Research Article

Adsorption Kinetics for the Removal of Hazardous Dye Congo Red by Biowaste Materials as Adsorbents

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The present work aims to investigate the removal of dye congo red from aqueous solutions by two low-cost biowaste adsorbents such as ground nut shells charcoal (GNC) and eichhornia charcoal (EC) under various experimental conditions. The effect of contact time, ionic strength, temperature, pH, dye concentration, and adsorbent dose on the removal of dye was studied. The kinetic experimental data were fitted to pseudo-first order, pseudo-second order, intraparticle diffusion, Elovich model, and Bangham's model. Results imply that adsorption of congo red on these adsorbents nicely followed the second order kinetic model and maximum adsorption capacity was found to be 117.6 and 56.8 mg g⁻¹ for GNC and EC at 318 K, however it increases with increase in temperature for both adsorbents. Equilibrium isotherms were analyzed by Langmuir, Freundlich, Temkin, Dubinin and Radushkevich, and Generalized Isotherms. Freundlich isotherm described the isotherm data with high-correlation coefficients. The results of the present study substantiate that biowaste material GNC and EC are promising adsorbents for the removal of the dye congo red.

1. Introduction

Dye, a constituent that is widely used in textile, paper, plastic, food, and cosmetic industries is an easily recognized pollutant [1]. Decolourizing of textile and manufacturing waste water is currently a major problem for environmental managers [2]. Dyes may significantly affect photosynthetic activity in aquatic life due to the presence of aromatics, metals, chlorides, and so forth, in them [3]. Many of the dyes used in the industries are stable to light and oxidation, as well as resistant to aerobic digestion [4]. However, dyes usually have a synthetic origin and complex aromatic molecular structure which makes them more stable so they are not biodegradable and photodegradable, it brings some difficulties for the treatment of these pollutants [5]. Congo red (CR) (1-naphthalenesulfonic acid, 3,3'-(4,4'-biphenylene bis (azo)) bis (4-amino-) disodium salt) is a benzidine-based anionic disazo dye, this dye is known to metabolize to benzidine, a known human carcinogen [6].

Physicochemical processes are generally used to treat dyes laden waste water. These processes include flocculation, electro flotation, precipitation, electrokinetic coagulation,

ion exchange, membrane filtration, electrochemical destruction, irradiation, and ozonation. However, all these processes are costly and cannot be used by small industries to treat wide range of dye waste water [7]. The adsorption process provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pretreatment step before its application [8]. Adsorption is known to be a better technique, which has great importance due to the ease of operation and comparable low cost of application in decoloration process [9].

Activated carbon is the most widely used adsorbent with great success due to its large surface area, microporous structure, and high-adsorption capacity. However, its use is limited because of its high cost. This has led to search for cheaper substitutes [10]. Investigators have studied the feasibility of using low-cost substances, such as waste apricot [11], coconut shell [12], dairy sludge [13], bamboo grass treated with concentrated sulfuric acid [14], peat [15], orange peels [16], pea nut hulls [17], rice husk [18], ground nut shells charcoal and bagasse [19], bamboo [20], jack fruit peels [21], pistachio nut shells [22], and date stone and palm tree waste [23] as adsorbents for the removal of dyes and heavy

metals from waste water. The purpose of present work is to study the mechanism of adsorption of congo red on ground nut shells charcoal (GNC) and eichhornia charcoal (EC). Eichhornia crassipes is one of the worst weeds in the world. Its vigorous grower is known to double their population within two weeks. Large, dense Eichhornia crassipes mat can degrade water quality and can choke water ways. The kinetics, equilibrium, and thermodynamic parameters are studied to describe the rate and mechanism of adsorption to determine the factor controlling the rate of adsorption and to find out the possibility of using these biomaterials as low-cost adsorbents for the removal of dye CR. The effect of solution concentration, adsorbent dose, ionic strength, temperature, and pH on CR adsorption has been evaluated.

2. Experimental

2.1. Materials and Methods

2.1.1. Adsorbents. Groundnut shells was used as an adsorbent, was collectively obtained from the local shop, Amritsar (India) washed with tap water and finally with double distilled water to remove the suspended impurities, dust, and soil and then dried in oven. Eichhornia was collected from pond at Ram Tirath Road, Amritsar. Charcoal of both the materials was prepared in a very economical way, that is, by burning in the absence of free excess of air and then charcoal was sieved through sieves to remove coarse particles.

