Green synthesis and characterisation of L-Serine capped magnetite nanoparticles for removal of Rhodamine B from contaminated water

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ABSTRACT
This paper describes a green one-pot synthesis of L-Serine (L-Ser) capped magnetite nanoparticles (Fe₃O₄ NPs) and its potential application for adsorption of RhB dye from aqueous solution. The surface property, structure, morphology and magnetic properties of as prepared L-Ser capped Fe₃O₄ NPs were characterised through UV-Visible spectroscopy, Fourier transform-infrared spectroscopy, X-Ray Diffraction (XRD), scanning electron microscope, transmission electron microscope (TEM) and vibrating sample magnetometer (VSM). The XRD results were indicated the formation of high crystalline spinel type Fe₃O₄ NPs. TEM images were shown the spherical shape of L-Ser capped Fe₃O₄ NPs with particle size of 5.9 nm. The VSM curve showed the superparamagnetic behaviour of L-Ser capped Fe₃O₄. A plausible interaction mechanism of L-Ser and Fe₃O₄ NPs was also investigated. L-Ser capped Fe₃O₄ NPs due to its large surface area and a strong magnetism was shown potential adsorption efficiency towards RhB dye from aqueous solution. The adsorption isotherm data fitted well with Langmuir isotherm model and the monolayer adsorption capacity (qₑₑₓₑ) was found to be 6.82 mg/g at pH 7.4 and 300 K. The experimental kinetic data fitted very well with the pseudo-second-order model. The thermodynamic studies reveal that adsorption efficiency is critically dependent on temperature.

1. Introduction
In recent years, numerous industries have been troubling the water quality by release of various contaminants such as dyes, heavy metal ions and many other organic pollutants [1–3]. Particularly, dyes because of their long time stability and enormous effluents have been released per year, which causes for adverse effect on human health such as pain, vomiting, skin irritation, severe headaches, acute diarrhoea, etc. [3]. However, the conventional water treatment methods such as precipitation and flocculation are unsuccessful for the complete removal of dyes. Instead, adsorption is promising technology for an effective treatment of polluted water due to it is low-cost, simply designed, easy to handle, and
provides sludge-free output [4,5]. Activated carbon has been long known for an effective colour removal adsorbent, but its expensive operation cost unable to address for a wide range of consumers [6]. Hence developing of alternative adsorbents of less cost, ease of operation and simplistic design has been the focus of recent research.

In the last decades, many approaches have been studied for the development of low-cost and more effective adsorbents such as silica gel [7], perlite [8], lignite [9], fly ash [10], etc. Most of these adsorbents due to their highly porous in nature provide sufficient surface area for adsorption. Nanostructured materials due to its high surface area to volume ratio and can easily functionalise their surface by different molecules have been used for an efficient adsorption. Moreover, its unique structural, electrical, optical and magnetic properties can provide outstanding opportunities for the adsorption of dyes [11,12]. Notably, superparamagnetic nanoparticles as a result of easily manipulated by external magnetic field have been used for numerous applications including the environmental remediation [13]. Superparamagnetic Fe₃O₄ NPs emerged as a potential candidate for advanced technological applications due to their biocompatibility, low toxicity and high magnetic saturations [14]. However, Fe₃O₄ NPs below their critical particle size (≈20 nm) without surface capping could be easily aggregated during the course of chemical reaction [15]. This phenomenon hampers to exploit the effectiveness of Fe₃O₄ NPs for their potential application.

In order to arrest aggregation of Fe₃O₄ NPs, surface capping or immobilisation using appropriate capping agents has been used such as polymers [16] and hydrocarbons [17] and others. However, these organic capping agents have a potential toxicity to the environment and public health. So, it is still a great challenge to develop biocompatible synthesis methods. More recently, amino acids have been showing a fascinating interest because of their biocompatibility and good capping capability towards Fe₃O₄ NPs [18,19]. Syntheses of Fe₃O₄ NPs with amino acids as a capping agent have often done in the absence of toxic organic solvents which increases the popularity of amino acids as capping materials [19].

