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Preparation of composite of bentonite clay and *Azadirachta indica* (neem) leaves powder for the removal of Congo red from an aqueous solution

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ABSTRACT

In this study, a composite of bentonite clay and powdered neem leaf was used to investigate the adsorption of the anionic dye Congo red (CR) from an aqueous solution. The designed adsorbent was characterized through scanning electron microscopy and Fourier-transform spectroscopy. In order to estimate the percentage CR discharge, the impacts of several parameters, such as contact duration, adsorbent dose, initial dye concentration, pH and temperature were evaluated. Adsorption kinetics was investigated using nonlinear pseudo-first-order and pseudo-second-order models. Results indicated that CR adsorption onto composite fitted to nonlinear pseudo-second-order model. Experimental data of CR adsorption was subjected to several linear isotherm models. Attained results exhibited that CR adsorption fitted to linear Freundlich isotherm. Adsorption thermodynamic studies revealed that CR adsorption was an endothermic and spontaneous process. Moreover, the composite regeneration and removal of dye by column were also illustrated.

Keywords: Congo red; Bentonite clay; Pseudo-second-order model; Endothermic process; *Azadirachta indica*

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1. Introduction

Congo red (CR) is a prominent anionic diazo dye used extensively in industries like pigmentation and wood working despite its association with adverse health effects [1,2]. High concentrations of CR can wreak havoc on the human body, exerting cytotoxic, mutagenic, carcinogenic, and neurotoxic effects [3]. Its intricate aromatic structure renders it stable and non-biodegradable, making it exceptionally water-soluble and challenging to eliminate. Furthermore, CR's carcinogenic properties can pose severe risks to the skin, eyes, reproductive, and respiratory systems [4,5]. Its versatility extends to applications in various sectors, including wool, silk, textiles, food, and even laboratory settings, where it is used to diagnose conditions like amyloidosis and as a pH indicator. Unfortunately, CR is also known for its benzidine (4,4′-diaminobiphenyl or 1,1′-biphenyl-4,4′-diamine) and naphthoic acid (2-naphthoic acid) derivatives, which can degrade into cancer-causing substances, adding to its notoriety [6,7]. Exposure to CR may result in respiratory issues, drowsiness, and alterations in blood parameters such as coagulation [8]. Given these concerns, developing effective strategies for removing CR from wastewater in these sectors is paramount.

Effluents containing CR can be treated through many techniques, encompassing biological treatment [9], coagulation/flocculation [10], ozone treatment [11], chemical oxidation [12], membrane filtration [13], ion exchange [14], photocatalysts [15], and adsorption [16]. Among these methods, adsorption stands out due to its simplicity, high efficiency, and wide array of available adsorbents.

Commercially, activated carbon has proven successful in removing colorants, but its widespread use is hindered by its high-cost [17]. Researchers have demonstrated the usage of components such as walnut husk [18], mixtures [19], biochar made from agricultural waste [20], clinoptilolite in its native state [21], husk of a sesame [22], Penicillium YWO1 biomass [23], zeolite in its natural state [24], succinyl chitosan that has been cross-linked [25], substituted bentonite [26], eucalyptus barks [27] modified attapulgite [28], ion exchange membranes [3,4,29–33], clay substance [34–36], activated charcoal [37], rice husk [38,39], dehydrated beet pulp carbon [40], leave powder of different plant leaves [41–46], polyurethane foam [47], agricultural by-products, in particular, have exhibited capacity as cost-effective adsorbents in this context and are often chemically modified to enhance their colorant adsorption capabilities [48]. Due to the majority of them having anionic or hydrophobic surfaces, several adsorbents do not have good anionic dye adsorption capabilities [49].

This study presents a novel approach towards the synthesis of a composite using powdered *Azadirachta indica* (neem) leaves and bentonite clay. The composite's characteristics were thoroughly examined through morphology analysis and FTIR spectroscopy. We comprehensively demonstrate CR removal from an aqueous solution, elucidating the influence of composite dosage, contact duration, CR concentration, pH, and temperature. Our investigation also employs nonlinear kinetics and nonlinear isotherm models to present and analyze the experimental results of CR adsorption onto the prepared composite. Furthermore, the thermodynamics governing CR adsorption onto the synthesized composite are explored, and the potential for adsorbent regeneration is demonstrated. The removal of CR dye by column study was also discussed.