2.1.2. Dye Solution Preparation. The dye congo red (C.I name = Direct Red 28, C.I No. = 22120, Chemical formula = $C_{32}H_{22}N_6O_6S_2Na_2$, Formula weight = 696.65) is supplied by S.D fine Chemicals, Mumbai, India, was used as such without further purification. An accurately weighed quantity of dye was dissolved in double distilled water to prepare the stock solution (65 mg L^{-1}). Serial dilutions were made by diluting it with double distilled water.

2.1.3. Adsorption Experiments. Adsorption experiments were carried out by agitating 100 mg of adsorbent with 100 mL of dye solution, of the desired concentration and pH, at different temperatures (308, 313, and 318 K) in a thermostated metrex water bath shaker with a shaking of 120 rpm. The samples were withdrawn from the shaker at predetermined time intervals and dye solutions were separated from the adsorbent using whatman filter paper. The absorbance of supernatant solution was measured spectrophotometrically by monitoring the absorbance at 497 nm using a UV-vis spectrophotometer (1800, Shimadzu, Japan). Effect of pH was studied by adjusting the pH of dye solutions (2.0, 4.0, 6.0, 8.0, 10.0, and 12.0) using 0.1 N HCl and 0.1 N NaOH solutions. Batch equilibrium adsorption experiments were carried out by shaking 100 mL solution of various dye concentrations at pH 7.0 with 100 mg of adsorbents at 308, 313, and 318 K, respectively.

The amount of dye adsorbed by the adsorbent was calculated using the following equation:

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

where C_o and C_e (mg L^{-1}) are the concentrations of dye before and after adsorption.

The pH of zero point charge (pH_{zpc}) plays an important role in the adsorption process. The pH_{zpc} of GNC and EC was determined by the method reported by Rivera-Utrilla et al. 2001 [24]. For this purpose, 50 mL of a 0.01 M sodium chloride (NaCl) solution was placed in a 100 mL erlenmeyer flask. The pH was then adjusted to successive initial values between 2 and 12, by using either sodium hydroxide or hydrogen chloride (0.1 N), and 0.15 g of adsorbents (GNC or EC) were added to the solution. After a contact time of 24 h, the final pH was measured and plotted against the initial pH. The pH at which the curve crosses the line $\text{pH}(\text{final}) = \text{pH}(\text{initial})$ is taken as the pH_{zpc} .

3. Results and Discussion

3.1. FTIR Analysis. Measurements were carried out by means of a Varian Resolutions Pro-FTIR spectrometer. One centimeter diameter and constant-weight KBr pellets were prepared by mixing the samples with KBr at 1:5 ratio. The spectra were measured in the wave number range of $400\text{--}4000 \text{ cm}^{-1}$. Figures 1(a) and 1(b) shows the FTIR spectra of dye, adsorbent and dye loaded adsorbents. The band at 1366 cm^{-1} shows the asymmetric stretch of S=O. The peak values from $1350\text{--}1000 \text{ cm}^{-1}$ may be due to C-N bond of amine. The value 1615 cm^{-1} can be assigned to bending vibration of primary amine.

FTIR spectra of CR + GNC and CR + EC shows that peaks in the low frequency region ($<1000 \text{ cm}^{-1}$) which are present in the dye alone and are not observed in the dye loaded adsorbents because of the adsorption of dye CR on the adsorbent surface. Decreased intensity of sharp peaks concluded that dye has been functionalized by both the adsorbents.

3.2. Scanning Electronic Micrographic Studies (SEM). SEM is widely used to study the morphological features and surface characteristics of the adsorbent material. It also reveals the surface texture and porosity of adsorbent. Figure 2 shows that the surface of the adsorbent GNC and EC become smooth due to adsorption of congo red. It also plays an important role in determining the surface availability for the adsorption of dye on adsorbents.

3.3. X-Ray Diffraction Studies. The X-ray diffraction pattern was recorded in the scanning mode on an XRD 7000 (Shimadzu, Japan) analytical instrument operated at 40 KV and a current of 30 mA with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). X-ray diffraction (XRD) technique is a powerful technique to analyze the crystalline and amorphous nature of the material under investigation. In crystalline material, well defined

FIGURE 1: (a) FTIR spectra of GNC, CR, and dye loaded GNC. (b) FTIR spectra of EC, CR, and dye loaded EC.

peaks are observed whereas in noncrystalline or amorphous material shows broad peaks instead of sharp peaks. Figures 3(a) and 3(b) shows that well-defined peaks are observed for the adsorbent EC as compare to GNC which indicates that EC is more crystalline as compare to GNC. When the adsorbent get loaded by the dye molecules the crystalline nature of the dye changed into amorphous nature. It has been concluded that the dye molecules diffused into the micro- and macropores of the adsorbent molecules. XRD study reveals the change in crystallinity of the dye and adsorbent due to adsorption.