In this paper, we report a facile green synthesis of L-Ser capped Fe₃O₄ NPs via a co-precipitation of Fe³⁺ and Fe²⁺ salts in the presence of L-Ser as a capping agent. The as synthesised L-Ser capped Fe₃O₄ NPs were characterised through using UV-Visible, Fourier transform-infrared (FTIR), X-ray diffraction (XRD), scanning electron microscope/energy dispersive X-ray spectroscopy (SEM/EDS), transmission electron microscope (TEM) and vibrating sample magnetometer (VSM). The plausible interaction between L-Ser and Fe₃O₄ surface was investigated based on FTIR and UV-Visible spectroscopic techniques. Furthermore, the adsorption efficiency of L-Ser capped Fe₃O₄ NPs was investigated using RhB under various experimental parameters such as concentration of dye, contact time and temperature. The adsorption kinetics, thermodynamics and isotherms of RhB by using L-Ser capped Fe₃O₄ NPs were also investigated.

2. Experimental

2.1. Materials

Iron (III) chloride hexahydrate (FeCl₃.6H₂O) and Iron (II) sulphate heptahydrate (FeSO₄.7H₂O) used for synthesis of Fe₃O₄ NPs were purchased from Merck, India and used as without further purification. L-Ser and NH₃ (25%) were received from HiMedia,
India. All other reagents were analytical graded and used without further purification. Milli-Q water was used throughout the whole synthesis process.

2.2. Synthesis of L-Serine capped Fe$_3$O$_4$ NPs

Syntheses of Fe$_3$O$_4$ NPs were carried out through single-pot co-precipitation reaction in the presence of L-Ser as a capping agent. In a typical synthesis, 2:1 molar ratio of metal salts Fe$^{3+}$ (0.54 g FeCl$_3$.6H$_2$O) and Fe$^{2+}$ (0.278 g FeSO$_4$.7H$_2$O) was added in 250 mL round-bottomed flask, respectively, and the reaction was kept for one hour under constant stirring in atmospheric nitrogen at 80 °C. Then, 5 mL 2 M of L-Ser was added to the reaction mixture and then 5 mL ammonia solution (25%) was rapidly injected into reaction mixture. The reaction was further allowed to proceed for 2 hours at 80 °C under constant stirring. Then finally, the black precipitate was obtained and separated by external magnet, washed several times with Milli-Q water, and then dried in vacuum at room temperature. Similarly, L-Ser capped Fe$_3$O$_4$ NPs were also prepared by varying the concentration of L-Ser while all other reaction parameters were kept the same.

2.3. Characterisation

The UV-Visible absorption spectra were recorded using a Shimadzu 2450 – SHIMADZU spectrometer. FTIR spectra were recorded using a SHIMADZU-IR PRESTIGE-2 spectrometer. Powder samples were mixed thoroughly with KBr and pressed into thin pellets. The powder XRD patterns were obtained by PANalytical X’pert pro diffractometer at 0.02°/sec scan rate with Cu-k$\alpha_1$ radiation (1.5406 Å, 45 kV, 40 mA). Transmission electron microscopy images were obtained (TEM model FEI TECNAI G2 S-Twin) at an accelerating voltages of 120 and 200 kV. SEM images were acquired JEOL-JSM6610 LV equipped with an electron probe-micro analyser. Magnetic property measurement was carried out at room temperature (300 K) using VSM (Lakeshore 665, Coeur D Alene, ID, USA).

2.4. Batch mode adsorption studies

Batch adsorption efficiency of L-Ser capped Fe$_3$O$_4$ NPs experiments was carried out using RhB as a model dye at room temperature (300 K). In a typical experiment, 50 mg of L-Ser capped Fe$_3$O$_4$ NPs was added in 50 mL of known concentration of dye solution. The pH of solution was adjusted by NaOH (0.1 M) or HCl (0.1 M). The flasks were stirred for the specified time period and samples from each flask were withdrawn at the desired time of reaction until adsorption equilibrium was achieved. The L-Ser capped Fe$_3$O$_4$ NPs were collected by an external magnet. The residual dye concentration was determined by UV-Visible spectrophotometer by measuring the absorbance at a wavelength of maximum absorbance of RhB (554 nm). The amount of RhB adsorbed, $q$ (mg/g) on L-Ser capped Fe$_3$O$_4$ NPs was calculated by

