Biopolymer-Grafted, Magnetically Tuned Halloysite Nanotubes as Efficient and Recyclable Spongelike Adsorbents for Anionic Azo Dye Removal

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ABSTRACT: The quest for sustainable development and green chemistry had led to the design and synthesis of advanced adsorbent materials for efficient removal of pollutants in industrial effluents. Magnetic halloysite nanotubes with chitosan nanocomposite sponges were prepared by combining solution-mixing and freeze-drying. Magnetic@chitosan/halloysite (Fe₃O₄−HNT/CS) and spongelike chitosan/halloysite (HNT/CS) were used as adsorbents for the removal of Congo red dye in aqueous solution in a batch process. The as-prepared composites were characterized using scanning electron microscopy, energy-dispersive X-ray analysis, X-ray diffraction, vibrating-sample magnetometry, thermal gravimetry–differential scanning calorimetry, and Fourier transform infrared spectroscopy. Data from kinetic study were analyzed with pseudo-first-order and pseudo-second-order models, whereas the mechanism was analyzed using Bangham’s, Elovich’s, intraparticle, and double-exponential diffusion models. The equilibrium data were evaluated using Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models. The adsorption kinetics of dye removal followed the pseudo-first-order model with average rate constants of 0.260 and 0.196 min⁻¹ for Fe₃O₄−HNT/CS and HNT/CS, respectively. The Langmuir adsorption isotherm best fitted the equilibrium data with R² > 0.9 with maximum adsorption capacities of 41.54 and 54.49 mg g⁻¹ obtained for HNT/CS and Fe₃O₄−HNT/CS, respectively. Negative values of ΔG° obtained from thermodynamic studies revealed that the adsorption process was spontaneous. The values of ΔH° and ΔS° obtained for Congo red dye removal were 69.46 and 39.54 kJ mol⁻¹ and 240.5 and 145.1 J mol⁻¹ K⁻¹ for HNT/CS and Fe₃O₄−HNT/CS, respectively. The results indicated that CS–HNT is an excellent adsorbent; however, its magnetic modification further improved its recyclability and enhanced the performance for the removal of Congo red dye from aqueous solution.

1. INTRODUCTION

Industrial and domestic processes require water that is free from colors and related compounds. On the contrary, however, effluents from industries such as textile, paper and pulp, dye and dye intermediates, pharmaceutical, tannery, craft bleaching, food technology, hair coloring, rubber, paper, plastic, cosmetics, etc. contain dyes, organic colorants, and phenolic compounds.¹ These industries consume majority of tons of chemically different types of dyes that are currently manufactured.² When untreated effluents from these industries are released in aquatic environment, development of aquatic animals and plants is inhibited because of outright blocking of sunlight, resulting in reduced photosynthesis, increased biological oxygen demand, and reduced dissolved oxygen to sustain the aquatic life. Furthermore, these pollutants exhibit toxic effects on microbial and aquatic populations and become toxic and carcinogenic to mammals when they enter the food chain.³

The first contaminants to be recognized in wastewater effluents are colorants, and the presence of a synthetic dye in water even in a very small amount (≤1.0 mg L⁻¹) is typically highly visible, affecting the aesthetic merit and transparency of the water bodies. The complex structure and synthetic origin of dyes made their removal through conventional wastewater treatment a colossal task. Moreover, they are designed to resist breakdown with time and defy exposure to harsh conditions such as sunlight, water, soap, and oxidizing agents, thus making their removal challenging during wastewater treatment. The Congo red (CR) dye is a sodium salt of 3,3′-(1,1′-biphenyl)-4,4′-diyl)bis(4-aminonaphthalene-1-sulfonic acid), and it is the first synthetic dye produced with a complex chemical structure and capability of dying cotton directly;⁴ hence, its application in a wide field of industrial processes involve dyeing. Unfortunately, it metabolized to benzidine, a compound implicated as a carcinogenic and a mutagenic agent,⁵ therefore, exposure to this dye posed a potential danger of bioaccumulation and allergy.

Various methods including physical, chemical, physicochemical, and biological methods have been developed for the removal of dye and other contaminants from wastewater.
Adsorption has been the most common physicochemical treatment method with potential applications because of its low cost, effectiveness, and efficiency. Mostly, activated carbon has been widely accepted in commercial systems as an adsorbent for the removal of the contaminants in wastewater including dyes because of its significant adsorption capacity; nevertheless, its high capital cost, complicated synthesis process, low capacity, slow kinetics property, and the harmful byproducts of the treatment process are major setbacks for using activated carbon.\textsuperscript{7−9}

