Adsorption removal of Congo red onto L-cysteine/rGO/PANI nanocomposite: equilibrium, kinetics and thermodynamic studies

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ABSTRACT
In this paper, adsorption of Congo red (CR) onto L-cysteine decorated with reduced graphene oxide/polyaniline composite at room temperature was investigated. The morphology and structure properties of as-prepared nanocomposite were verified by UV–visible spectroscopy (UV–visible), powder X-ray diffraction (XRD), Fourier transform infrared spectrophotometry (FTIR), scanning electron microscopy (SEM), and Brunauer Emmett Teller (BET) studies. Effect of absorbent dosage, contact time, initial dye concentration and temperature were studied and optimal conditions for the adsorption process of Congo red dye were found. The obtained results indicated that isotherms data fitted well to Langmuir model. While kinetics data fitted well to the pseudo-second-order kinetic equation and the adsorption process was generally governed via intra-particle diffusion. Thermodynamic data showed that adsorption process of CR was endothermic and spontaneous in nature. At optimal conditions, the maximum adsorption capacity of CR was calculated and found to be 56.57 mg/g, which shows that L-cysteine functionalized reduced graphene oxide/polyaniline based nanocomposite can be efficiently used for wastewater management.

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1. Introduction
Various industries, particularly food and textile industries frequently use pigments and dyes to colour their products. As a result, these industries discharge huge amounts of their coloured effluents into the environment. The release of these coloured substances poses a serious threat to the environment [1]. Their discharge in freshwater sources leads to carcinogenesis, mutagenesis, teratogenicity, chromosomal fractures and respiratory toxicity. Due to their non-biodegradable nature, they tend to cause skin irritation, allergic dermatitis, mutations and cancer in humans and disorder in photosynthesis activity of aquatic plants, manifestation of eutrophication phenomena, increasing manure hardness, turbidity, death and demolition of aquatic beings [2–4]. Congo red a azo dye [5] can affect blood factors for instance clotting, induced somnolence, respiratory problems, serious irritations to eyes, skin and alimentary tract and is also mutagenic and carcinogenic [6,7]. Despite the need of dyes removal to overcome the damaging concerns in the environment and living beings, treatment of dye-contaminated wastewater is a global problem as they demonstrate resistance to breakdown with exposure to water, sunlight, soap [8]. Therefore, several techniques like adsorption, flocculation, coagulation, ozonation, membrane filtration, radiolysis, electrochemical and advanced oxidation processes are used for decolorizing the industrially polluted water on the basis of various properties like high efficiency, economic feasibility and easy handling [9–11]. Among all these methods, adsorption proved itself as a promising removal method credited to the merits of cost effectiveness, high design flexibility, high performance in removal of small molecules, least fluctuations, resistance to toxic matter, low discharge ratio and easy handling [12–14]. For dye removal, various types of adsorbents are extensively studied including activated carbon [15], metal oxides [16], polymers [17], zeolites [18], agricultural residues [19] CuO–ZnO tetrapodal hybrid [20], Cu–WO3 [21] tpolydimethylsiloxane@zinc oxide tetrapod@iron oxide nanorod nanohybrid [22], ZnO-tetrapods/activated carbon (ZnO–T/AC) nanocomposite [23] and carboxylated cellulose nanofibril films [24]. But among them, few
adsorbents face some difficulties like low adsorption capacity, insufficient extraction and issues of recycling and reuse [25].