XRD crystallite size is calculated using Scherrer formula [25]

$$D = K \frac{\lambda}{\beta} \cos \theta, \quad (2)$$

where K is the shape factor, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle. The dimensionless shape factor, K , has a typical value of about 0.9, but varies with the actual shape of the crystallite. Peak width is inversely proportional to crystalline size, results show that as crystalline size get smaller, peak get broader. Peak intensity is usually weakest at large angle 2θ . Particle size at maximum

intensity was found to be 42.4 and 13.4 nm for EC and GNC, respectively. Similar method was adopted by Prema et al. 2011 [26] to calculate the average size of the particles.

3.4. Effect of Contact Time. Figure 4 illustrates the effect of contact time on the adsorption of dye CR at different temperatures using different adsorbents. It is indicated that uptake of the dye is rapid in the beginning and then it becomes constant. The adsorption curves are single, smooth, and continuous leading to saturation and indicate the possible monolayer coverage on the surface of adsorbents by the dye molecules [27]. The equilibrium time for EC is 90, 60, and 40 minutes and for GNC is 80, 60, and 30 minutes at 308, 313, and 318 K, respectively.

3.5. Effect of pH. The percentage of dye adsorption at different pH is shown in Figure 5. The initial pH of dye solution plays an important role particularly on the adsorption capacity by influencing the chemistry of both dye molecule and adsorbents (GNC and EC) in aqueous solutions. The color of CR in aqueous solution is solid red at pH around 7. The color of CR changes to dark blue at acid pH and to red at alkaline pH (10–12), but this red color is slightly different from original red at the neutral pH. CR exists as an anionic

FIGURE 2: Scanning electron microscope (SEM) images of ground nut shell (GNC) (a) before adsorption, (b) after adsorption; Eichhornia charcoal (EC), (c) before adsorption, (d) after adsorption.

form at basic pH (sulfonate groups) and as a cationic form at acid pH. The zero point charge (pH_{zpc}) of GNC and EC was determined [24]. Adsorption of cation is favored at $pH > pH_{zpc}$, while the adsorption of anion is favored at $pH < pH_{zpc}$ [28]. The pH_{zpc} value for GNC and EC was found to be 9.1 and 7.8, respectively. As illustrated in the Figure 5, when pH value of dye solution increased from 2 to 12, the percentage of dye adsorption sharply reduced from 94 to 73% in case of GNC and 75 to 51% in case of EC. At pH 2.0 a significantly high-electrostatic attraction exists between the positively charged surface of the adsorbent and anionic dye. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent does not favor the adsorption of dye anions due to the electrostatic repulsion. Also, lower adsorption of CR at alkaline pH is due to the presence of excess OH^- ions competing with the dye anions for the adsorption sites. Nevertheless, significant adsorption of anionic dye on the adsorbent still occurred above pH_{zpc} due to the fact that a chemical interaction between the dye and GNC and EC, respectively. Similar results have been reported for the adsorption of CR on waste orange peel [29] and activated carbon [30].

3.6. Effect of Temperatures. The sorption experiments were reported at three temperatures ranging 308, 313, and 318 K for GNC and EC. Figure 4 shows that percentage colour removal increases with increase in temperature implying that high temperature favors for the removal of CR from aqueous solutions. Increase in temperature decreases the solubility of dye and hence adsorption increases. Increased adsorption may also be as a result of increase in the mobility of the large dye ion with temperature. An increasing number of molecules may acquire sufficient energy to undergo an interaction with active site at the surface [31]. Therefore increase in sorptive uptake of CR with increase in temperature may be partly attributed to chemisorptions.

3.7. Effect of Adsorbent Dose. The effect of adsorbent dose on the removal of congo red by GNC and EC at initial concentration ($C_0 = 65 \text{ mg L}^{-1}$) is illustrated in Figure 6. Results describe that CR removal increases upto a certain limit and then it remains almost constant. With increase in the adsorbent dose from 0.1 to 1.2 g, dye uptake increases from 83–95% and 60–82% for GNC and EC, respectively. Increase in adsorption with adsorbent dosage can be attributed to increased adsorbent surface area and availability of more adsorption sites.