$$q = (C_o-C)V/m$$

where $C_o$ is the initial RhB concentration (mg/L), $C$ is RhB concentration (mg/L) in solution after adsorption, $V$ is the volume (L) of the aqueous solution and $m$ is the mass (g) of
L-Ser capped Fe$_3$O$_4$ NPs. Common adsorption isotherms and kinetic models were used to demonstrate the adsorption process.

3. Result and discussion

The UV-Visible spectra of uncapped and L-Ser capped Fe$_3$O$_4$ NPs are shown in Figure 1. UV-Visible spectrum of both L-Ser capped and uncapped Fe$_3$O$_4$ NPs shows a broad absorption peaks which originates primarily from the absorption and scattering of light by Fe$_3$O$_4$ NPs [20]. This characteristic peak was observed for both uncapped and L-Ser capped Fe$_3$O$_4$ NPs around 350 nm. The strong absorption peak at 200 nm for L-Ser capped Fe$_3$O$_4$ NPs is due to L-Ser (Electronic supplementary information [ESI], Figure S1); and it indicates effective capping of Fe$_3$O$_4$ NPs using L-Ser.

The phase structure and crystalline nature of uncapped and L-Ser capped Fe$_3$O$_4$ NPs were investigated using powder XRD. The XRD pattern of both uncapped and L-Ser capped

Figure 1. UV-Visible spectra of (a) uncapped and (b) L-Ser capped Fe$_3$O$_4$ NPs.

Figure 2. The powder XRD patterns of (a) uncapped Fe$_3$O$_4$ NPs and (b) L-Ser capped Fe$_3$O$_4$ NPs.
Fe$_3$O$_4$ NPs is shown in Figure 2, in which all peaks may be indexed to the inverse spinel phase of Fe$_3$O$_4$ (JCPDS card No. 19-0629). The XRD pattern shows peaks at 2$\theta$ = 30.77°, 35.82°, 43.4°, 57.52° and 63.02° corresponding to the planes of (220), (311), (400), (511) and (440). No peaks associated from other impurities were observed. The sharp and intense peaks indicate high crystallinity of the as synthesised Fe$_3$O$_4$ NPs. The average crystalline size of uncapped and L-Ser capped Fe$_3$O$_4$ NPs was estimated using Scherer formula [21] and found to be 32.6 and 10.5 nm for uncapped and L-Ser capped Fe$_3$O$_4$ NPs, respectively. This attributed to the L-Ser act as a protective material for the growing of Fe$_3$O$_4$ NPs during the synthesis process and which is in accordance to the reported literatures [22].

The structural information of as prepared Fe$_3$O$_4$ NPs was investigated through FTIR spectra. The FTIR spectra of uncapped and capped Fe$_3$O$_4$ NPs are presented in Figure 3. Uncapped Fe$_3$O$_4$ NPs have two prominent peaks at 1629 and 3424 cm$^{-1}$ which ascribed to the O-H bending and stretching vibrations respectively and indicated that the water molecule is coordinated with unsaturated Fe atom in uncapped Fe$_3$O$_4$ surface [22]. FTIR spectrum of L-Ser is shown in Figure S2, ESI which is in a good agreement with previously reported data [23] and it has two peaks at 1602 and 1407 cm$^{-1}$ which were due to asymmetric and symmetric stretching frequencies of COO$^-$, respectively. FTIR of L-Ser capped Fe$_3$O$_4$ NPs (Figure 3(b)) shows that the peaks at 1598 and 1345 cm$^{-1}$ were assigned to the $\nu_{as}$(COO$^-$) and $\nu_{s}$(COO$^-$) stretching vibrations of carboxyl group of L-Ser, respectively [24]. The energy differences between these asymmetric and symmetric stretching frequencies of carboxyl groups in L-Ser capped Fe$_3$O$_4$ give hint about the nature of interaction of carboxyl group with the metal surface. Hence, the energy differences between the asymmetric and symmetric stretching frequencies ($\Delta\nu_{as,s} = 1598 - 1345$ cm$^{-1} = 223$ cm$^{-1}$) were observed in the range of the bidentate complexing of carboxyl group with unsaturated Fe cation [24]. The strong peaks at 585 and 412 cm$^{-1}$ were associated to the intrinsic Fe–O vibrations of L-Ser capped Fe$_3$O$_4$ NPs [25]. The FTIR confirms that the L-Ser was coated on the surface of Fe$_3$O$_4$ NPs.