The concept of adsorption has been completely revolutionized by the discovery of two-dimensional single layer of carbon atoms named as graphene by Sir Novoselov and Sir Geim in 2004 [26]. Since its discovery, graphene and its composites has attracted tremendous attention of researchers in many fields due to its special properties like super large surface area, flat structure and good chemical stability [27,28]. It has sp² hybridized honeycomb like structure and has applications in electronic devices, solar cells and sensors [29–31]. In recent years, graphene based materials are being utilized for the effective abstraction of toxins from wastewater. It has wide range of properties like novel electronic properties, elastic properties and extraordinary electronic conductivity, which suggested that this material can be used for removal of dyes [32–34]. In recent years, various metal and metal oxides nanoparticles (Fe₂O₃, Ag, CuO, NiO) and conducting polymers (PANI, PP, PEDOT) have been utilized as effective adsorbents towards the adsorption of various dyes [35,36]. Rajumon et al. studied the adsorption of Basic Fuchsin (BF) and Methylene Blue (MB) on rGO. The high adsorption capacity for the removal of these dyes was found which is due to electrostatic attraction, π–π and n–π interactions of rGO [37]. Li et al. prepared rGO/PANI nanocomposite for adsorption of aqueous Hg [38]. The adsorption capacity of polyaniline was enhanced with the incorporation of rGO which was revealed by SEM, TEM and BET studies. Ghahramani et al. studied the removal of malachite green dye with the help of rGO coated polyaniline [39]. The prepared composite followed pseudo-first-order kinetics and showed a very high adsorption capacity. PANI possess a delocalized structure and electrochemical units of benzenoid and quinonoid. It also has good environmental stability, ease of synthesis and fine-tuned properties [40,41]. Whereas L-cysteine has a high metal chelating capability and it has been extensively utilized for adsorptive removal of various organic dyes [42,43]. Therefore, introduction of L-cysteine in rGO/PANI could further enhance the surface area of graphene sheets which may help in more efficient adsorption of Congo red.

In this work, we have employed reduced graphene oxide composite with the dispersion of polyaniline and L-cysteine on graphene sheets as a novel adsorbent material for the effective removal of carcinogenic dye Congo red (CR). The prepared nanocomposite has been characterized with several techniques like UV–visible spectroscopy, XRD, FTIR, SEM and BET. The adsorption properties of the nanocomposite toward CR dye in aqueous solution were investigated. Furthermore, adsorption mechanism has also been studied via isotherms, kinetic models and thermodynamic analysis.

1. **Novelty statement**

In this study the utilization of L-Cys/rGO/PANI nanocomposite for the removal of congo red is reported, the novelty points of this study are

1. L-Cys/rGO/PANI nanocomposite was not reported for the removal of congo red from wastewater.
2. It is an efficient, cheap and rapid method for the removal of dyes.
3. Non-linear forms of kinetic and isotherms models are applied.

2. **Experimental details**

2.1. **Reagents and materials**

All the required chemicals including graphite powder, potassium permanganate, sodium nitrate, hydrogen peroxide, L-cysteine, ammonium peroxydisulfate (APS) were purchased from standard international supplied, i.e. Sigma–Aldrich. They were of analytical grade and most of them have purity ≥ 99.9%. Furthermore, we have not carried out any purification of these chemicals. They were used as received.

2.2. **Instrumentation**

UV–visible spectrophotometer (Agilent Technologies Cary 60) was used for analysing optical absorption spectra of samples. FT-IR spectrum was measured via spectrophotometer (Nexus 470) in the range of 400–4000 cm⁻¹. Structure measurements were done by XRD. The XRD spectrometer (Philips X pert PRO) used Cu Kα as a radiation source. The surface morphology of sample was investigated by ZEISS LEO SUPRA 55 SEM.

2.3. **Adsorption studies**

For adsorption of CR, an amount of composite from 0.005 to 0.030 g was added to dye solution (10 mL) in concentrations range from 30 to 180 mgL⁻¹ at temperature of 10–60°C. After 1 h of continuous shaking on an orbital shaker, the composite was taken out from the solution by filter paper. The equilibrium concentration of nanocomposites was calculated by UV–visible spectrophotometer at λ max (498 nm⁻¹).

\[
C_{eq} = \frac{(C_0 \times A_f)}{A_i}
\]

where \(C_0\) (mgL⁻¹) denotes the initial dye amount. \(A_i\) and \(A_f\) are the initial and final absorbance.

The percentage removal was find out by following equation:

\[
\% \text{removal } = \frac{(C_0 - C_{eq})/C_0} \times 100
\]
The adsorbed amount of dye from solution was determined by

\[ Q_{eq} = (C_0 - C_{eq}) \frac{m}{V} \]  

(3)

where \( C_0 \) (mgL\(^{-1}\)) and \( C_{eq} \) (mg L\(^{-1}\)) signifies initial dye amount and equilibrium dye concentration, while \( V \) (L) is the volume and \( m \) (g) is the mass of composite.

To optimize nanocomposite amount, different doses of reduced graphene nanocomposite (0.005–0.03 g) were added in 30 mgL\(^{-1}\) of reduced graphene nanocomposite (0.005–0.03 g) were added in 30 mgL\(^{-1}\) dye solution (10 mL). After 1h of shaking, the adsorbent was removed from aqueous solution of CR and the subsequent solution was examined to find the amount of dye remaining in solution.