2. Methodology

2.1. Reagents

The materials utilized were Congo red dye and a composite of bentonite and neem leaf powder. Distilled water was utilized throughout this work. Congo red (99%) was acquired from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Sodium hydroxide (98%) of Sigma-Aldrich (Germany) was used.

2.2. Adsorbate

Congo red is a chemical molecule that occurs naturally. The melting temperature of CR is over 360°C, and it is soluble in water and ethanol while becoming orange in acetone and almost insoluble in ether. It is a particular azo dye. Although it dissolves more effectively in organic solvents, CR may be dissolved in water and creates a red colloidal solution. The molecular weight of Congo red dye is 696.665 g/mol. Its chemical formula is $C_{32}H_{22}N_6Na_2O_6S_2$.

2.3. Preparation of composite

Neem leaves were collected from neem tree, washed and dry in sunlight. Neem leaves were grinded and powder was prepared. Distilled water was used for washing the powder. After washing, powder was dried at 80°C in an oven. Bentonite clay was taken and converted to powder. In a round bottom flask, equal amounts of bentonite and neem leaves (*Azadirachta indica*) powder (20 g each) were mixed followed by the addition of 300 mL of 0.1 M NaOH solution with constant stirring. After that, the content was dried in an oven set at 105°C. The sample was added in crucible and calcined for 6 h at 300°C. The resulting black powdered material was thoroughly cleaned to eliminate any remaining NaOH before being drying at 105°C in the oven.

2.4. Batch binding assay

When adding composite to the determined volume of an anionic dye aqueous solution, 200 rpm of shaking was done in order to conduct batch adsorption studies [30,32,50–53]. Using a UV/VIS spectrophotometer (UV-2550, SHIMADZU), the dye's concentration was determined and a corresponding calibration curve was produced. Maximum absorbance of Congo red was obtained at a wavelength of 490 nm. The effect of adsorbent dosage on the removal of CR from aqueous solution was investigated by varying the amount of adsorbent while maintaining the other parameters constant at room temperature, such as contact time of 40 min, the initial dye concentration of 30 mg/L, solution volume of 30 mL, and shaking rate of 200 rpm. The estimated mass of the composite (0.04 g) was put into the measured volume of the solution (30 mL) with a set initial dye concentration (30 mg/L) and shaking rate of 200 rpm constant at room

temperature for various time intervals in order to study the impact of contact time on the CR % removal. Similarly, the concentration's effect was studied by changing initial concentration and keeping other factors constant. Further, the optimum pH for maximum adsorption was also investigated. In addition, the temperature's effect was illustrated by varying temperature and keeping mass of composite (0.04 g), volume of solution (30 mL), starting dye concentration (30 mg/L), shaking rate of 200 rpm and contact time constant.

2.5. Column adsorption experiment

Column adsorption experiments were carried out in a glass column of 1.6 cm internal diameter and height of 30 cm. Each bed of the adsorbent was underlined by 0.5 mm of glass wool. The column was packed to a height of 8 cm with 100 g of composite on layer of glass wool placed at the bottom of the column. Congo red dye solution having an initial concentration of 20 mg/L was passed through the column at 5mL/min. The eluate was continuously collected from the exit of the column at a time interval of 2 min in 50 mL beakers. The solution in each beaker was then analyzed using visible spectrophotometer in order to group the beakers containing the dye. The solutions in the beakers with the dye were collected in a single beaker and concentration was determined. The percentage removal was calculated through Eq. (1):

$$\%\text{Removal} = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \quad (1)$$

where C_{in} (mg/L) and C_{out} (mg/L) are the influent and effluent dye concentrations, respectively.

3. Results and discussion

3.1. SEM and FTIR tests

The morphology of the composite was examined using scanning electron microscopy (SEM). Results indicate their amorphous nature. These images revealed that flakes like structures are present in these composites. Their particle size revealed that they are present as microns. The basic composition of this composite is mainly carbon along with minerals like Al, Zn, Ca, K etc. according to EDX analysis.

Fig. 1 indicates the hydroxyls connecting to the octahedral and tetrahedral layers. Water's asymmetric OH stretch (deformation mode) results in a highly sharp and intense band at 1,630 cm^{-1}, a structural component of bentonite clay. The maximum absorption sharp band at 1,012 cm^{-1} is due to silicon-oxygen bond.