Morphology of L-Ser capped Fe$_3$O$_4$ NPs was investigated using SEM and TEM. SEM images clearly showed that the L-Ser capped Fe$_3$O$_4$ NPs have nearly spherical shape (Figure 4). EDS spectra (Figure 4(d)) confirm that the presence of Fe and O atoms with 82% and 16% weight value, respectively, which were near to the theoretical percent weight values of pure magnetite. TEM images of as prepared L-Ser capped Fe$_3$O$_4$ NPs dried
powder dispersed in dimethyl sulfoxide are depicted in Figure 5 and clearly have the spherical morphology with average particle size of 5.9 nm and standard deviation 1.58 nm of L-Ser capped Fe$_3$O$_4$ NPs. A selected area electron diffraction pattern obtained from the particles is given in Figure 5(c) and in good agreement with the characteristic electron diffraction pattern of Fe$_3$O$_4$ NPs of spinel structure [26]. Figure 5(d) shows the particle size distribution of L-Ser capped Fe$_3$O$_4$ NPs.

The room temperature magnetisation curves of L-Ser capped Fe$_3$O$_4$ NPs are depicted in Figure 6. The magnetisation curve shows the absence of hysteresis loop and zero coercivity at room temperature indicating that the superparamagnetic behaviour of L-Ser capped Fe$_3$O$_4$ NPs. The saturation magnetisation (Ms) was found to be 85 emu/g, and smaller than bulk Fe$_3$O$_4$ of 92 emu/g [25]. The decrease in the Ms value of L-Ser capped Fe$_3$O$_4$ NPs could be ascribed to size and surface effects induced by the nanoscale particle size of L-Ser capped Fe$_3$O$_4$ NPs. Moreover, the nonmagnetic capping agent (L-Ser) adsorbed on the surface of Fe$_3$O$_4$ NPs and thus resulted in decrease of Ms value.

3.1. Plausible interaction mechanism of L-Ser on to Fe$_3$O$_4$ surface

In general, amino acids are amphiprotic in nature and their charge critically depends on pH of a solution and thus, very small variations in pH could change in the charge of amino acid. At isoelectric point (pI) (pH = 5.68), L-Ser predominantly exists as zwitterion form (as shown in Scheme 1). When the pH of solution is less than pI, then L-Ser exists as cationic
form (-NH$_3^+$, -COOH), while it is present in anionic form (-NH$_2^-$, -COO$^-$) at higher pH value. Therefore, at high pH value, L-Ser behaves as a strong nucleophile and able to form a bond with an electron deficient species. Nanoparticles due to their high surface to volume ratio, coordinative unsaturated surface species undergo either defects or chemical interaction.

Figure 5. (a,b) Representative TEM images of L-Ser capped Fe$_3$O$_4$ NPs, (c) selected area electron diffraction patterns and (d) size distribution histogram.

Figure 6. Vibrating sample magnetometer (VSM) curve of L-Ser capped Fe$_3$O$_4$ NPs at room temperature.
to gain their stability. Fe₃O₄ NPs are inverse spinel structure where Fe³⁺ occupied both Tₐ and half of O₈ sites and Fe²⁺ half of O₆ of the unit cell. However, Fe³⁺/Fe²⁺ found on surface Fe₃O₄ NPs not fully bound to adjacent oxygen atoms and undergo interaction with L-Ser to fulfil their stability. L-Ser at pH > 9.15, predominantly exists in its anionic form (COO⁻ and NH₂) which is strong nucleophile and could be form a bond with Fe³⁺/Fe²⁺ (Figure 7).