The kinetic mechanism of dye was studied with the addition of 25 mg of nanocomposite in 10 ml dye solutions of 30 mgL\(^{-1}\) in flasks. Then these flasks were placed on an orbital shaker for different time intervals. At different time intervals, the adsorbent was removed from dye solution with the help of filter paper. The remaining dye concentration and relative dye adsorption were calculated.

Adsorption isotherms for CR were determined by adding 25 mg graphene nanocomposite into 10 mL of different concentrations (30–180 mgL\(^{-1}\)) of aqueous solutions of CR. The nanocomposite was separated from solution after 10 min. shaking and resultant solution was analysed for the dye concentration.

The thermodynamic studies of dye adsorption were carried out via addition of 25 mg of nanocomposite into 10 mL of 30 mgL\(^{-1}\) aqueous solution of Congo red dye at different temperatures ranging from 283 to 333 K. After shaking, the nanocomposite was separated and the solution was analysed for remaining dye concentration.

**2.4. Preparation of GO and rGO**

Graphene oxide was prepared by oxidation of graphite powder using modified Hummer’s method [44]. According to this approach, 1 g of sodium nitrate was added in 1 g of graphite powder. Here, sodium nitrate acts as an oxidizing agent. To the above solution, 50 mL of H\(_2\)SO\(_4\) was added gradually with continuous stirring for half an hour while keeping it in ice bath. Then 6 g of K\(_2\)MnO\(_4\) was mixed to the subsequent black coloured solution under constant stirring for about 180 min. After that, 300 mL of distilled water and 20 mL of H\(_2\)O\(_2\) were added in slurry to remove the excess of K\(_2\)MnO\(_4\). Furthermore, solution of H\(_2\)SO\(_4\) (6%) and H\(_2\)O\(_2\) (1%) was also added in the above solution to remove the residual K\(_2\)MnO\(_4\). After the addition of H\(_2\)SO\(_4\) and H\(_2\)O\(_2\), the solution was rinsed till the pH approaches to 7.0. The obtained product is GO.

The synthesized graphene oxide was then converted into reduced graphene oxide with help of hydrazine (NH\(_2\)NH\(_2\)) and ammonia (NH\(_3\)). In a standard process, for the conversion of GO into rGO, the suspension of GO (10 mL) was diluted with distilled water (90 mL) and then sonicated for 30 min to get good suspension. After that, 5 \( \mu \)L of hydrazine and 35 \( \mu \)L of ammonia were added in the above solution with the help of micropipette and at the same time solution was heated at 95°C for 60 min. The resulting black suspension of reduced graphene oxide was dried and stored for further use.

**2.5. Preparation of L-cysteine decorated rGO/PANI (Cys/rGO/PANI)**

An efficient and simple approach was used to synthesize amino acid based nanocomposite (L-Cys/rGO/PANI). In this process, APS acts as an oxidizing agent. Firstly, 100 mg powder rGO was added in 0.1M L-cysteine solution. The obtained mixture was ultra-sonicated for 30 min. Afterwards; 1 mL of aniline monomer was added in this mixture under constant stirring of 10 min with magnetic stirrer. Subsequently, 20 mL of 3 M APS solution was added drop wise to the above suspension at the same time while holding constant magnetic stirring. After that, the resultant mixture was removed from the stirrer and kept undisturbed for the 12 h. The appearance of black colour precipitates confirmed the reaction completion. The product was rinsed with the distilled water and acetone. The as-prepared nanocomposite was dried at 70°C. Scheme 1 shows the procedure of L-Cys/rGO/PANI preparation.

**3. Results and discussion**

**3.1. Characterization of L-Cys/rGO/PANI nanocomposite**

**3.1.1. SEM and BET analysis**

Figure 1(A) shows the scanning electron microscope image of composite L-Cys/rGO/PANI. The result clearly confirms the formation of nanocomposite of L-cysteine, polyaniline and nanosheets of rGO. BET surface area was determined with the help of N\(_2\) adsorption isotherm. BET isotherm of as-prepared nanocomposite is shown in Figure 1(B). The BET specific surface area of prepared adsorbent is calculated and found to be 45 m\(^2\)/g. The high surface area of nanocomposite can be attributed to the favourable fictionalization of polyaniline and L-cysteine onto the sheets of rGO.