The quest for sustainable development and green chemistry had led to the design and synthesis of advanced adsorbent materials for efficient adsorption, separation, and purification. These include natural or synthetic zeolite,\textsuperscript{10} organically modified porous silica,\textsuperscript{11} natural or modified clays,\textsuperscript{12} macroporous polymeric adsorbents,\textsuperscript{13} and so on. However, high costs in terms of operation and consumption time, low selectivity, limited adsorption capacities, and difficulties in their regeneration and reuse are major challenges for such materials. Therefore, it is of great theoretical and practical significance to develop high-performance, low-cost, and recyclable adsorbents. Significant attention had also been paid to polymer–clay nanocomposites, which are low-cost, environment-friendly, and abundant materials with good chemical, mechanical, and structural stability.\textsuperscript{14,15} Most clays have cationic exchange capacity, thereby limiting their applications to cationic pollutants; therefore, functionalization is envisaged to confer enhanced performance. Halloysite (HNT), an aluminosilicate clay with a hollow nanotube structure, has been used as a nanocomposite, a catalyst, in molecular hydrogen storage, and as an adsorbent because of the presence of hydroxyl groups and large pore volume and surface area.\textsuperscript{16} Chitosan is a biopolymer derived from chitin, an abundant precursor, by deacetylation. Its richness in hydroxyl and amino functional groups makes it one of the substances that has been most exploited in the field of adsorption of substances.\textsuperscript{16} Its use has been limited by its pH sensitivity and low mechanical properties; hence, for practical operations, these properties require improvement to increase the adsorption capability of chitosan.\textsuperscript{17} The introduction of clay into the polymer structure increases not only the adsorption capacity of the adsorbent but also the mechanical and thermal stability, thereby resulting in an adsorbent with superior properties compared to those of either the clay or the polymer; nevertheless, the difficulty encountered from separation of the suspended polymer–clay composite after use is a big challenge. This challenge can be circumvented by incorporation of iron oxide nanoparticles into the clay–polymer moiety, thereby creating adsorbents with magnetic properties that significantly impact the adsorption process on the surface with accelerated separation and improved efficiency of water treatment.\textsuperscript{18} Although various reports on the use of the HNT/CS composite are available in the literature, the inclusion of magnetic particles is less reported.

This study reports the synthesis and characterization of a biopolymer-grafted, magnetically tuned halloysite composite (Fe\textsubscript{3}O\textsubscript{4}–HNT/CS) and its unmagnetized precursor. Their performances as adsorbents for the removal of Congo red dye were also investigated. The effects of the initial concentration of dye, contact time, pH, and adsorbent dosage on Congo red dye removal as well as recyclability were reported. Kinetic and equilibrium data as well as thermodynamics data from the batch adsorption studies were analyzed with appropriate models and reported.

2. RESULTS AND DISCUSSION

2.1. Characterization of the Adsorbent. The surface morphologies of CS, HNT/CS, and Fe\textsubscript{3}O\textsubscript{4}–HNT/CS were observed by scanning electron microscopy (SEM) presented in Figure 1. It is clear from the figure that the presence of HNT modified the surface morphology of the CS (Figure 1a). The rough surface of the chitosan becomes more collapsed, and the uniformly smooth surface is gradually transformed to three-dimensional morphologies as HNT and Fe\textsubscript{3}O\textsubscript{4} were incorporated into the composite.

Energy-dispersive X-ray (EDX) analysis of CS, HNT/CS, and Fe\textsubscript{3}O\textsubscript{4}–HNT/CS is shown in Figure 2. The presence of O and C in chitosan was revealed by Figure 2a and the incorporation of HNT was confirmed by the presence of Al Na and Si in Figure 2b, whereas the presence of Fe in Figure 2c confirmed the incorporation of magnetic particles into the structure of Fe\textsubscript{3}O\textsubscript{4}–HNT/CS.

The decomposition process of CS/HNT and Fe\textsubscript{3}O\textsubscript{4}–CS/HNT could be described in three main steps as shown by the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves in Figure 3a,b. The weight loss in TGA curves of CS/HNT is shown at around 91, 285, and 527 °C. The weight loss at these temperatures could be attributed to the dehydration due to loss of surface and interlayer water, decomposition of the remaining low-molecular-weight species, and dehydration and dehydroxylation of structural water. Similarly, Fe\textsubscript{3}O\textsubscript{4}–CS/HNT displayed weight loss at 108, 257, and 484 °C, whereas the first could be attributed to the evaporation of adsorbed water, the last two stages could be attributed to decomposition of the chitosan in the hybrid material.

The Fourier transform infrared (FTIR) spectra of HNT/CS and Fe\textsubscript{3}O\textsubscript{4}–HNT/CS before and after adsorption are presented in Figure 4. The double peaks at 3600 cm\textsuperscript{-1} and
above are due to the stretching vibration of the surface hydroxyl group on the two composites. The peaks at 471, 529, and 928 cm\(^{-1}\) in HNT/CS and those at 464, 558, and 913 cm\(^{-1}\) in Fe\(_3\)O\(_4\)–HNT/CS were assigned to deformation of Si–O–Si, Si–O–Al, and OH of inner hydroxyl groups. The peaks at 1087 and 1014 cm\(^{-1}\) in HNT/CS and Fe\(_3\)O\(_4\)–HNT/CS, respectively, are assigned to Si–O. The NH\(_2\) vibration frequency could be assigned to the peaks at 1588 and 1515 cm\(^{-1}\) of HNT/CS and Fe\(_3\)O\(_4\)–HNT/CS, respectively, whereas the peak at 594 cm\(^{-1}\) found in Fe\(_3\)O\(_4\)–HNT/CS is due to Fe–O. A shift in band position and broadening of peaks were prominent after the adsorption, suggesting further interaction between the dye and the adsorbents.