Carboxylate ions have two possible interaction modalities to Fe³⁺/Fe²⁺ either uni- or bi-dentate as shown in Figure 7(a,b); however, FTIR analysis was ascribed the bi-dentate [24]. The amino group of L-Ser (Figure 8(c)) through nitrogen atom could coordinate to Fe³⁺ of Fe₃O₄ NP. The alcoholic terminal also has plausibly made a bond with unsaturated Fe atom of Fe₃O₄ NPs.

### 3.2. Adsorption studies

In general, adsorption efficiency is highly dependent on surface characteristics, size distribution and extent of functional groups on adsorbent [12]. Nanosize distribution of L-Ser capped Fe₃O₄ NPs along with the presence of active functional groups (COO⁻ and NH₂) on its surface develops better adsorption for RhB dye. In the present study, it was obtained that L-Ser capped Fe₃O₄ NPs have shown better adsorption efficiency than uncapped Fe₃O₄ (Figure 8(a)). At adsorption equilibrium (180 min) the percent removal (%) efficiency of L-Ser capped Fe₃O₄ NPs (Figure 8(b)) at 300 K, pH = 7.4, were found to be 85.5%, 65.6% and 45.4% for concentration of 5, 10 and 15 ppm of RhB, respectively.

### 3.3. Adsorption kinetics

Adsorption kinetics of RhB by L-Ser capped Fe₃O₄ NPs was investigated by Lagergren pseudo-first-order (Equation (2)) and pseudo-second-order equation (Equation (3))
The first-order kinetic model of Lagergren is applied for fast adsorption of any solute from solution and the process mainly controlled by diffusion [27]:

\[
\log (q_e - q_t) = \log q_e - \left( K_1 / 2.303 \right) \times t
\]  

(2)

where \( K_1 \) is the rate constants of the pseudo-first-order and \( q_e \) denotes the amount of dye adsorption at equilibrium.

Instead, the pseudo-second-order model proposes that chemiadsorption is the rate-limiting step and that adsorption occurs on localised sites where no interactions between adsorbates take place [28].

\[
t/q_t = 1/K_2 q_e^2 + (1/q_e) \times t
\]  

(3)

where \( K_2 \) is pseudo-second-order kinetic models.

The adsorption kinetics analysis of RhB on to L-Ser capped Fe\(_3\)O\(_4\) Nps was investigated by two models as shown in Figure 9. A correlation coefficient value (\( R^2 \)) as shown in

**Figure 8.** (a) Effect of adsorbent type for adsorption of RhB (5 mg·L\(^{-1}\)) and (b) effect of RhB concentration on percent removal (%) onto L-Ser capped Fe\(_3\)O\(_4\) NPs.

**Figure 9.** (a) Pseudo-first-order and (b) pseudo-second-order plots for adsorption of RhB on L-Ser capped Fe\(_3\)O\(_4\) NPs at varying initial concentration of RhB (error bar represents 5% error).
Hence, the adsorption kinetics of RhB onto L-Ser capped Fe₃O₄ NPs was found to follow pseudo-second-order kinetics, and the rate-determining step is predominantly chemiadsorption [29]. The maximum adsorption efficiency of L-Ser capped Fe₃O₄ NPs towards RhB was calculated from pseudo-second-order kinetics (qₑ/cal) found to be good agreement to experimental (qₑ/exp) (Table 1). The pseudo-second-order kinetics further predicts that adsorption proceed through chemiadsorption process, in which the adsorption process predominantly affected by electrostatic interaction between the cationic dyes and the L-Ser capped Fe₃O₄ NPs.

### 3.4. Adsorption isotherm

In order to develop a suitable adsorption system for RhB on to L-Ser capped Fe₃O₄ NPs, Langmuir, Freundlich and Temkin adsorption isotherm models were investigated and their corresponding curves are depicted in Figure 10. The Langmuir [30] equation can be expressed in a linearised form:

\[
\frac{C_e}{q_e} = \frac{1}{Q_o} + \frac{C_e}{Q_o} b_L
\]

where \( q_e \) (mg/g) is the equilibrium amount of dye adsorption, \( Q_o \) (mg/g) refers to the maximum adsorption capacity of L-Ser capped Fe₃O₄ NPs and \( b_L \) (L/mg) is the Langmuir equilibrium constant related to the enthalpy of the process.