3.2. Effect of operating factors on the CR removal

3.2.1. Influence of adsorbent dose

The % discharge of CR from an aqueous solution is shown in Fig. 2a in relation to adsorbent mass. It was observed that increasing the amount of adsorbent caused the adsorption to rise and that, once it reached a specific point, the adsorption stayed nearly constant. It was increased from 67% to 75% as the adsorbent dosage increased to 0.01–0.045 g. Because there are more active sites per mass of adsorbent, this can be possible. This optimized mass was 0.040 g, and it was used for further studies. At 0.040 g, adsorption was 74%. Similar behavior was noted in our previous work [54,55].

3.2.2. Influence of contact duration

Fig. 2b depicts the impact of contact time on CR discharge from an aqueous solution. It was discovered that increasing contact time improved CR absorption. After 40 min, there was a maximum amount of CR adsorption onto the composite. The adsorption did not alter significantly after this. Initially adsorption rate was higher because all pores and active sites were free for dye molecules to adsorb. With the passage of time, the reduced active sites became accessible, which reduced the rate of adsorption. This behavior was also reported in the literature [39,56,57]. Thus, the optimized time was 40 min, which was used for further data collection.

3.2.3. Influence of initial dye concentration

Initial dye concentration has a significant impact on how effectively a dye can be removed from an aqueous solution. Fig. 2c illustrates how the initial CR concentration affected the rate of CR elimination. The percentage of CR elimination was found to be decreased with a rise in CR initial concentration at room temperature, according to the results. Active sites have reached saturation due to the rising concentration [51,58,59]. Due to the presence of free active sites, the adsorption capacity was greater at low concentrations. Similar outcomes were obtained in our earlier research [60].

3.2.4. Influence of pH variation

The variation in solution's pH indirectly influences the charge on adsorbent's surface during the adsorption

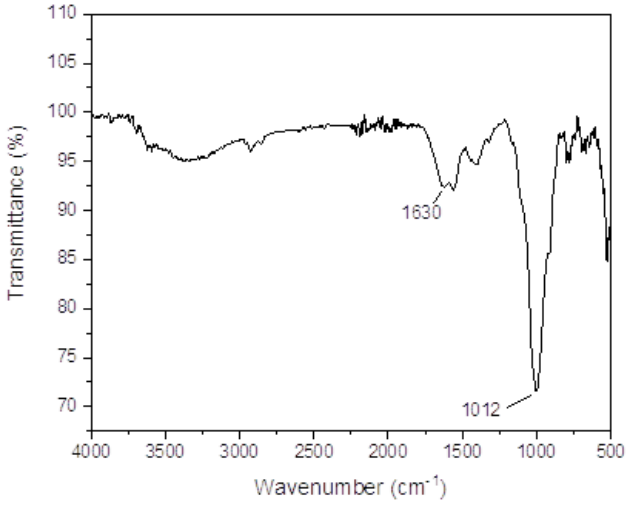

Fig. 1. FTIR spectrum of the prepared composite.

process and might affect its capacity to bind with the pollutant ultimately impacting on its percentage removal. In case of the neem-bentonite clay composite, a maximum percentage removal was achieved at pH 2.5. The effect of pH on CR removal in represented in Fig. 3a. Results showed that the CR removal was decreased with increase in pH of medium. As Congo red being an anionic dye possesses negative charge in solution. It is associated to the electrostatic