X-ray diffraction (XRD) spectra of CS, HNT, HNT/CS, and Fe\(_3\)O\(_4\)–HNT/CS are presented in Figure 5. The characteristic
peaks of CS are shown at 14.4 and 20.5°. The XRD spectra of HNT/CS showed that CS is well incorporated into the HNT as all of the peaks in the individual samples were retained in their composite. The XRD patterns of Fe₃O₄−HNT/CS displayed distinct peaks at 2θ values of about 30.6, 35.9, 43.8, 57.2, and 63.1, as marked in the figure. These peaks are characteristics of Fe₃O₄, thereby indicating that the composite had been magnetically incorporated in agreement with previous studies.¹⁹

Magnetic properties of the Fe₃O₄−HNT/CTS composite are shown in Figure 6. The curves showed that magnetization increased with an increase in the magnetic field, and also they displayed symmetrical nature and passed through the origin. The hysteresis loop shows zero coercivity with zero remanence, implying that the composite has a super-
paramagnetic property. When compared with pure Fe₃O₄ with a magnetization value of 0.78 emu mg⁻¹ (inset), Fe₃O₄−HNT/CS shows a lower saturation magnetization of 0.12 emu mg⁻¹, and this can be attributed to the presence of larger fractions of CTS and HNT in the composite.

2.2. Effects of Contact Time and Initial Concentrations on Adsorption Capacities. The effects of contact time and initial concentrations on the uptake of CR by HNT/CS and Fe₃O₄−HNT/CS are presented in Figure 7a,b. A rapid adsorption of dye was noticed in about 10–15 min of the experiment, then a quasi-equilibrium was established, and the process displayed no significant increase in dye uptake after 30 min in the solutions with the two adsorbents, inferring a dynamic equilibrium (30–180 min). The adsorption capacity at equilibrium increases from 9.2 to 35.0 and 8.7 to 30.9 mg g⁻¹ for Fe₃O₄−HNT/CS and HNT/CS, respectively, as the initial concentrations of CR increase from 50 to 200 mg L⁻¹.

2.3. Effect of pH on the Removal Efficiency of the Adsorbent. The chemistry of the adsorption medium, to certain extent, is a determinant in the adsorbent and adsorbate interaction, thereby making adsorption highly pH-dependent. The efficiency of CR removal from its aqueous solution as a function of pH between pH values of 2 and 10 is presented in Figure 8. The pKₐ of CR is 4.1; therefore, at lower pH, the negatively charged molecules of the dye predominate in the solution (Figure 8a), making part of the adsorbent soluble and leading to inefficiency of the composite. As the pH increases, the composite becomes more stable and the surface charge leads to an increase in electrostatic interaction between the dye molecule and the adsorbent. Fe₃O₄−HNT/CS adsorbed slightly higher than the HNT/CS composite, which may be due to additional surface charges provided by the magnetic nanoparticles.

2.4. Effect of Adsorbent Dosage on Removal Efficiency. The effect of adsorbent dosage on the removal efficiency of CR by Fe₃O₄−HNT/CS and HNT/CS is shown in Figure 9. The increase in adsorbent dosages from 10 to 40 mg of Fe₃O₄−HNT/CS led to a corresponding increase in adsorption efficiency from 97.9 to 99.6%, whereas the efficiency of HNT/CS increased from 96.07 to 97.85% as the dosage increased from 10 to 30 mg. These increase in efficiencies may be attributed to increment in the number of adsorption sites available for adsorption. However, a further increase in adsorbent dosages led to reduced efficiency; these observations may be a result of particle aggregation, leading to a decrease in the total surface area of the adsorbent and an increase in the diffusional path length.

2.5. Adsorption Isotherms. Adsorption models are mathematical and fundamental equations used to quantify and explain the mechanism of the adsorbent–adsorbate equilibrium. In this study, the equilibrium data were analyzed with nonlinear models of Langmuir, Freundlich, Dubinin–Radushkevich, and Tempkin isotherms presented in Table 1. The details of these models had been given elsewhere.

| Table 1. Isotherm Models for the Adsorption Study |
|----------------|----------------|----------------|
| name           | model          | parameters     |
| Langmuir       | \( Q_{eq} = \frac{Q_{max} C_{eq}}{1 + bC_{eq}} \) | \( Q_{max}, b, R_L \) |
| Freundlich     | \( Q_{eq} = \frac{Q_{max} C_{eq}}{1 + bC_{eq}} \) | \( K_f, n \) |
| Tempkin        | \( Q_{eq} = \frac{Q_{max}}{1 + aT_{eq}} \) | \( a, b, T \) |
| Dubinin–Radushkevich | \( Q_e = \frac{Q_{max}}{1 + \beta e^{-\beta C_{eq}}} \) | \( Q_{max}, \beta, E \) |

The isotherm models were fitted into the experimentally determined \( Q_e \) vs \( C_{eq} \) by nonlinear regression using the Scientist 2.0 software package for Windows (Micromath Scientific Software, Salt Lake City, UT). The adequacy and fitness of the isotherm equation to the adsorption data were based on the values of the correlation coefficients, \( R^2 \). Figure 10 shows isotherm fits for CR adsorption by HNT/CS and Fe₃O₄−HNT/CS, and they were obtained through the parameters presented in Table 2. From the figure, it is obvious that the experimental and the theoretical data displayed a higher level of agreement, which is evident in the values of \( R^2 \) obtained for isotherm parameters.