**3.1.2. UV–visible analysis**

Figure 2(A and B) displays the UV–visible absorption bands of graphite powder, rGO, GO, L-cysteine and L-Cys/rGO/PANI nanocomposite. The graphite powder peak observed at 268 nm is moved to 233 nm in GO, which is due to the \( \pi - \pi^* \) transitions of C=C functionalities in ring. And another peak at 261 nm is appeared, which is accredited to \( \pi - \pi^* \) transitions of functional group C=O. The red shift in peak from 233 to 261 nm is indorsed to the reduction of GO into

\[ \text{\pi - \pi^* transitions of functional group C=O. The red shift in peak from 233 to 261 nm is indorsed to the reduction of GO into} \]
rGO, which shows the effective abstraction of oxygen containing groups from the interior of GO rendering it as rGO [45]. L-cysteine exhibits a distinct peak at about 217 nm which signifies the close resemblances with literature values [46]. The UV−visible spectra of composite L-Cys/rGO/PANI depicted three absorption peaks (220, 271, 360 nm) with an additional peak at 591 nm corresponding to rGO, L-cysteine, and polyaniline, which recommend the successful coating of L-cysteine and PANI onto the surface of rGO sheets.

3.1.3. FTIR and XRD analysis

FTIR was recorded to identify various active functional groups of as-prepared nanocomposite. FTIR patterns of rGO and L-cys/rGO/PANI are exhibited in Figure 3(A). The characteristic peak of rGO is observed at 1524 cm$^{-1}$ which shows the relocation of $\text{C}=\text{C}$ matrix of graphene nanosheets achieved after the reduction of GO into rGO [47]. In composite, S−H stretching peak at 2562 cm$^{-1}$ and O−H stretching peak at 3440 cm$^{-1}$ exhibits the presence of L-cysteine [48]. The various bands of PANI appeared at 852, 1173 and 1591, 1270, 1366, 1680 and 3232 cm$^{-1}$ associated to NH and CH stretching vibrations, benzoid ring and NH2 bending modes. N−H stretching peak occurs at 3232 cm$^{-1}$. C−H bending peak and benzoid ring of PANI exhibited at 1173 and 1591 cm$^{-1}$ [49]. The corresponding peaks of −CN stretching appeared at 852, 1270 and 1366 cm$^{-1}$. C=$\text{N}$ stretching peak marked at 1680 cm$^{-1}$. All these peaks expressed the presence of active amalgamation of precursors (rGO, L-cysteine and PANI).

XRD spectra of rGO and L-Cys/rGO/PANI are shown Figure 3(B). The observed peak of reduced graphene oxide lies on $2\theta = 23.64^\circ$ along with d-spacing of 0.38 nm. The broad XRD peak at $2\theta = 23.64^\circ$ along with d-spacing of 0.38 nm confirmed the effective conversion of GO into rGO. The observed signal of rGO ($2\theta = 23.64^\circ$) was very close to the reported literature which confirms the removal of oxygen functionalities in intervening spaces of graphite nanostructures. In composites, sharp peaks are documented at 19.45°, 24.17°, 26.20°, 30.38° and 44.09° with inter-planar d-spacing 0.45, 0.83, 0.33, 0.20 and 0.20 nm. The peaks at 26.20°
Figure 2. UV–visible plots of (A) Graphite powder, rGO, GO and (B) L-cysteine and L-Cys/rGO/PANI.

Figure 3. (a) FTIR spectra and (b) XRD spectra of rGO and L-Cys/rGO/PANI.

and 30.38° are ascribed to the PANI [50], whereas the peak signals at 19.45° and 44.09° are of L-cysteine.

3.2. Adsorption measurements

3.2.1. Effect of composite dosage, initial dye amount and contact time

Effect of composite dosage on Congo red removal was investigated at room temperature and obtained results are given in Figure 4(A), that the maximum removal of Congo red dye was obtained in just 01 hr at 0.025 mg absorbent dosage. This high adsorption efficiency of nanocomposite can be credited due to the exceptionally large surface area of reduced graphene oxide based nanocomposite. There was no further significant change in adsorption takes place with the increase in adsorbent dosage. Therefore, 0.025 g of nanocomposite is optimized weight for further experimentation.