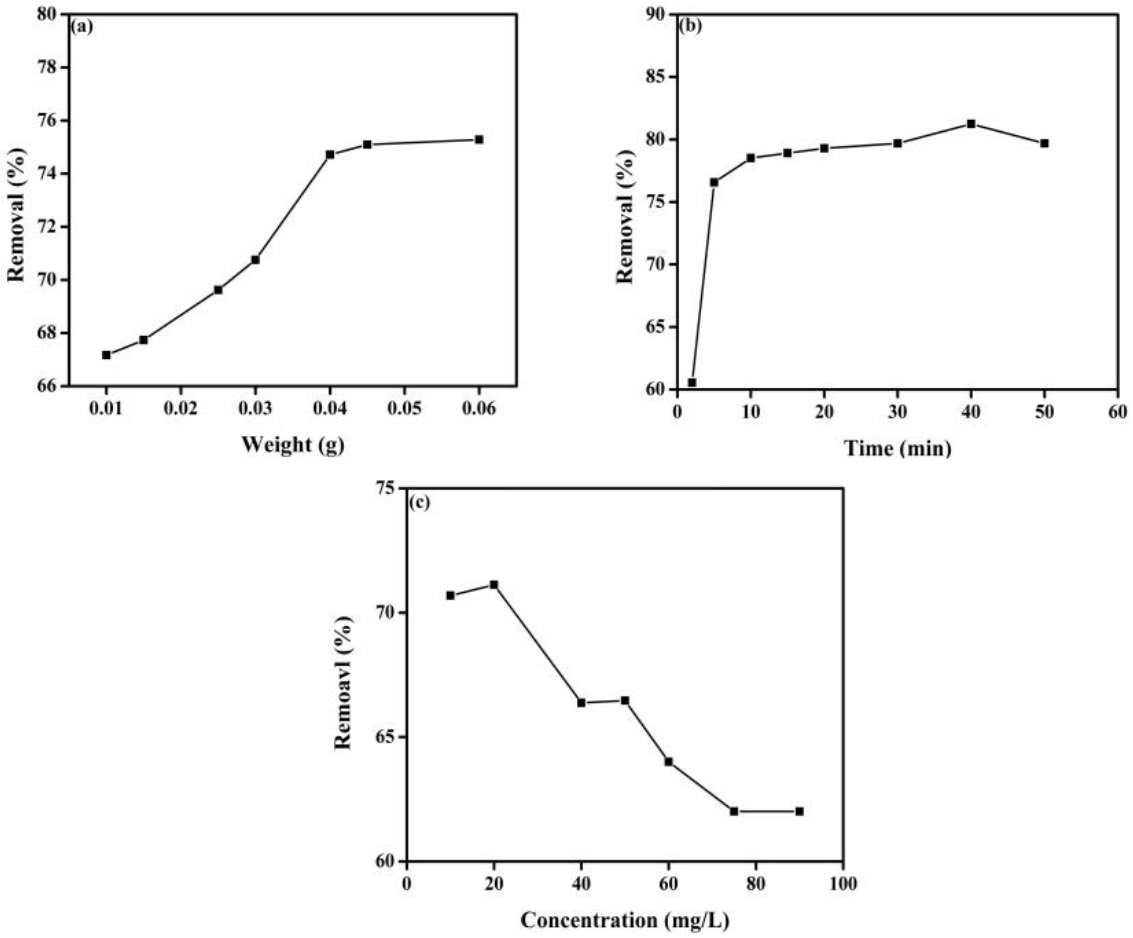

Fig. 2. (a) Effect of weight of adsorbent, (b) contact duration, and (c) initial dye concentration on the removal of CR from an aqueous solution.

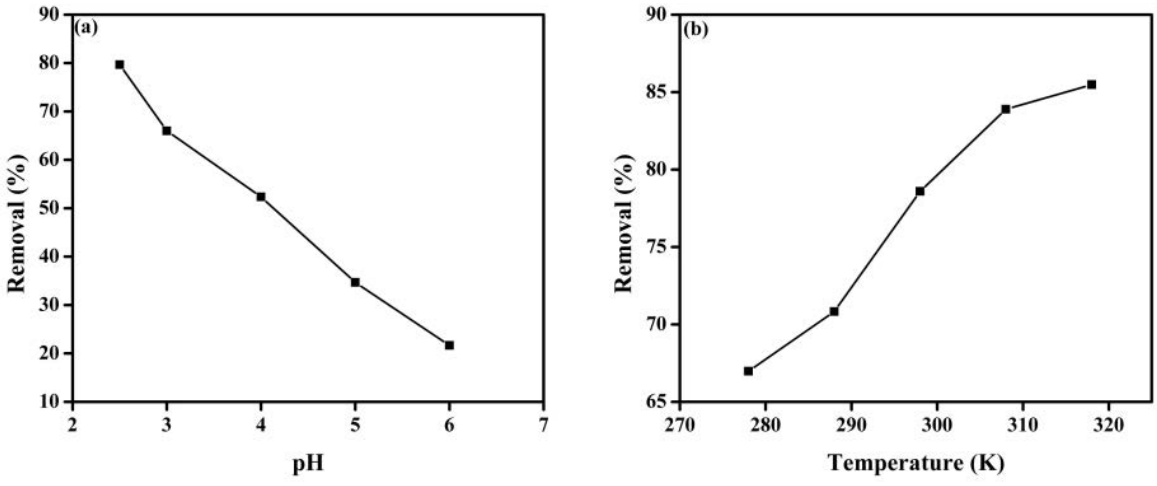

Fig. 3. (a) Effect of pH and (b) temperature on the removal of CR from an aqueous solution.

of attractions between negatively charged CR molecules and positively charges adsorbent in acidic media [38]. With increase in the value of pH, the removal of CR from an aqueous solution was found to be declined (Fig. 3a).