Figure 9. Effects of adsorbent dosage on adsorption of CR by Fe₃O₄−HNT/CS and HNT/CS.
model was used to investigate the diffusion-rate-controlling steps affecting the surface reaction, to properly recognize the adsorption kinetics. The Elovich kinetic model was used to study the influence of pore diffusion on the adsorption kinetics, and the Bangham model was used to study the influence of pore diffusion on the adsorption kinetics, whereas double-exponential kinetic models properly analyzed the two-step adsorption mechanism, i.e., the rapid and slow adsorption steps, respectively.

The kinetic models were fitted into the experimentally determined \( Q_t \) vs \( t \) by linear regression, as described for the isotherm fits. The adequacy as well as the fitness of the kinetic equations to the experimental data was based on the values of the correlation coefficients, \( R^2 \), and sum square error function (%SSE).

The pseudo-first-order fits (Figure 11a,b) and second-order kinetic fits (Figure 12c,d) for the adsorption of CR on \( \text{Fe}_3\text{O}_4 \)–\( \text{HNT/CS} \) were also shown in Tables 4 and 5. Pseudo-first-order adsorption kinetics by the \( \text{Fe}_3\text{O}_4 \)–\( \text{HNT/C} \) composite displayed correlation coefficients, \( R^2 \), ranging between 0.982 and 0.995 with the experimental values of \( Q_e \) showing a wide deviation from the calculated values (Table 4). The pseudo-second-order parameter \( R^2 \) ranged between 0.989 and 0.997, the experimental values of \( Q_e \) are a bit close to the calculated values, and the %SSE showed that the adsorption process for this adsorbent is best explained by the pseudo-second-order kinetic model. The rate constant \( k_2 \) is in the magnitude of \( 10^{-3} \); it decreases with an increase in concentration, and the lower values obtained suggest a longer equilibrium time.

The adsorption by HNT/CS displayed a contrary mechanism (Table 5); the %SSE and calculated \( Q_e \) supported the pseudo-first-order kinetic mechanism.

The fitting results by the Elovich model (Figure 12a,b) and Bangham model (Figure 12c,d) were as displayed, whereas the corresponding parameters are given in Tables 4 and 5. The Elovich model displayed a better fit for adsorption by the two adsorbents; variation in \( \beta \) was noted as the CR concentration increased, which could be attributed to the relationship between the surface activation energy and dye concentration; and the \( R^2 \) and %SSE values showed that the model perfectly fitted the data from the two adsorbents. The Bangham model displayed good agreement with the experimental data from the adsorption processes, and the Bangham constant \( k_0 \) depicts the

### Table 2. Isotherm Parameters for the Adsorption of CR by HNT/CS and \( \text{Fe}_3\text{O}_4 \)–\( \text{HNT/CS} \)

| Isotherm          | Parameter | HNT/CS | \( \text{Fe}_3\text{O}_4 \)–\( \text{HNT/CS} \) |
|-------------------|-----------|--------|-----------------------------------------------|
| Langmuir          | \( Q_{max} \) (g mg\(^{-1}\)) | 41.535 | 54.491 |
|                   | \( b \) (L mg\(^{-1}\)) | 0.133 | 0.024 |
|                   | \( R_k \) | 0.075 | 0.299 |
|                   | \( R^2 \) | 0.999 | 0.996 |
| Freundlich        | \( K_f \) (g mg\(^{-1}\) min\(^{-1/2}\)) | 9.499 | 2.267 |
|                   | \( 1/n \) | 0.373 | 0.558 |
|                   | \( R^2 \) | 0.995 | 0.994 |
| Tempkin           | \( b_t \) (L mol\(^{-1}\)) | 278.645 | 223.282 |
|                   | \( a_t \) (L mg\(^{-1}\)) | 1.337 | 0.262 |
|                   | \( R^2 \) | 0.998 | 0.997 |
| Dubinin–Radushkevich | \( Q_s \) (g mg\(^{-1}\)) | 30.293 | 28.737 |
|                   | \( \beta \times 10^3 \) (mol kJ\(^{-1}\)) | 1.97 | 2.19 |
|                   | \( E \) (kJ mol\(^{-1}\)) | 15.914 | 15.126 |
|                   | \( R^2 \) | 0.982 | 0.993 |

The kinetic models were fitted into the experimentally determined \( Q_t \) vs \( t \) by nonlinear regression, as described for the