To investigate parameter of contact time, time span from 01 min to 120 min was studied with optimized weight of 0.025 g at room temperature. The results (Figure 4(B)) were just magnificent as only after 10 min almost 98% removal of Congo red was observed and no significant development was seen after 10 min which shows the excellent adsorption capacity of our synthesized nanocomposite for dye removal.

Initial dye concentration has an important impact on adsorption process so this parameter was also studied. Concentrations of 30–180 mg/L of Congo red dye were investigated by carrying out their adsorption with 0.025 g nanocomposite dosage and 10 min. Figure 4(C) shows that maximum removal of 92% was observed at 30 mgL⁻¹ while at higher concentrations, % removal of dye was also considerable which predicts higher adsorption capacity of composite for even highly concentrated dyes.

The temperature factor plays an important role in dye adsorption, therefore, its effect was investigated in a range of 283–333 K with 0.025 g amount of composite in 10 ml volume of 30 mgL⁻¹ concentrated dye solution,
10 min. contact time and at neutral pH. The results indicated that adsorption of Congo red dye increased from 85% to 96% with the increase in temperature from 283 to 333 K. The reason behind enhanced amount of adsorption with the increase in temperature may be either due to spurt of certain initially slow adsorption steps or owing to increase in active sites.

3.3. Kinetic of adsorption

Adsorption kinetic models provide useful information about equilibrium adsorption and clarify the mechanism of adsorption. In this research work, experiments were performed at room temperature and neutral pH. Various adsorption kinetic equations namely pseudo-first-order (PFO), pseudo-second-order (PSO) along with both linear and non-linear models and Elovich model with linear models were used to investigate the adsorption kinetics of CR on nanocomposite.

3.3.1. PFO kinetic equation

The first kinetic process of adsorption was elaborated by Lagergren (1898) through rate equation [51]. It is considered as the first kinetic model for describing adsorption rate on the basis of adsorption capability. The non-linear plot can be described as

\[ Q_t = Q_e \left(1 - e^{-kt}\right) \]  

The graphs of non-linear plots of this model for CR are plotted against t and are represented in Figure 5(C).

Table 1. Non-linear and linear variables of PFO and PSO model for adsorption of Congo red on graphene composite.

| System                  | Pseudo-first-order kinetic model | Pseudo-second-order kinetic model |
|-------------------------|----------------------------------|-----------------------------------|
|                         | Linear form                      | Non-linear form                   |
| \( Q_e \) (mg/g)        | 7.85 \times 10^{10}              | 38.393                            |
| \( k_1 \) (min\(^{-1}\)) | -0.051                           | 2.084                             |
| \( R^2 \)               | 0.880                            | Chisquare 9.44                    |
|                         |                                  | Pseudo-second-order kinetic model |
|                         | Linear form                      | Non-linear form                   |
| \( Q_e \) (mg/g)        | 11.76                            | 39.061                            |
| \( K_2 \) (min\(^{-1}\)) | 0.345                            | 0.16                              |
| \( R^2 \)               | 1                                | Chisquare 1.32                    |

The parameter values of this model are shown in Table 1.
The linear form of kinetic equation can be described as
\[ \frac{dq_t}{dt} = k_1(q_e - q_t) \]  
(5)

here \( q_e \) and \( q_t \) are the sorption capacity at equilibrium and any time. While \( k_1 \) is the rate constant. The graphical representation of linear plots for Congo red adsorption on graphene composites is given in Figure 5(A). The value of correlation coefficient (R²) is 0.880 which depicted that adsorption of CR does not follow this model.

3.3.2. PSO kinetic equation

This model is used to predict the behaviour of entire path of adsorption process [52]. The non-linear kinetic plot can be described as
\[ Q_t = \frac{t}{k_2 q_e^2} \left( e^{\frac{t}{q_e}} + e^{\frac{t}{q_e}} - 1 \right) \]  
(6)

The non-linear graphs of this model for CR are plotted between \( Q_t \) and \( t \) are represented in Figure 5(C). Values of parameters are specified in Table 1.