3.2.5. Influence of temperature

Temperatures ranging from 278 to 318 K were used to examine the effect of temperature on CR discharge from an aqueous solution. The obtained findings are shown in Fig. 3b. With an increase in temperature, it was shown that the CR elimination increased from 66% to 85%. It was proposed that the removal of CR from an aqueous solution is an endothermic reaction [41,61]. Table 1 provides an interesting comparison of adsorption capability of the prepared composite with other adsorbents reported in the literature.

3.2.6. Comparative study

Our study focuses on preparing a composite material using bentonite clay and *Azadirachta indica* (neem) leaves powder for removing Congo red dye from an aqueous solutions. In a comparative study for Congo red (CR) dye removal, activated carbon and metal–organic frameworks out perform with 95% removal efficiency. Neem leaves and silica gel demonstrate moderate efficiency at 60%–75%, while other materials like hydrogel beads and bentonite clay exhibit intermediate removal capabilities at around 70%–80%.

3.3. Adsorption kinetics

In order to illustrate adsorption kinetics, nonlinear pseudo-first-order and pseudo-second-order models were applied to the adsorption of CR. Herein, adsorption kinetic variables were assessed using the Wave Metrics module of the IGOR Pro 6.1.2 software.

Nonlinear pseudo-first-order is represented as [65,66]:

$$\frac{dQ_t}{dt} = k_1\left(Q_e - Q_t\right) \tag{2}$$

Nonlinear pseudo-second-order is represented as [65,66]:

$$\frac{dQ_t}{dt} = k_2\left(Q_e - Q_t\right)^2 \tag{3}$$

where Q_e (mg/g) denotes the amount adsorbed at equilibrium, t (min) denotes the passage of time, and Q_t denotes the amount adsorbed at "t". In addition, k_1 (min^{-1}) and k_2 (g/mg·min) denote the pseudo-first-order and pseudo-second-order rate constants, respectively.

Nonlinear pseudo-first-order equation is given as:

$$Q_t = Q_e\left(1 - e^{-kt}\right) \tag{4}$$

Nonlinear pseudo-second-order equation is written as:

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \tag{5}$$

In Fig. 4 the nonlinear pseudo-first-order and pseudo-second-order kinetics graphs are indicated. To evaluate which model supported the kinetic equations with best fit, the Chi-square test 'χ^{2}' was utilized.

$$\chi^2 = \sum \frac{\left(Q_e - Q_{e,m}\right)^2}{Q_{e,m}} \tag{6}$$

where Q_e (mg/g) is the equilibrium capacity as determined using experimental data, and $Q_{e,m}$ (mg/g) is the equilibrium capacity as estimated by a model. The comparison of experimental data with model-derived data generally revealed that whether the data are identical in this instance 'χ^{2}' would indicate a limited number and vice versa. To calculate kinetic constants for the adsorption pseudo-second-order model is more trustworthy as confirmed by the obtained lower 'χ^{2}' (nonlinear) values. Analyzing and contrasting the nonlinear CR adsorption kinetic parameters of pseudo-first-order and pseudo-second-order on the adsorbent. PFO has an equilibrium adsorption capacity Q_e of 17.836 mg/g, an adsorption kinetic rate k_1 of 0.944 min^{-1}, and χ^2 value of 0.458. Adsorption kinetic rate k_2 for the PSO is 0.143 g/mg. min, equilibrium adsorption capacity Q_e is 18.259 mg/g, and χ^2 will be 0.184.

Table 1
Comparison of adsorption capacity of the prepared composite with other adsorbents reported in the literature.