### Table 3. Kinetic Models for the Adsorption Study

| Name                | Model                                                                 | Parameters |
|---------------------|-----------------------------------------------------------------------|------------|
| pseudo-first-order  | \( Q_t = Q_e(1 - e^{-kt}) \)                                        | \( Q_e, k \) |
| pseudo-second-order | \( Q_t = \frac{k_2Q_{\text{eq}}^2}{1 + 4kt} \)                         | \( Q_{\text{eq}}, k_2 \) |
| Elovich             | \( Q_t = \frac{1}{\beta} \ln(\alpha \beta t + 1) \)                  | \( \alpha, \beta \) |
| intraparticle diffusion | \( Q_t = Q_{\text{eq}} - (D_1e^{-k_1t} + D_2e^{-k_2t}) \) | \( k_{\text{eq}}, C_i \) |
| Bangham             | \( Q_t = Q_{\text{eq}} - [D_1e^{-k_1t} + D_2e^{-k_2t} + D_3e^{-k_3t}] \) | \( D_1, D_2, k_{\text{eq}}, k_i \) |
adsorption rate of the adsorbent. From the tables, it is obvious that the rate increases as the concentration of the dye increases. The correlation coefficient $R^2$ and %SSE obtained for this model indicate that the model perfectly explains the kinetics of adsorption as pore-diffusion-controlled adsorption.32,33

The intraparticle diffusion and double-exponential models’ fitting results are displayed in Figure 13a–d for further understanding of adsorption of CR on HNT/CS and Fe$_3$O$_4$–HNT/CS, respectively. The corresponding parameters in the tables indicate high correlation coefficient, $R^2$, and reasonably lower values of %SSE, suggesting better fittings. The intraparticle model fitting and parameters for the two adsorbents show that the curves do not pass through the origin, i.e., $C_1 \neq 0$, which is a confirmation that although the process involved intraparticle diffusion, it is not the sole rate-controlling step. The adsorption process is best described by the two-step mechanism, as confirmed by the intraparticle diffusion model. Using the double-exponential model, the fits from this model (Figure 13c,d) displayed good agreement with the data and the process could be described as having the first step of rapid dye uptake involving external and internal diffusion followed by a prevailing slow step controlled by intraparticle diffusion adsorption until equilibrium is reached.

2.7. Thermodynamics of the Adsorption Process. The thermodynamics of the adsorption processes was studied by subjecting equilibrium data at various temperatures to respective thermodynamic eqs 1–3. These equations enable the determination of the free energies ($\Delta G^0$), enthalpies ($\Delta H^0$), and changes in entropy ($\Delta S^0$) associated with the adsorption processes.33

$$K_d = \frac{m \times Q_e}{C_e}$$

(1)

where $m$ is the adsorbent dosage, $Q_e$ is adsorption capacity at equilibrium, and $C_e$ is the equilibrium concentration of the dye.

$$\Delta G^0 = -RT \ln K_d$$

(2)

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

(3)

The van’t Hoff plot for the adsorption of CR by Fe$_3$O$_4$–HNT/CS and HNT/CS is shown in Figure 14, whereas the thermodynamics parameters are presented in Table 6.

The thermodynamic parameters obtained for the two adsorbents revealed that the enthalpies of adsorption, $\Delta H^0$, were positive, connoting an increase in the adsorption efficiency with an increase in the process temperature, whereas the positive values of entropies, $\Delta S^0$, indicated that there was an affinity between the CR molecules and adsorbent surfaces and that the degree of dispersion of the process increased with an increase in temperature. The spontaneity of the adsorption of CR by the adsorbents was revealed by the negative Gibbs free energy ($\Delta G$) values obtained at various temperatures, suggesting favorable adsorption of CR by the adsorbents at a higher temperature.

2.8. Regeneration Study. One of the important factors usually considered for the selection of adsorbent is reusability;
the higher the reusability, the lower the cost. To investigate the reusability of Fe₃O₄–HNT/CS and HNT/CS, the adsorption regeneration test were carried out according to the method described by Wang et al. The solution of Congo

![Figure 12. Elovich (a, b) and Bangham kinetic model (c, d) fits for the adsorption of CR on Fe₃O₄–HNT/CS and HNT/CS, respectively.](image)

Table 4. Kinetic Parameters for the Adsorption of CR by Fe₃O₄–HNT/CS

|                | pseudo-first-order kinetics model parameters | pseudo-second-order kinetics model parameters |
|----------------|---------------------------------------------|-----------------------------------------------|
| Cₒ (mg L⁻¹)   | 50  75  100  150  200                       | Cₒ (mg L⁻¹)                                   |
| Qₑₑ (mg g⁻¹)  | 75  90  105  120  135                       | Qₑₑ (mg g⁻¹)                                 |
| Qₑₑ (mg g⁻¹)  | 9.798 10.19 11.32 12.68 13.96               | Qₑₑ (mg g⁻¹)                                 |
| kₑₑ (min⁻¹)   | 0.525 0.149 0.199 0.184 0.244                | kₑₑ × 10^3 (g mg⁻¹ min⁻¹)                    |
| R²             | 0.992 0.995 0.982 0.988 0.989                | R²                                           |
| % SSE          | 0.107 0.304 0.335 1.62 1.907 % SSE            |