Linear plot of PSO kinetic model is symbolised as
\[ \frac{t}{q_t} = 1/k_2 q_e^2 + \frac{t}{q_e} \]  
(7)

Here, \( q_e, K_2 \) and \( q_t \) are the adsorption capacity, rate constant and the adsorbed amount at \( t \). The graphical representation of this model for the removal of CR dye is illustrated in Figure 5(B). The graph was plotted among \( t \) and \( t/q_t \). The R² had the value exactly unity (1) for adsorption of Congo red which depicted that adsorption process of Congo red dye on graphene composite can be best illustrated by this model.

3.3.3. Elovich model

Elovich model only gives information about the nature of adsorption process and does not give any illustration about the mechanism of whole adsorption method. Elovich model shows that process is chemisorption [53]. The equation for Elovich model can be represented as
\[ q_t = \frac{1}{B} \ln (\alpha B) + \frac{1}{B} \ln t \]  
(8)

here \( \alpha \) is adsorption rate. The constant B is the adsorption constant. The value of B which is correlated to the range of the surface saturation and activation energy required for chemisorption. The Elovich model for Congo red dye is shown in Figure 6(A). The value of R² is 0.993 which is slightly less than pseudo-second-order.

Figure 5. (A) PFO kinetic equation (B) PSO kinetic equation and (C) Non-linear forms of Both models.
3.3.4. Adsorption mechanism

The adsorption mechanism of attachment of an adsorbate on adsorbent surface comprehends a chain of steps. The overall rate of the process of adsorption is originally controlled by the slowest step among the chain of steps. To understand the adsorption mechanism, intra-particle diffusion theory was proposed by Weber and Morris [54]. This theory was used for adsorption mechanism and the mathematical form of this theory is

$$Q_t = k_{id} \sqrt{t} + C \quad (10)$$

where C signifies intercept which give information about the thickness of borderline and $k_{id}$ is the rate constant, and value of this constant can be assessed from the slope of graph between $Q_t$ versus $t^{1/2}$ and the parameters values are given in Table S1. A linear plot of this model for adsorptive removal of CR is represented in Figure 6(C) which clearly depicts that three steps are involved in mechanism. During the first 3 min, an instant adsorption appeared due to high initial Congo red concentration. In the next stage, decline was observed in the adsorption rate. This stage is rate the limiting stage. The last stage is the final equilibrium phase with the minimum amount of Congo red concentration, ensuing to the additional slowdown of diffusion process.

The electrostatic and hydrophobic interactions between the L-Cysteine decorated rGO/PANI and organic dyes are shown in Scheme 2. The exceptional removal ability of reduced graphene oxide based nanocomposite is due to the role of all three components (L-cys, rGO, PANI) in adsorption of Congo red dye. rGO nanosheets possess exceptionally large surface area along with the electrostatic interaction between cationic dye and anionic oxygen containing functional groups which could offer good circumstances for adsorption process. As Congo red has aromatic structure so the adsorbility should be mostly attributed to the $\pi-\pi$ stacking between dye and $\pi$-conjugation regions of the rGO nanosheet. Polyani-line is the most stable conjugate polymer and is helpful for adsorption as it causes an increase in active sites for attachment of dye molecules. This polymer can solely be used for adsorption of Congo red dye with good results [55]. Addition of L-cysteine imparts the L-Cys-rGO an optimum water dispersity as well as a conjugate structure. Such a particular characteristic enables adsorption of dye molecules on the rGO nanosheets [56].

3.4. Adsorption isotherms

The adsorption isotherm gives information about the interactions between adsorbate and adsorbent along with adsorption capacity. Over many years, a broad range of equilibrium isotherms like Langmuir, Dubinin–Radushkevich, Freundlich and Tempkin isotherms have been studied.

3.4.1. Langmuir isotherm

This isotherm adopts monolayer adsorption on the surface having a fixed number of active sites with uniform attitudes for adsorption [57]. The non-linear plot
Figure 7. (A) Langmuir (B) Freundlich (C) Tempkin and (D) Dubinin–Rawdushkivich (DRK) isotherms for CR adsorption.

of Langmuir model is represented as

\[ Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \]  \hspace{1cm} (11)

where \( K_L \) and \( Q_m \) represents Langmuir constant and adsorption capacity. The non-linear model for Langmuir isotherm is represented in Figure 7(A). The value of \( K_L \) and \( Q_m \) are represented in Table S2. The value of chi square for Congo red is \( 1.227 \times 10^{-11} \). The linear plot of Langmuir isotherm is denoted as

\[ \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \]  \hspace{1cm} (12)

here \( q_m \), \( K_L \) and represents Langmuir constants associated with adsorption capacity and maximum adsorption capacity, while \( q_e \) and \( C_e \) are the adsorbed amount and amount of dye at equilibrium. \( C_e/q_e \) verses \( q_e \) graph was plotted for linear plot of isotherm as shown in Figure 7(A). The value of \( R^2 \) for adsorption of Congo red is 0.987 which specified the high applicability of the Langmuir model for Congo red dye adsorption.