Adsorbents	Removal of CR (%)	References
Bottom ash	96.95	[62]
De-oiled soya	97.14	[62]
Guar gum/activated carbon nanocomposite	78.0	[63]
Modified rice husk	91.0	[38]
Leaves powder of *Syzgium cumini*	90.20	[46]
Activated carbon	90.0	[64]
Anion exchange membrane BII	99.57	[54]
Neem-bentonite composite	70.0	This work

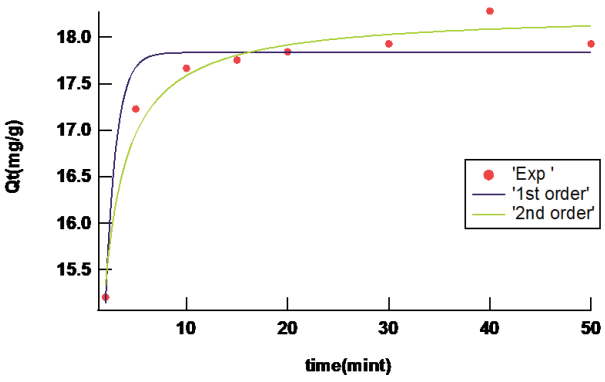

Fig. 4. CR adsorption models with nonlinear pseudo-first-order and pseudo-second-order kinetics.

3.4. Adsorption isotherms

3.4.1. Langmuir isotherm

Langmuir isotherm is based on the maximum adsorption corresponding to the saturated monolayer of liquid molecules on the solid surface. It is shown as [44]:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \tag{7}$$

where Q_m is Langmuir monolayers adsorption capacity, C_e is supernatant concentration at equilibrium state of the system (mg/L), K_L is Langmuir constant (L/mg) (mg/g), and q_e is the amount of dye adsorbed at equilibrium state of system (mg/g). The Langmuir isotherm essential characteristics can be shown in term of dimensionless constant separation factor R_L that is shown as [44].

$$R_L = \frac{1}{1 + K_L C_0} \tag{8}$$

The value of R_L showed the shape of the isotherm to be either unfavorable (R_L > 1), linear (R_L = 1), favorable (0 < R_L > 0), or irreversible (R_L = 0) [4,44].

The plot of Langmuir adsorption isotherm is denoted in Fig. 5a. Determined values of its endowments are shown in Table 2. The correlation coefficient (R^2 = 0.975) value was close to unity indicating that CR adsorption followed Langmuir isotherm. The value of R_L (R_L = 7.10 × 10^{-6} – 7.88 × 10^{-7}) represented that it was a favorable process.

3.4.2. Freundlich isotherm

It is expressed as [67]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{9}$$

where K_f and n_F are Freundlich constant. Freundlich adsorption isotherm's graph is represented in Fig. 5b and the determined values of its parameters shown in Table 2. The value of correlation coefficient (R^2 = 0.994) exhibited that CR adsorption fitted to Freundlich isotherm. The value of Freundlich constant '*n*' was found to be 1.24 representing that CR adsorption was favorable because the value of "*n*" ranges from 2–10 exhibiting good adsorption, 1–2 moderate adsorption and less than one denotes poor adsorption [65,68,69].

3.4.3. Temkin isotherm

Temkin isotherm is given as [41]:

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{10}$$

where B_T = RT/b_T, R is gas constant (8.31 J/mol·K) and T is absolute temperature (K). The constant b_T is related to the heat of adsorption and A_T is equilibrium binding constant coinciding to the maximum binding energy. Temkin isotherm's plot for CR adsorption is represented in Fig. 5c. Measured b_T and A_T values are shown in Table 2. The value correlation coefficient value (R^2 = 0.955) exhibited that CR adsorption obeyed Temkin isotherm.