Elovich Model Parameter

|                | Bangham Model Parameter                          |
|----------------|-----------------------------------------------|
| Qₑₑ (mg g⁻¹)  | 10.885 16.725 19.819 26.83 41.088              |
| a (mg (g min)⁻¹) | 129.681 500.707 2742.43 906.472 3854.9       |
| β (g mg⁻¹)     | 1.337 0.476 0.489 0.302 0.225                 |
| R²             | 0.998 0.997 0.998 0.999 0.999 % SSE            |
| % SSE          | 0.00555 0.00279 0.00211 1 × 10⁻⁶ 0.0001 % SSE   |

Intraparticle Diffusion Model Parameters

|                | Double-Exponential Model Parameters            |
|----------------|-----------------------------------------------|
| Kₑ⁄ (mg g⁻¹ min⁻¹/²) | 2.574 3.104 4.133 5.199 8.43             |
| Cₙ (mg g⁻¹)   | 1.027 0.975 1.065 1.632 2.8                |
| R²             | 0.995 0.986 0.979 0.958 0.973 % SSE          |
| % SSE          | 0.733 3.449 0.983 3.533 2.132                |
| Kₑ⁄ (mg g⁻¹ min⁻¹/²) | 0.077 0.47 0.382 1.051 1.48             |
| Cₙ (mg g⁻¹)   | 9.371 11.323 15.153 15.97 26.007 % SSE     |
| R²             | 0.999 0.996 0.999 0.999 0.999 % SSE          |
| % SSE          | 0.206 2.977 1.495 6.37 5.339                |

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red dye was poured into a syringe previously loaded with the adsorbents, and the syringe was then inverted into a sample collection bottle (Figures 15a and 16). The solution from outlet becomes clearer and the concentration of the dye in the outlet by comparing its absorbance with that of dye solution. The strong electrostatic interaction between the adsorbent and the dye molecules makes it difficult for the dye to be eluted by deionized water (Figure 15b); however, squeezing with 0.1 M

![Figure 13](https://acs-somega.org/article/acsomega.8b02960/2019/4/2425-2436)

**Figure 13.** Intraparticle diffusion (a, b) and double-exponential model (c, d) fits for the adsorption of CR on Fe₃O₄–HNT/CS and HNT/CS, respectively.

Table 5. Kinetic Parameters for the Adsorption of CR by HNT/CS

| Parameter | pseudo-first-order | pseudo-second-order |
|-----------|-------------------|---------------------|
| C₀ (mg L⁻¹) | 50 | 75 | 100 | 150 | 200 |
| Qe₁ (mg g⁻¹) | 10.94 | 13.03 | 24.392 | 32.316 | 40.708 |
| Qe₂ (mg g⁻¹) | 11.078 | 12.904 | 24.97 | 32.661 | 42.518 |
| k₁ (min⁻¹) | 0.191 | 0.277 | 0.142 | 0.189 | 0.179 |
| R² | 0.994 | 0.998 | 0.999 | 0.999 | 0.999 |
| %SSE | 0.016 | 0.009 | 0.056 | 0.011 | 0.198 |

Elovich Model Parameters

| Parameter | pseudo-first-order | pseudo-second-order |
|-----------|-------------------|---------------------|
| Qe₁ (mg g⁻¹) | 11.439 | 13.316 | 25.1 | 33.301 | 43.365 |
| α (mg (g min⁻¹)) | 115.005 | 540.046 | 73.209 | 548.771 | 364.25 |
| β (g mg⁻¹) | 0.747 | 0.949 | 0.284 | 0.273 | 0.192 |
| R² | 0.998 | 0.999 | 0.991 | 0.994 | 0.989 |
| %SSE | 0.0021 | 0.0005 | 0.0008 | 0.0009 | 0.0043 |

Bangham Model Parameters

| Parameter | pseudo-first-order | pseudo-second-order |
|-----------|-------------------|---------------------|
| Qe₁ (mg g⁻¹) | 9.547 | 11.841 | 20.26 | 28.216 | 36.165 |
| k₁ (mg g⁻¹ min⁻¹) | 6.78 | 9.475 | 13.59 | 20.76 | 25.923 |
| s | 0.126 | 0.082 | 0.146 | 0.113 | 0.123 |
| R² | 0.998 | 0.999 | 0.998 | 0.993 | 0.989 |
| %SSE | 0.016 | 0.008 | 0.029 | 0.016 | 0.012 |