FIGURE 3: (a) XRD spectra of GNC, CR, and dye loaded GNC. (b) XRD spectra of EC, CR, and dye loaded EC.

3.8. Effect of Ionic Strength. Different concentrations of KCl and NaCl (0.01–0.05 M) were added to investigate the effect of ionic strength on adsorptive removal of CR. Figure 7 narrates that increase in ionic strength causes increase in the adsorption of congo red. Salt addition increases the aggregation of dye molecules and decreases the solubility. An increase in aggregation promotes the adsorption of dye molecules [32]. Another plausibility is that increase in ionic strength increases the positive charge of the adsorbent surface thus increases the electrostatic attraction between dye (CR) and adsorbent. Thus increase in ionic strength was found to have an increase in adsorption of CR.

3.9. Effect of Initial Concentration. The effect of initial concentration on the removal of CR by both the adsorbents is indicated in Figure 8. Experiment was done at constant adsorbent dose 1 g L^{-1} . It is evident from the figure that percentage CR removal decreases with increase in CR concentration, however actual amount of the dye adsorbed (q_t) is increased. This is due to increase in CR concentration, surface area,

and active sites of the adsorbent were saturated and hence percentage removal decreases.

3.10. Adsorption Kinetic Study

3.10.1. Pseudo-First Order and Pseudo-Second Order Models. The pseudo-first-order equation is given as [33]

$$\frac{dq_t}{dt} = k_f (q_e - q_t), \quad (3)$$

where q_t (mg g^{-1}) is the amount of dye adsorbed at time t . q_e (mg g^{-1}) is the adsorption capacity at equilibrium, k_f (min^{-1}) is the pseudo first order rate constant, and t is the contact time (min). The integration of (3) with initial condition ($q_t = 0$ at $t = 0$) leads to following equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303} t. \quad (4)$$

(a)

(b)

FIGURE 4: The effect of contact time on the adsorption of congo red by GNC and EC at different temperatures (sorbert dose = 1 g L^{-1} , $C_o = 65 \text{ mg L}^{-1}$, $\text{pH} = 7.0$).

The values of k_f , calculated from the linear plots of $\log(q_e - q_t)$ versus t , for the adsorption of dye CR on both the adsorbents are given in Table 1. These plots are linear, however linearity of these curves does not necessarily assure first order mechanism [34] due mainly to the inherent disadvantage of correctly estimating equilibrium adsorption capacity (q_e). The q_e values obtained from Lagergren plots are different from the experimental q_e values, therefore first order kinetic is less likely to explain the rate processes.

The pseudo-second order model is represented as [35]:

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2, \quad (5)$$

where k_s is the pseudo-second order rate constant ($\text{g mg}^{-1} \text{ min}^{-1}$). Integrating (5) and noting that $q_t = 0$ at $t = 0$, the following equation is obtained

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

The equilibrium adsorption capacity, q_e is obtained from the slope and k_s is obtained from the intercept of linear plot

FIGURE 5: Effect of pH values on the adsorption of congo red by GNC and EC (sorbert dose = 1 g L^{-1} , $C_o = 65 \text{ mg L}^{-1}$).

FIGURE 6: Effect of adsorbent dose on adsorption of congo red onto GNC and EC ($C_o = 65 \text{ mg L}^{-1}$, $\text{pH} = 7.0$).

of t/q_t versus t . The values are furnished in Table 1. The q_e experimental and the q_e calculated values from the pseudo second-order kinetic model are very close to each other. The calculated correlation coefficients are also close to unity ($R^2 = 0.99$) for pseudo-second order kinetic than that for the pseudo-first order kinetic model. Therefore, the sorption can be approximated more appropriately by pseudo-second order kinetic model than the first-order kinetic model for both the biosorbents.

3.10.2. Intraparticle Diffusion Study. An empirically found functional relationship common to most adsorption process is that the uptake varies almost proportionally with $t_{1/2}$, the Weber-Morris plot (q_t versus $t_{1/2}$), rather than with the contact time, t [36]:

$$q_t = k_{id} t_{1/2} + C, \quad (7)$$

where k_{id} is the intraparticle diffusion rate constant. Values of the intercept (C) gives an idea about the thickness of boundary layer, that is, larger the intercept the greater is the

TABLE 1: Kinetic parameters for the adsorption of congo red by GNC and EC at different temperatures.