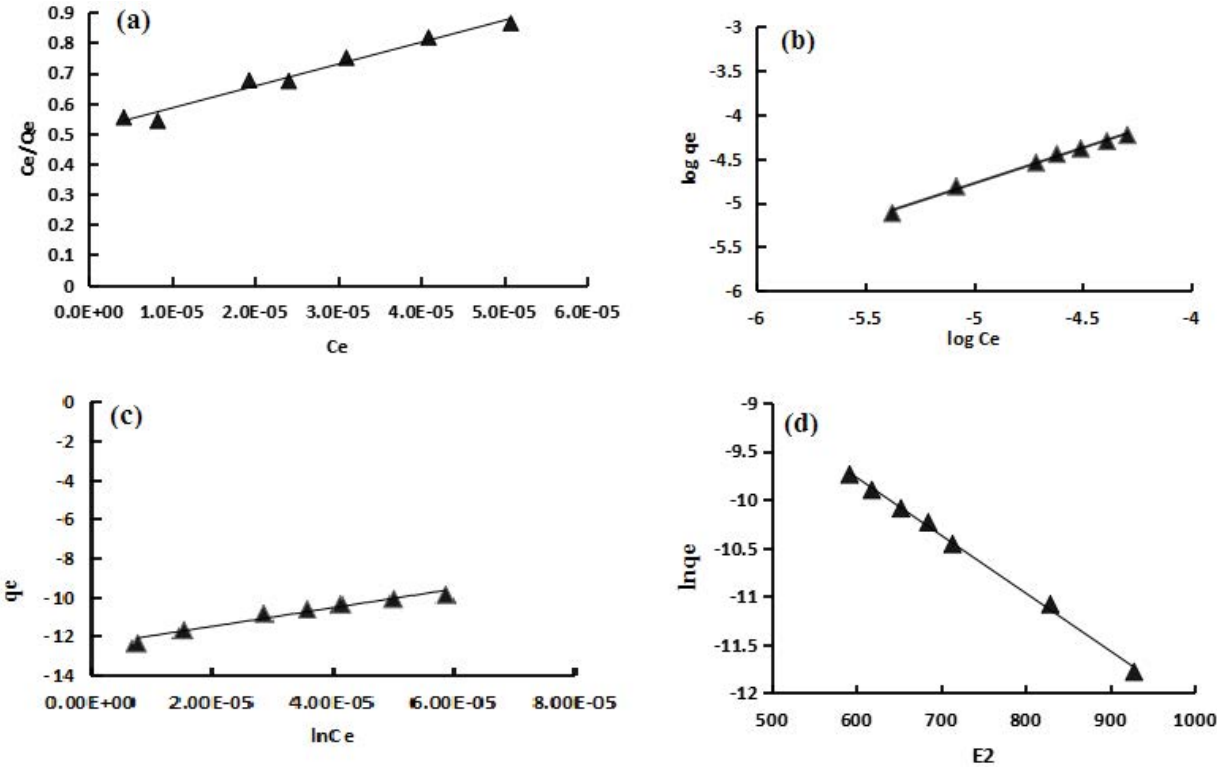

Fig. 5. For the adsorption of CR onto composite of bentonite clay and *Azadirachta indica* (neem) leaves powder, linearized versions of the (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) Dubinin–Radushkevich isotherm models were developed.

Table 2
CR adsorption measured isotherm factors

Adsorption isotherms		Determined parameters	
Langmuir isotherm	Q_m	K_L	R^2
	1.40×10^{-4}	1.41×10^4	0.975
		$R_L = 7.10 \times 10^{-6} - 7.88 \times 10^{-7}$	
Freundlich isotherm	n	K_f	R^2
	1.24	5.48	0.994
Temkin isotherm	b_T	A_T	R^2
	0.052	1.0	0.955
Dubinin–Radushkevich (D-R) isotherm	Q_m	B	R^2
	2.0×10^{-3}	0.006	0.997
		E = 9.57	

C_m: mg/g; E: kJ/mol; Q_m: mg/g; K_L: L/mol; K_f: mol/g; b_T: kJ/mol; A_T: L/mg; β: mol²/J²

3.4.4. Dubinin–Radushkevich (D-R) isotherm

It is represented as [41]:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{11}$$

where β (mol²/kJ) is constant related to the adsorption energy and ε is the Polanyi potential can be determined by using Eq. (12):

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \tag{12}$$

where T is absolute temperature (K) and R is gas constant (8.31 kJ/mol). The mean free energy E (kJ/mol) can be calculated by Eq. (13):

$$E = \frac{1}{\sqrt{2\beta}} \tag{13}$$

Fig. 5d shows the graph of D-R adsorption isotherm and measured values of its factors are shown in Table 2. Determined value of mean adsorption energy (E) was 9.57 kJ/mol (Table 2). It exhibited that CR adsorption was chemical adsorption process [53,57]. The value of E lower than 8 kJ/mol is the characteristic of physical adsorption process while higher than 8 kJ/mol is characteristic of chemical adsorption process [44,70].

3.5. Thermodynamics of adsorption

Here, the thermodynamics of CR adsorption was studied by calculating the changes in Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) by using Eqs. (14)–(16):

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{14}$$

$$K_c = \frac{C_a}{C_e} \tag{15}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{16}$$

where C_a, K_c, R, C_e, and T represent the quantity of dye (mol/L) adsorbed on the adsorbent per litre (L) of the solution, the equilibrium constant, the general gas constant (8.31 J/mol·K), the equilibrium concentration of dye in solution (mol/L), and the absolute temperature (K), respectively. A graph of lnK_c vs. 1/T for CR adsorption is shown in Fig. 6. The endothermic nature of the adsorption process for CR was demonstrated by the positive values of enthalpy (ΔH° = 21.28 kJ/mol) [4,65]. The increase in randomness at the adsorbate–adsorbent interface during CR adsorption is shown by the positive value of entropy (ΔS° = 0.082 kJ/mol) [57]. At all temperatures, the value of Gibb's free energy (ΔG°) was negative, indicating that CR adsorption was a practical and spontaneous reaction [5,71].

