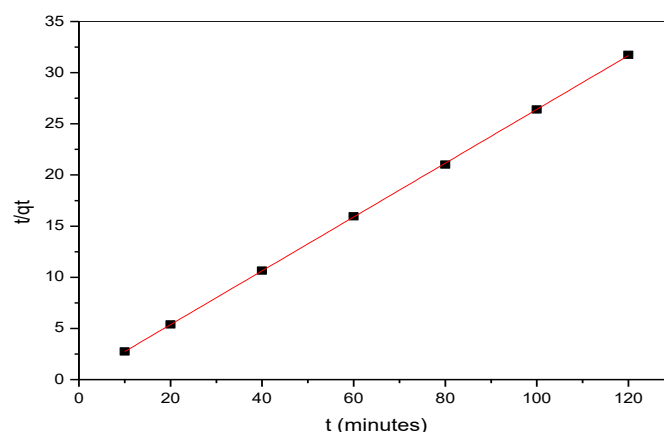


Fig. 12: Pseudo second-order plot for adsorption of CR onto BFSSP

Table 2: Pseudo-first and second order kinetic model parameters for CR adsorption

Pseudo-First Order Model				Pseudo-Second Order Model			
q_e (exp) (mg/g)	k_1 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	q_e (cal) (mg/g)	R^2	h ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$)	K_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	q_e (cal) (mg/g)	R^2
3.96	0.844	0.846	0.179	8.87	0.166	3.802	0.999

4.9. Adsorption Thermodynamics

The linear Van't Hoff equation plot for the adsorption of CR onto BFSS powder is shown in Fig. 13. Table 3, presents ΔH° and ΔS° values obtained from the Van't Hoff plot including the calculated ΔG° values.

Negative ΔG° values obtained at all temperatures (Table 3) indicated the feasibility and the spontaneous nature of CR adsorption onto BFSS powder. It was observed that the values of ΔG for the adsorption of CR onto BFSS increased with increase in temperature suggesting a rapid and more spontaneous adsorption at the lower temperature. The negative ΔH° value confirmed the exothermic nature of the adsorption process. The negative value of ΔS° revealed decreased randomness at the solid/solution interfaces [35].

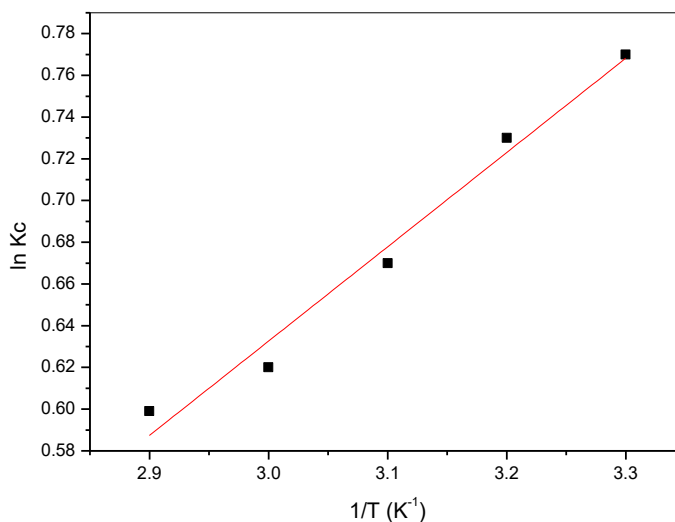


Fig. 13: Van't Hoff plot for the adsorption of CR onto BFSS powder

Table 3: Thermodynamic parameters for the adsorption of CR dye onto BFSSP

Temperature (K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol. K)
303	-1940.08		
313	-1935.12		
325	-1907.05	-23.30	-49.99
333	-1717.23		
343	-1708.34		

V. CONCLUSION

The potential of Breadfruit seed shell (BFSS) powder as an effective adsorbent for the removal of CR dye from aqueous medium has been identified. The adsorption of CR onto BFSS powder was found to be influenced by contact time, adsorbent dose, initial CR concentration, temperature and initial pH of the solution. The optimum adsorption of CR dye was found at pH 2. Maximum adsorption capacity was 16.00mg/g at 50mg/L initial CR concentration. Temperature had strong influence on the adsorption process and the maximum removal was observed at 303K. The equilibrium was attained at 60 min, after which there was no increase in CR adsorption. The kinetic studies revealed that the adsorption process followed the pseudo-second-order kinetic

model. The study on equilibrium sorption revealed that Freundlich isotherm model gave the best fit to the experimental data. The nature of adsorption of CR onto BFSS powder was chemical adsorption as inferred from Freundlich isotherm model. The calculated thermodynamic parameters indicated a spontaneous and exothermic nature of the adsorption of CR dye onto BFSS powder. The present study showed that BFSS powder can be effectively used as an inexpensive and efficient adsorbent without any modification for the treatment of dye effluents.

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