Equations	Parameters	Adsorbents					
		308 K	313 K	318 K	308 K	313 K	318 K
Pseudo-first order	$q_e \text{exp (mg g}^{-1}\text{)}$	51.30	53.02	54.20	35.85	37.98	41.38
	$q_e \text{cal (mg g}^{-1}\text{)}$	6.33	6.09	7.69	17.01	13.25	12.99
	$k_f \text{ (min}^{-1}\text{)}$	0.083	0.081	0.059	0.058	0.064	0.065
	R^2	0.98	0.99	0.97	0.99	0.88	0.98
Pseudo-second order	$q_e \text{exp (mg g}^{-1}\text{)}$	51.30	53.02	54.20	35.85	37.98	41.38
	$q_e \text{cal (mg g}^{-1}\text{)}$	51.81	53.44	55.86	37.05	39.65	42.97
	$k_s \text{ (g/mg min)}$	0.035	0.034	0.020	0.012	0.008	0.011
	R^2	0.99	0.99	0.99	0.99	0.99	0.99
Intraparticle diffusion	$k_{id} \text{ (mg/g min}^{1/2}\text{)}$	1.06	0.937	1.03	1.79	1.59	2.42
	$C \text{ (mg g}^{-1}\text{)}$	44.98	47.07	47.94	22.87	26.81	26.80
	R^2	0.95	0.91	0.99	0.95	0.98	0.99
Bangham	$k_o \text{ (g)}$	115.6	123.5	129.1	39.59	48.84	51.84
	A	0.07	0.08	0.09	0.17	0.14	0.17
	R^2	0.98	0.96	0.96	0.98	0.97	0.98
Elovich	$a \text{ (mg/g min)}$	1.15×10^{10}	5.47×10^{10}	3.29×10^{11}	8.69×10^2	4.88×10^3	2.11×10^3
	$b \text{ (g mg}^{-1}\text{)}$	0.509	0.524	0.525	0.264	0.298	0.242
	R^2	0.98	0.96	0.96	0.98	0.96	0.99

FIGURE 7: Effect of ionic strength on sorption of congo red by GNC and EC (sorbent dose = 1 g L⁻¹, C₀ = 65 mg L⁻¹, pH = 7.0).

boundary layer effect [37]. This is attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. The values of k_{id} and C obtained from the slope and intercept of linear plots are listed in Table 1.

3.10.3. Elovich Model. The most interesting model to describe the activated chemisorptions is Elovich equation [38]:

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t, \quad (8)$$

where a and b are constants. The constant a is considered as the initial sorption rate (mg/(g min)) and b is related

to the extent of surface coverage and activation energy for chemisorption (g mg^{-1}) and q_t (mg g^{-1}) is the amount of dye adsorbed at time t (min). The values of a and b obtained from the linear plots of q_t versus $\ln t$, are comprised in Table 1.

3.10.4. Bangham's Equation. Kinetic data were further used to know about the slow step occurring in the present adsorption system using Bangham's equation [39]:

$$\text{Log log} \left(\frac{C_0}{C_0 - q_t m} \right) = \text{log} \left(\frac{k_o m}{2.303V} \right) + \alpha \text{log } t, \quad (9)$$

where C_0 is the initial concentration of dye in solution (mg L^{-1}). V is the volume of the solution (mL), m is

FIGURE 8: Effect of initial concentration of dye congo red on colour removal by GNC and EC. (sorbet dose = 1 g L^{-1} , $C_o = 65 \text{ mg L}^{-1}$, pH = 7) at different temperatures.

the weight of adsorbent per liter of solution (g L^{-1}), q_t (mg g^{-1}) is amount of dye adsorbed at time t , and $\alpha (<1)$ and k_o are constants and are accommodated in Table 1. Linear plot ($\text{Log log } (C_o/C_o - q_t m)$ versus $\text{log } t$) demonstrated that the diffusion of adsorbate into pores of adsorbents is not the only rate controlling step [40].

3.11. Adsorption Isotherm. To describe the equilibrium nature of adsorption various isotherm equations have been used such as Langmuir, Freundlich, Dubinin and Radushkevich, Temkin equations, and Genralized Isotherm.

3.11.1. Freundlich Isotherm. This isotherm is an empirical equation employed to describe heterogeneous system. Freundlich isotherm is also applied to plot the equilibrium data of the adsorption. The linear form of Freundlich equation can be expressed as [41]:

$$\log \frac{x}{m} = \log K_F + \frac{1}{n} \log C_e, \quad (10)$$

where x is the amount of dye adsorbed (mg), m is the weight of the adsorbent used (g), and C_e is the equilibrium concentration of the dye in solution (mg L^{-1}). K_F and $1/n$ are Freundlich constant. $1/n$ is heterogeneity factor and K_F indicates the adsorption capacity. The value of $n > 1$, reflecting the favorable adsorption. The values of n and K_F are calculated from the slopes and intercepts of the linear plots of $\log (x/m)$ versus $\log C_e$ and are given in Table 2. Adsorption capacity increases with increase in temperature.