3.4.2. Freundlich isotherm

This isotherm is an exponential equation assuming that increase in adsorbate amount leads to increase in the concentration of adsorbate on adsorbent surface [58]. The non-linear plot of Freundlich isotherm can be stated as

\[ q_e = K_f C_e^{1/n} \]  \hspace{1cm} (13)

here \( C_e \) is the superfluidity amount at equilibrium stage, \( q_e \) is adsorbed dye’s amount at equilibrium, \( n \) and \( K_f \) are the parameters and all constant values are specified in Table S2. The value of chi square for CR is \( 2.990 \times 10^{11} \). The linear plot of isotherm can be represented as

\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]  \hspace{1cm} (14)

here \( n \) and \( K_f \) are the constants. The \( n \) tells about the promising adsorption process and \( K_f \) illustrates the comparative adsorption capacity of the adsorbent. The graph between \( \log q_e \) and \( \log C_e \) was plotted as shown in Figure 7(B). The \( R^2 \) value for Congo red dye is 0.997 which indicates that Congo red follows Freundlich kinetic model. The value of Freundlich constant \( nF \) determines the favourability of adsorption process. The value of \( nF \) for CR adsorption onto graphene composite was greater than 1 and less than 10 representing favourable adsorption process of dye.

3.4.3. Tempkin isotherm

This model explains that decrease in adsorption heat is linear function [59]. The non-linear Tempkin isotherm
can be stated as

\[ q_e = \frac{RT}{b_T} \ln(a_T C_e) \]  

(15)

here \( R, T, b_T \) and \( a_T \) are constants states to gas constant, temperature (K), heat of adsorption and equilibrium binding constant as presented in Figure 7(A). The value of \( a_T \) and \( b_T \) constants are obtained from the non-linear plot of Tempkin isotherm and specified in Table S2. The value of Chi square of Tempkin isotherm for Congo red dye is \( 1.158 \times 10^{-10} \). The linear plot of Tempkin model can be stated as

\[ q_e = \beta \ln A + \beta \ln C \]  

(16)

\[ B = \frac{RT}{b} \]  

(17)

here \( T(K) \) and \( R \) specify the temperature and gas constant. While \( b \) and \( \alpha \) refers to the Tempkin constant and equilibrium binding constant. A graph was plotted between \( \ln C e \) and \( q_e \) and slope of the graph provides the value of constant \( \alpha \) while value of Tempkin constant \( b \) is calculated from the intercept of this graph (Figure 7(C)). The value of correlation factor is 0.975.

3.4.4. Dubinin–Radushkevich (D–R) isotherm

This model is used for explaining both heterogeneous and homogeneous surfaces of adsorbate. It can also be utilized to assess free energy, porosity and properties of adsorbent. It explains the subcritical vapours adsorption on to microscopic solids ensuing a pore packing procedure [58]. The non-linear form of Dubinin–Radushkevich can be stated as

\[ q_e = C_m \exp(-\beta \varepsilon^2) \]  

(18)

Non-linear plot of D–R isotherm is given in Figure 7(A). The value of Chi square for the removal of CR is \( 9.844 \times 10^{-12} \). The linear form of DRK isotherm can be stated as

\[ \ln q_e = \ln q_m - \beta \varepsilon^2 \]  

(19)

\[ \varepsilon = \frac{RT \ln(1 + 1/C_e)}{\beta} \]  

(20)

here, \( q_m \) represents the maximum adsorption capacity, \( \varepsilon \) is Polanyi potential and \( \beta \) shows activity coefficient constant. The slope of the plot of the graph between \( \ln q_e \) and \( \varepsilon^2 \) provides the value of \( \beta \) and the value of \( q_m \) can be evaluated from the intercept of this graph (Figure 7(D)). The adsorption performance of L-Cys/rGO/PANI is compared with other recently reported adsorbents as presented in Table 2.