To ascertain spontaneity, type of adsorption, and forecast the size of changes on the adsorbent's surface, the thermodynamic parameters were evaluated using a graphical technique based on the Van't Hoff equation. The feasibility of the adsorption process and the impact of temperature may be estimated via the examination of these factors. We calculated the change in Gibbs' standard enthalpy, entropy, and free energy (ΔG°, ΔH°, and ΔS°). When doing adsorption tests, the temperature was varied from 29.8°C to 81°C while taking into account the parameters set out in the experiment design.

3.6. Environmental application

The applicability of the procedure is an important factor and was checked by making a solution of dye in tap water. The solution was added to conical flasks after mixing with an optimized weight and shaking for an optimized time with a 100 mg/L dye concentration. The solution in conical flasks was separated after the first cycle, and optimized weight was added to the solution for the second cycle. After the second cycle, the solution was separated and optimized weight was added once more. After the third cycle, the solution was separated out and the initial and final absorbance

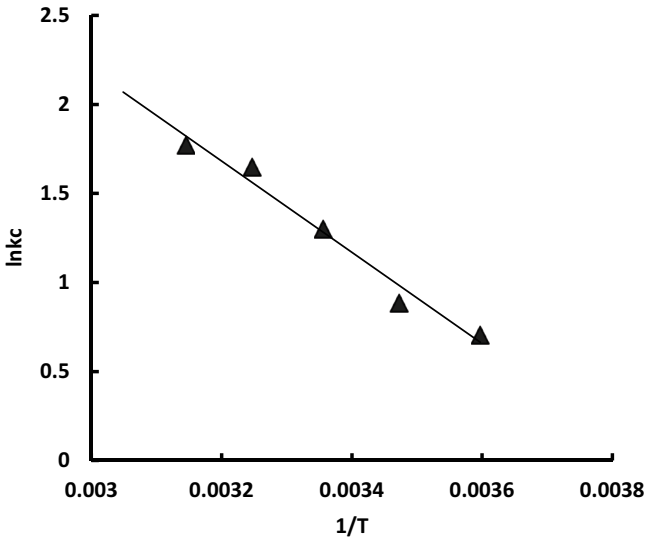

Fig. 6. $1/T$ vs. $\ln K_c$ plot for CR adsorption.

was checked. According to the findings, the % of CR dye removed in the first cycle, second cycle and third cycle was around 95%, 92% and 85%, respectively.

3.7. Economic evaluation

Based only on the adsorbent's ability to retain the dye, a preliminary estimate of the capital cost of employing newly designed composite for CR was made without taking additional cost elements like regeneration.

The relative cost of designing 1 g of adsorbent was used as a standard to determine the adsorption system cost which approximates to 1 US dollar when converted from local currency. The basic reason of such a low cost is the type of precursors selected to obtain the adsorbent. Both of the components of newly designed composite are easily available in nature in access quantities.

3.8. Removal of dye by using column

The maximum removal of Congo red dye by column study was calculated by using equation 1 and was found to be 65%.

4. Conclusion

In conclusion, a new adsorbent bentonite clay and powdered neem leaf composite for the effective removal of CR dye from an aqueous solution was produced. SEM was used to depict the morphology of the synthetic composite. The synthesis of composite was studied by FTIR test. The resulting composite was utilized to adsorb CR from an aqueous solution. The elimination of CR increased with composite mass, contact duration, and temperature while decreasing with pH and initial concentration CR in solution. Adsorption of CR fitted to nonlinear pseudo-second-order kinetic model. Adsorption isotherm results indicated that CR adsorption fitted to linear Freundlich isotherm with correlation coefficient (R^2 = 0.994) close to unity. In addition, the value of mean adsorption energy (E = 9.57 kJ/mol) represented that adsorption of CR onto the prepared composite was chemical adsorption process. Adsorption thermodynamic study showed that adsorption of CR onto the composite was a spontaneous and endothermic process. The results demonstrated that the bentonite clay and powdered neem leaf composite that was made is an exceptional adsorbent for CR at room temperature.

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