3.11.2. Langmuir Isotherms. The Langmuir isotherm model is valid for monolayer adsorption onto a surface containing a

finite number of identical sites. The linear form of Langmuir Isotherm is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{C_m} + \frac{1}{K_L C_m}, \quad (11)$$

where C_e is the concentration of dye solution (mg L^{-1}) at equilibrium and q_e (mg g^{-1}) is the adsorption capacity at equilibrium. The constant C_m signifies the adsorption capacity (mg g^{-1}) when monolayer is complete and K_L is related to the affinity of the binding sites. The values of K_L and C_m (monolayer concentration) were calculated from the intercept and slope of the plots (C_e/q_e versus C_e) are included in Table 2. Monolayer concentration increases with increase in temperature.

The essential feature of the Langmuir isotherm to identify the feasibility and favorability of the adsorption process can be expressed by a dimensionless constant called separation factor (R_L) was adopted. The separation factor (R_L) was calculated in each case using the following equation:

$$R_L = \frac{1}{(1 + K_L C_o)}, \quad (12)$$

where C_o is the initial dye concentration (mg L^{-1}). The value of R_L lies between 0 and 1 for favorable adsorption, while $R_L > 1$ represent unfavorable adsorption, and $R_L = 1$ represent linear adsorption while the adsorption process is irreversible if $R_L = 0$ [42]. The values of " R_L " were found to be less than unity for the studied adsorbents and are contained in Table 4, states highly favorable adsorption for the dye congo red on studied biosorbents.

3.11.3. Temkin Isotherm. The Temkin isotherm equation suggests a linear decrease of sorption energy as the degree

TABLE 2: Isotherm parameters for the removal of congo red by GNC and EC at different temperatures.

Equations	Parameters	Adsorbents					
		308 K	313 K	318K	308 K	313 K	318 K
Freundlich	$K_F (\text{mg/g})(\text{L/mg})^{1/n}$	9.44	10.36	12.02	6.38	7.70	9.82
	N	1.56	1.58	1.57	2.23	2.25	2.28
	R_2	0.99	0.99	0.96	0.98	0.98	0.99
Langmuir	$K_L (\text{L mg}^{-1})$	0.064	0.067	0.078	0.059	0.071	0.088
	$C_m (\text{mg g}^{-1})$	106.38	112.35	117.64	45.24	49.75	56.81
	R^2	0.98	0.96	0.99	0.97	0.98	0.99
Dubinin Radushkevich	$q_s (\text{mg g}^{-1})$	51.26	55.25	60.78	30.29	33.58	39.36
	$E (\text{KJ mol}^{-1})$	0.380	0.381	0.412	0.223	0.250	0.294
	R^2	0.96	0.97	0.99	0.91	0.94	0.96
Temkin	$K_T (\text{L mg}^{-1})$	0.574	0.584	0.676	0.475	0.571	0.705
	B_1	23.73	25.36	26.97	10.93	12.00	13.75
	R^2	0.98	0.99	0.99	0.98	0.98	0.99
Generalized	N	0.97	0.99	1.00	0.98	0.98	0.99
	$K_G (\text{mg L}^{-1})$	15.32	14.75	16.24	16.00	13.42	11.01
	R^2	0.98	0.99	0.99	0.96	0.98	0.99

of completion of the sorptional centres of an adsorbent is increased. This model takes into account the presence of indirect adsorbate/adsorbent interactions and suggests that because of these interactions the heat of adsorption of all molecules in the layer would decrease linearly with coverage [43]. The Temkin isotherm has generally been applied in the following form:

$$q_e = B_1 \ln K_T + B_1 \ln C_e. \quad (13)$$

The constant K_T and B_1 can be calculated using a linear plot of q_e versus $\ln C_e$. K_T is the equilibrium binding constant (L mg^{-1}) corresponding to maximum binding energy and the value increased with increase in temperature for both the adsorbents suggestive of the corresponding increase of maximum binding energy and constant B_1 is related to heat of adsorption. The values of the constants are presented in Table 2.