Double-Exponential Model

| Parameter | pseudo-first-order | pseudo-second-order |
|-----------|-------------------|---------------------|
| K₁d (mg g⁻¹ min⁻⁰·⁵) | 2.488 | 3.249 | 5.718 | 7.84 | 10.866 |
| C₁ (mg g⁻¹) | 0.73 | 0.889 | 0.178 | 1.166 | 0.092 |
| R² | 0.98 | 0.982 | 0.997 | 0.991 | 0.991 |
| %SSE | 0.275 | 0.114 | 0.719 | 0.059 | 0.13 |

| Parameter | pseudo-first-order | pseudo-second-order |
|-----------|-------------------|---------------------|
| K₂d (mg g⁻¹ min⁻⁰·⁵) | 0.293 | 0.189 | 0.274 | 0.455 | 0.584 |
| C₂ (mg g⁻¹) | 8.975 | 11.659 | 22.424 | 28.976 | 37.552 |
| R² | 0.998 | 0.999 | 0.999 | 0.999 | 0.999 |
| %SSE | 0.575 | 0.24 | 0.138 | 0.238 | 0.048 |
enthalpy, and entropy changes proved that the present processes. The thermodynamic parameters of free energy, models are suitable for the prediction of the adsorption followed by a prevailing slow step controlled the rate. The

\[ \Delta G = -RT \ln K \]

respectively. The kinetic models showed that intraparticle removal.

are promising adsorbents and highly economical for CR removal.

that the adsorbent exhibited excellent resilience, recyclability, and durability with better reusability; therefore, the composites are promising adsorbents and highly economical for CR removal.

\[ \text{Table 6. Thermodynamic Parameters for Adsorption of CR by Fe}_3\text{O}_4\text{--HNT/CS and HNT/CS} \]

| temp (K) | \( K \) | \( \Delta G \) (kJ mol\(^{-1}\)) | \( \Delta H \) (kJ mol\(^{-1}\)) | \( \Delta S \) (J mol\(^{-1}\) K\(^{-1}\)) | \( R^2 \) |
|---------|-------|----------------|----------------|----------------|------|
| 303     | 1.132 | -2.852         | 69.469         | 240.458        | 0.949|
| 313     | 3.246 | -8.447         | 1.235          | 5.678          | 0.893|
| 323     | 3.505 | -9.411         | 3.893          | 3.578          | 0.849|
| 333     | 3.838 | -10.625        | 6.372          | 6.372          | 0.803|
| 343     | 4.316 | -12.308        | 8.447          | 8.447          | 0.753|

\[ \text{Figure 14. van’t Hoff fit for adsorption of CR by Fe}_3\text{O}_4\text{--HNT/CS and HNT/CS.} \]

NaOH solution for about 30 s and washing several times with distilled water until neutral pH restores the adsorbent for reuse (Figure 15c). Similar processes were repeated for the magnetic composite (Figure 15d) with similar observations. A series of compression and recycling procedures were performed, and it is amazing to note that the adsorbents were recovered with little or no deformation, with intact efficiency of the adsorbents until after about 6 cycles when it was reduced to ≈95 and 87% for HNT/CS and Fe\(_3\)O\(_4\)--HNT/CS, respectively. This implied that the adsorbent exhibited excellent resilience, recyclability, and durability with better reusability; therefore, the composites are promising adsorbents and highly economical for CR removal.

3. CONCLUSIONS

The synthesis of Fe\(_3\)O\(_4\)--HNT/CS and HNT/CS was successful according to the results of characterizations, as well as their use as adsorbents for the removal of CR from aqueous solution. However, the adsorption processes for the removal of CR dye depend on the contact time, initial pollutant concentration, solution pH, adsorbent dosage, and temperature. The isotherm fits well with the adsorption data with the Langmuir isotherm model showing the maximum monolayer adsorption capacities of 41.54 and 54.49 mg g\(^{-1}\) for adsorption of CR by Fe\(_3\)O\(_4\)--HNT/CS and HNT/CS, respectively. The kinetic models showed that intraparticle diffusion was not the sole rate-determination step for the adsorption process; rather, rapid external and internal diffusion followed by a prevailing slow step controlled the rate. The models are suitable for the prediction of the adsorption processes. The thermodynamic parameters of free energy, enthalpy, and entropy changes proved that the present adsorption process is feasible, spontaneous, endothermic, and random in nature. The overall analysis by kinetics, isotherms, and thermodynamics suggested that the adsorption of CR by Fe\(_3\)O\(_4\)--HNT/CS and HNT/CS is through chemisorption involving interaction between dye molecules and the functional groups present on the adsorbent surfaces. Consequently, it is obvious that Fe\(_3\)O\(_4\)--HNT/CS and HNT/CS are effective adsorbents for the removal of Congo red dye from aqueous solution.

4. MATERIALS AND METHOD

4.1. Materials. Halloysite clay nanotube (HNT), chitosan (90% deacetylation degree), iron(III) chloride hexahydrate (FeCl\(_3\)-6H\(_2\)O), and iron(II) chloride tetrahydrate (FeCl\(_2\)-4H\(_2\)O) (AR grade) were products of Sigma-Aldrich. Hydrochloric acid and sodium hydroxide were procured from Merck, India. Congo red dye was a product of Loba Chemicals, India. Other reagents were of analytical grade, and MilliQ water was used for all of the experiments.