Hall et al. [31] correlate the characteristics of Langmuir isotherm constant (\( b_L \)) with a dimensionless factor \( R_L \) (Equation (5)) to describe the enthalpy of adsorption process:

\[
R_L = \frac{1}{1 + b_L Q_o}
\]

The value of separation factor \( R_L \) indicates the nature of the adsorption process as: \( R_L > 1 \) (unfavourable), \( R_L = 1 \) (linear), \( 0 < R_L < 1 \) (favourable) and \( R_L = 0 \) (irreversible). In this study, \( R_L \) was obtained between 0.03 and 0.08 (Table 2) and hence the values of \( R_L \) computed are <1, indicating that the adsorption process is favourable.

### Table 1. The pseudo-first-order and pseudo-second-order kinetics parameters of RhB adsorption on L-Ser capped Fe₃O₄ NPs.

| Parameters                  | 5 ppm   | 10 ppm  | 15 ppm  |
|-----------------------------|---------|---------|---------|
| \( q_e\text{,exp.} \) (mg/g) | 4.276   | 6.561   | 6.82    |
| Pseudo-first-order kinetics |         |         |         |
| \( k_1 \) (min⁻¹)           | 0.01492 | 0.01812 | 0.02222 |
| \( q_e\text{,cal} \) (mg/g)  | 2.723   | 6.11    | 4.739   |
| \( R^2 \)                    | 0.8489  | 0.9756  | 0.9605  |
| Pseudo-second-order kinetics|         |         |         |
| \( k_2 \) (g/mg/min)         | 0.048   | 0.0185  | 0.0296  |
| \( q_e\text{,cal} \) (mg/g)  | 4.535   | 7.940   | 7.270   |
| \( R^2 \)                    | 0.991   | 0.99    | 0.997   |
The Freundlich [32] isotherm can be applicable for modelling the adsorption of dye on heterogeneous surfaces and the linearised form of isotherm is expressed as

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e$$

(6)

where $K_f$ (mg/g) is Freundlich constant representing the adsorption capacity at unit equilibrium concentration that is defined as the adsorption or distribution coefficient and $1/n$ is related to the adsorption intensity. The value of Freundlich constant 'n' is greater than 1.0, as shown in Figure 10(d), indicating that RhB favourably adsorbed on L-Ser capped Fe$_3$O$_4$ NPs.

Tempkin [33] isotherm is based on the assumption that the heat of adsorption would decrease linearly with the increase of coverage of adsorbent is expressed as

$$q_e = \frac{RT}{b_T} \ln a_T + \left(\frac{RT}{b_T}\right) \ln C_e$$

(7)

where $a_T$ and $b_T$ are Tempkin constants.

The adsorption isotherms described by these three models for RhB adsorption by L-Ser capped Fe$_3$O$_4$ NPs are shown in Figure 10(b–d), and the parameters and $R^2$ values calculated from the three models are shown in Table 2. The regression coefficients ($R^2$) obtained from their values of Langmuir model ($R^2 = 0.99$), Freundlich model ($R^2 = 0.85$) and Tempkin model ($R^2 = 0.87$) were obtained, indicating that the data is best fit to the Langmuir
isotherm, and thus the RhB adsorption on L-Ser capped Fe₃O₄ NPs is monolayer adsorption. The maximum monolayer adsorption capacity ($Q_o$) was found to be 7.19 mg/g and it has competitive monolayer adsorption efficiency compared with common adsorbent (ESI Table 1).