3.11.4. Dubinin and Radushkevich (D-R) Isotherm. D-R isotherm is generally used to describe the sorption isotherms of single solute system. The D-R isotherm, apart from being analogue of Langmuir isotherm, is more general than Langmuir isotherm as it rejects the homogenous surface or constant adsorption potential [44]. It is expressed as

$$\ln q_e = \ln q_s - B\epsilon^2, \quad (14)$$

where q_e is D-R constant and ϵ can be correlated as

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right), \quad (15)$$

where q_s is the maximum amount of adsorbate that can be adsorbed on adsorbent, B is the constant related to energy, and C_e is the equilibrium concentration (mg L^{-1}). R is Universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, T is the temperature

(K). The mean free energy E of the adsorption per molecule of adsorbate can be calculated using the following equation:

$$E = \frac{1}{(2B)^{1/2}}. \quad (16)$$

The calculated D-R constant are given in provided 2. It is clear that adsorption energy value is more for congo red on ground nut shells charcoal as compare to EC.

3.11.5. Generalized Isotherm. The Generalized Isotherm has been used in the following form [45]:

$$\ln \left[\left(\frac{q_{\max}}{q_e} \right) - 1 \right] = \ln K_G - N \ln C_e, \quad (17)$$

where K_G is the saturation constant (mg L^{-1}), N is the cooperative binding constant, $q_{\max}$ is the maximum adsorption capacity of the adsorbent (mg g^{-1}). q_e (mg g^{-1}), and C_e (mg L^{-1}) are the equilibrium dye concentrations in the solid and liquid phase, respectively. The values of N and K_G are calculated from the slope and intercept of the plots and these values are produced in Table 2.

3.12. Error Analysis. Due to the inherent bias resulting from linearization, five different error functions of nonlinear regression basin were employed in this study to find out the best-fit isotherm model to the experimental equilibrium data.

The Sum of the Squares of the Errors (SSE). This error function, SSE, is given as

$$\text{SSE} = \sum_{i=1}^n (q_{e,\text{calc}} - q_{e,\text{exp}})_i^2. \quad (18)$$

Here, $q_{e,\text{cal}}$ and $q_{e,\text{exp}}$ are, respectively, the calculated and the experimental value of the equilibrium adsorbate solid

TABLE 3: Isotherm error analysis for adsorption of congo red by GNC and EC at different temperatures.

		SSE			SAE			ARE			HYBRID		
GNC													
Temp.	308 K	313 K	318 K	308 K	313 K	318 K	308 K	313 K	318 K	308 K	313 K	318 K	
Langmuir	7.11	3.21	8.79	6.07	4.70	6.51	1.94	1.49	1.98	0.06	0.48	−1.44	
Freundlich	4.34	2.02	12.89	4.97	3.50	7.91	1.53	1.11	2.37	−0.03	−0.12	−2.56	
Temkin	10.35	4.76	8.62	7.34	5.39	6.42	2.37	1.71	1.91	0.006	0.006	−2.64	
D-R	36.65	19.41	6.36	12.74	9.51	6.29	4.05	2.98	1.89	0.265	0.15	0.20	
EC													
Temp.	308 K	313 K	318 K	308 K	313 K	318 K	308 K	313 K	318 K	308 K	313 K	318 K	
Langmuir	1.85	3.87	0.72	3.29	3.23	0.39	1.62	1.57	0.19	0.03	0.07	−0.25	
Freundlich	1.34	2.53	0.45	2.83	3.52	1.42	1.38	1.67	0.56	0.01	−6.43	−24.64	
Temkin	1.80	4.59	31.15	3.17	4.95	15.23	1.56	2.42	6.79	1.44	−16.23	−46.59	
D-R	4.92	12.33	6.97	4.57	8.42	5.81	2.24	4.00	2.55	−32.25	−37.30	9.53	

TABLE 4: Thermodynamic parameters and R_L values for the adsorption of congo red on GNC and EC at different temperatures.

Adsorbents	Temp. (K)	R_L values	$-\Delta G$ (KJ mol ⁻¹)	ΔH (KJ mol ⁻¹)	ΔS (JK ⁻¹ mol ⁻¹)	R^2
GNC	308	0.20	27.41	16.06	141.0	0.98
	313	0.19	27.97			
	318	0.17	28.82			
EC	308	0.22	27.23	32.53	194.0	0.99
	313	0.19	28.15			
	318	0.16	29.17			

concentration in the solid phase (mg g⁻¹) and n is the number of data points. This is the most commonly used error function [46].