4.2. Synthesis of the Spongelike HNT/CS Composite.

HNT was activated by suspending 4 g of the powder in 40 mL of NaOH (24% w/v) and sonicated at 50 °C for 1 h. It was washed with distilled water and dried at 105 °C overnight, and the resulting solid was ground to ≈200 μm mesh size. CS was also activated by dissolving 1 g of the powder in 25 mL of acetic acid (2% v/v) solution under continuous stirring. Then, 1 g of the activated HNT was dispersed into the solution of the chitosan sonicated for 25 min and stirred further for 2 h. At that point, the arrangement was poured into a round and hollow plastic shape. Subsequently, it was frozen into ice at −20 °C, kept overnight in a freezer, and then lyophilized at −80 °C using a freeze dryer. The product was washed with distilled water until pH is neutral and dried in a vacuum oven overnight at 60 °C.

4.3. Preparation of the Fe\(_3\)O\(_4\)--HNT/CS Composite.

The mixed solution of 2 mmol of FeCl\(_3\)-6H\(_2\)O and 1 mmol of FeCl\(_2\)-4H\(_2\)O (50 mL) was prepared and stirred for 1 h, and 1 g of prepared HNT/CS was immersed in the solution mixture under mechanical shaking. It was then transferred into 50 mL of ammonia solution (35% v/v) to allow coprecipitation of the magnetic particles. The mixture was transferred into a water bath at 60 °C where 2 mL of glutaraldehyde (25% v/v) was slowly dropped into the reaction system and stirred for another 1 h. The product was washed thrice with ethanol and distilled water and then dried overnight in a vacuum oven.

4.4. Characterizations. The morphology and elemental composition of the prepared spongelike HNT/CS and Fe\(_3\)O\(_4\)--HNT/CS were investigated using SEM (Hitachi, Japan, S-4900H) equipped with energy-dispersive X-ray (EDX). X-ray diffraction (XRD) patterns of these samples were obtained by an X-ray diffractometer (PANalytical, XPert PRO, Netherlands) using Cu Kα (γ = 1.54178 Å) radiation. Fourier transform infrared (FTIR) spectra were recorded from 400 to 4000 cm\(^{-1}\).

\[ \text{Table 6. Thermodynamic Parameters for Adsorption of CR by Fe}_3\text{O}_4\text{--HNT/CS and HNT/CS} \]

| temp (K) | \( K \) | \( \Delta G \) (kJ mol\(^{-1}\)) | \( \Delta H \) (kJ mol\(^{-1}\)) | \( \Delta S \) (J mol\(^{-1}\) K\(^{-1}\)) | \( R^2 \) |
|---------|-------|----------------|----------------|----------------|------|
| 303     | 1.132 | -2.852         | 69.469         | 240.458        | 0.949|
| 313     | 3.246 | -8.447         | 1.235          | 5.678          | 0.893|
| 323     | 3.505 | -9.411         | 3.893          | 3.578          | 0.849|
| 333     | 3.838 | -10.625        | 6.372          | 6.372          | 0.803|
| 343     | 4.316 | -12.308        | 8.447          | 8.447          | 0.753|

\[ \text{Figure 15. Photos and SEM images of the prepared HNT/CS composites.} \]

\[ \text{Figure 15. Photos and SEM images of the prepared HNT/CS composites.} \]
4000 cm\(^{-1}\) in a TENSOR 27 spectrometer (Bruker, Germany) using the KBr pellet technique. The magnetic properties of the Fe\(_3\)O\(_4\) and Fe\(_3\)O\(_4\)−HNT/CS composites were characterized with a vibrating-sample magnetometer (VSM) (Lake Shore, 735 VSM, model 7304), whereas thermal stabilities were evaluated using thermogravimetric analysis (TGA) recorded by an SDT Q600 V8.3 Build 101 simultaneous DSC−TGA instrument.

**4.5. Preparations of Aqueous Solution of the Dye.** A stock solution containing Congo red dye was prepared by dissolving accurately weighed solute such that the solution contained 1 g equivalent of the dye in 1 L of MilliQ water, and working standard solutions were then prepared from the stock by dilution. The pH of the working solution was maintained with aliquot of HCl or NaOH prior to the adsorption study.

**4.6. Adsorption Studies.** The batch equilibrium and kinetic adsorption studies were conducted using Erlenmeyer flasks containing 25 mL of dye solutions with a concentration range of 50–200 mL\(^{-1}\) and with 0.4 g L\(^{-1}\) adsorbents. The contents were placed in a regulated water bath (30 ± 1 °C) with a shaker at 150 rpm, samples were collected at pre-set time intervals, and the dye concentrations in aqueous media were recorded by reading the absorbance at 497 nm on a UV−vis spectrophotometer (UV−vis−NIR, Varian 500 Scan Cary). The amounts of dye adsorbed (mg g\(^{-1}\)) by the adsorbents as a function of time \((Q_t)\) and at equilibrium \((Q_e)\) were estimated according to eqs 4 and 5 below

\[
Q_t = \frac{(C_0 - C_t)}{m} \times V
\]

\[
Q_e = \frac{(C_0 - C_e)}{m} \times V
\]

where \(C_0\), \(C_t\), and \(C_e\) are the initial, time \(t\), and equilibrium concentrations (mg L\(^{-1}\)) of the dye, respectively; \(V\) is the volume (L) of the solution; and \(m\) is the mass (g) of the adsorbent.
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