3.5. Adsorption thermodynamics

The thermodynamic variables of Gibb’s free energy (\( \Delta G^o \)), and entropy (\( \Delta S^o \)) and enthalpy (\( \Delta H^o \)) changes which were related with the adsorption of Congo red dye onto graphene composite were calculated with the help of Gibb’s free energy and vant Hoff equation.

\[ K_c = C_a / C_e \]  

(21)

\[ \ln K_c = \Delta S^o / R - \Delta H^o / RT \]  

(22)

\[ \Delta G^o = \Delta H^o - T \Delta S^o \]  

(23)

here \( T, K_c \) and \( R \) represents the temperature in kelvin, distribution coefficient of adsorption and gas constant. While \( C_a \) and \( C_e \) are equilibrium amount and solid phase amount at equilibrium. A graph was plotted between \( \ln Kc \) and \( 1/T \) for Congo red dye to find thermodynamic variables. The values of \( \Delta H^o \) and \( \Delta S^o \) were calculated as shown in Table 3. It is depicted that the values of Gibb’s free energy are negative for adsorption of Congo red dye on reduced graphene oxide composite and exhibited increase in Gibb’s free energy (\( \Delta G^o \)) values with rise in temperature. The value of enthalpy change (\( \Delta H^o \)) is Positive for Congo red dye which shows that the adsorption process is endothermic in nature. Similarly, the values of entropy (\( \Delta S^o \)) for Congo red dye is also positive demonstrating the increase in randomness during interactions.

4. Conclusion

A new adsorbent containing reduced graphene oxide functionalized with L-cysteine and polyaniline (L-Cys/rGO/PANI) was effectively prepared by simple and facile method for the removal of Congo red dye. Structural and morphological confirmation of as-prepared nanocomposites were verified effectively via XRD, UV-visible, SEM, FTIR and BET studies. The attained experimental results exhibited that the Congo red dye removal efficiency was remarkably dependent on various physico-chemical parameters including contact time, Congo red initial concentration, temperature

| Adsorbent                  | Solution concentration C0 (ppm) | Adsorption capacity qmax (mg/g) | References |
|----------------------------|---------------------------------|---------------------------------|------------|
| Fe3O4 NPs                  | 60, 300                         | 254                             | [60]       |
| MgO powder                 | 60, 100                         | 247.5                           | [61]       |
| NiO nanosheet              | 150, 500                        | 168                             | [63]       |
| porous ZnO                 | 100                             | 334                             | [64]       |
| NiO nanodiscuits           | 120                             | 193.2                           | [65]       |
| CoO/MoO2/Mo2C              | 200                             | 213                             | [66]       |
| L-Cys/rGO/PANI             | 30                              | 56.57                           | This Work  |

Table 3. Thermodynamic variables for CR adsorption at L-Cys/rGO/PANI composite.

Dye | Temperature (K) | \( \Delta G^o \) (kJ/mol) | \( \Delta H^o \) (kJ/mol) | \( \Delta S^o \) (kJ/mol) |
--- | --------------- | ----------------- | ----------------- | ----------------- |
Congo red | 283             | −8.2751           | 0.1583            | 0.0298            |
        | 293             | −8.5731           |                    |                  |
        | 323             | −9.4671           |                    |                  |
        | 333             | −9.7651           |                    |                  |

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[60] Absorption of Congo red dye on reduced graphene oxide composite.
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[62] Adsorption of Congo red dye on graphene oxide composite.
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[64] Adsorption of Congo red dye on graphene oxide composite.
[65] Adsorption of Congo red dye on graphene oxide composite.
[66] Adsorption of Congo red dye on graphene oxide composite.
and adsorbent dose. The optimal conditions for dye removal of time and adsorbent was 10 min and 0.025 g and maximum adsorption was found to be 56.57 mg/g. Experimental results subjected to various isotherms such as Langmuir, Tempkin, Freundlich, and Dubinin–Radushkevich (D–R) isotherms, indicated that the adsorption of Congo red followed both Freundlich and Langmuir isotherms. Moreover, the thermodynamic features exhibited that the adsorption of Congo red dye was thermodynamically spontaneous and endothermic in nature. It can be accomplished from this study that reduced graphene oxide based nanocomposite has huge potential to be employed for wastewater treatment.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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