The Sum of the Absolute Errors (SAE). SAE is given as

$$SAE = \sum_{i=1}^n \left(|q_{e,calc} - q_{e,exp}| \right)_i. \quad (19)$$

Isotherm parameters determined using the sum of the absolute errors (SAE) method provides a better fit as the magnitude of the errors increases, biasing the fit towards the high-concentration data [46].

The Average Relative Error (ARE). ARE is given as

$$ARE = \frac{100}{n} \sum_{i=1}^n \left| \frac{q_{e,calc} - q_{e,exp}}{q_{e,exp}} \right|_i. \quad (20)$$

The average relative error (ARE) function attempts to minimize the fractional error distribution across the entire concentration range [47].

The Hybrid Fractional Error Function (HYBRID). HYBRID is given as

$$HYBRID = \frac{100}{n-p} \sum_{i=1}^n \left[\frac{q_{e,calc} - q_{e,exp}}{q_{e,exp}} \right]_i. \quad (21)$$

This error function was developed [48] to improve the fit of the ARE method at low-concentration values. Instead of n as used in ARE, the sum of the fractional errors is divided by $(n-p)$, where p is the number of parameters in the isotherm equation.

Table 3 shows that Freundlich model best fits the removal of dye congo red by GNC and EC at 308 K, 313 K, and 318 K. Results also reveal that the error functions are less in case of EC as compare to GNC.

3.13. Thermodynamic Properties. The adsorption isotherm data obtained at different temperatures were used to calculate important thermodynamic parameters such as changes in Gibbs free energy ΔG , enthalpy change ΔH , and entropy change ΔS . The Langmuir constant, K_L (L mole⁻¹) was used to calculate changes in Gibbs free energy according to the following equations:

$$\Delta G = -RT \ln K_L, \quad (22)$$

$$\Delta G = \Delta H - T\Delta S.$$

From (22), we get

$$\ln K_L = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}. \quad (23)$$

The plot of $\ln K_L$ versus $1/T$ was found to be linear and ΔH and ΔS values were calculated from the slope and intercept of the plot by linear regression method and are listed in Table 4. The positive values of ΔH for GNC and EC suggest that adsorption process is endothermic in nature and increase of temperature activates the adsorption sites. The positive value of ΔS indicates increase in the randomness in the system [49]. The negative values of ΔG indicate the feasibility and spontaneity of the adsorption process. The ΔG value becomes more negative with increasing temperature supports that CR adsorption on GNC and EC is favored with the increase in temperature.

4. Conclusion

- (i) The adsorption of dye CR was examined at different experimental conditions. The results corroborate that adsorption increases with increase in temperatures, adsorbent dose, ionic strength, and contact time.
- (ii) The maximum removal of dye CR at 318 K was found to be 83 and 60 % for GNC and EC, respectively.
- (iii) Scanning electron microscope (SEM) study shows that the macro-pores on the surface of adsorbents are filled up by dye molecules after adsorption. It is also alluded in FTIR analysis that dye is loaded on the adsorbent surface.
- (iv) Particle size of adsorbent materials was calculated from XRD studies and was found to be 42.4 and 13.4 nm at maximum intensity for EC and GNC, respectively.
- (v) Kinetics study shows the adsorption reaction follows pseudo-second order kinetic model ($R^2 = 0.99$). The equilibrium data were found to be well represented by Freundlich isotherm which shows that the surface is heterogeneous in nature. It is also strengthened by error analysis.
- (vi) The maximum adsorption capacity increases with increase in temperature and was found to be 117.6 and 56.8 mg g⁻¹ for GNC and EC, respectively at 318 K.
- (vii) The negative value of change in Gibb's free energy implied that the reaction is spontaneous in nature, and values are more negative with temperature intimating that adsorption is favored with increase in temperature for both the studied adsorbents.
- (viii) Adsorption is favored at high temperature for both the studied adsorbents is also evident by the high values of various constants at high temperature, for example, Temkin constants K_T (equilibrium binding constant), Freundlich constant, K_F (adsorption capacity), Langmuir constant K_L (affinity to binding sites), C_m (monolayer concentration), and energy E (D-R isotherm), which is also confirmed by the positive values of enthalpy change.
- (ix) The R_L values also approve that biosorbents GNC and EC can be used favorably for the adsorption of dye CR.

The present research work established that GNC and EC were excellent low-cost bioadsorbents for the removal of dye congo red. The kinetics and thermodynamic data can be further explored for the design of an adsorber for industrial effluents treatment.

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