### 3.5. Adsorption thermodynamics

The effect of temperature on the adsorption efficiency of L-Ser capped Fe₃O₄ towards RhB at initial concentration of 10 ppm and pH = 7.4 is presented in Figure 11. The experiments were carried out at 290, 300, 310 and 320 K and as shown in Figure 11(a), the adsorption capacity increases from 6.8 to 8.3 mg/g with the increase of temperature from 290 to 320 K. It is apparent that the adsorption of RhB on the L-Ser capped Fe₃O₄ is an endothermic process, implying a chemical adsorption process [34]. The energy changes associated with the adsorption process were also investigated by evaluating thermodynamic parameters: standard Gibbs energy change ($\Delta G^\circ$), enthalpy change ($\Delta H^\circ$) and entropy change ($\Delta S^\circ$). The thermodynamic parameters for the adsorption process were obtained using Equations (8) and (9):

$$\ln b_L = \Delta S^\circ / R - 1/T * (\Delta H^\circ / R)$$  (8)

where $b_L$ is Langmuir isotherm constant obtained from Equation (4), $T$ is the temperature and $R$ is the gas constant, respectively. The $\Delta H^\circ$ and $\Delta S^\circ$ values were determined

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**Table 2. Langmuir, Freundlich and Tempkin adsorption isotherms’ parameters for the adsorption of RhB onto L-Ser capped Fe₃O₄ NPs.**

| Isotherm models | Parameters | $Q_o$ (mg/g) | $b_L$ (L/mg) | $R_L$ | $R^2$ |
|----------------|------------|-------------|-------------|-------|-------|
| Langmuir       |            | 7.19        | 2.31        | 0.03–0.08 | 0.99 |
| Freundlich     | $1/n$      |             | $k_f$ (mg$^{1−1/n}$ L$^{1/n}$ g$^{−1}$) | 4.7 | 0.85 |
| Tempkin        | $b_T$ (J/mol) | $\alpha_T$ (L/mg) | | 79.12 | 0.87 |

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Figure 11. Effect of temperature on (a) adsorption efficiency and (b) van’t Hoff plot (5% error bar) for adsorption of RhB (10 ppm) onto of L-Ser capped Fe₃O₄ NPs.
experimentally from the slope and intercept of van’t Hoff plots, i.e. \( \ln b_L \) versus \( 1/T \) (Figure 11(b)) and the calculated values are presented in Table 2. The standard Gibbs energy change \( (\Delta G^\circ) \) can be calculated using Equation (9):

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

The negative value (Table 3) of \( \Delta G^\circ \) at various temperatures remarks the spontaneous nature of adsorption of RhB onto L-Ser capped Fe\(_3\)O\(_4\) NPs, and amount of dye adsorbed \( (q_e) \) at equilibrium increases with increasing temperature. Positive value of \( \Delta H^\circ \) clearly shows that the adsorption process of RhB onto L-Ser capped Fe\(_3\)O\(_4\) is endothermic. The positive \( \Delta S^\circ \) confirms the randomness of the system and it results an increase in the rate of diffusion of RhB molecules across the surface of the L-Ser capped Fe\(_3\)O\(_4\) NPs rises, which leads to an increase in the adsorption efficiency [35].

### 4. Conclusion

In summary, a facile green synthesis of superparamagnetic L-Ser functionalised Fe\(_3\)O\(_4\) NPs was successfully developed by using a biocompatible capping agent, L-Ser. UV-Visible and FTIR results reveal the effective surface capping of Fe\(_3\)O\(_4\) NPs by using L-Ser. Pure phase and good crystalline nature of L-Ser capped Fe\(_3\)O\(_4\) NPs were confirmed by XRD. SEM and TEM techniques indicate spherical morphology of L-Ser capped Fe\(_3\)O\(_4\) NPs. VSM showed the superparamagnetic nature of L-Ser capped Fe\(_3\)O\(_4\) NPs. The adsorption behaviour of L-Ser capped Fe\(_3\)O\(_4\) NPs towards RhB was followed by a pseudo-second-order kinetic model, suggesting chemiadsorption. The adsorption mechanism best fit to Langmuir model which indicates the formation of a monolayer covering of the adsorbate at the outer surface of the adsorbent. The maximum adsorption capacity \( (q_{e,exp}) \) was found to be 6.82 mg/g at pH 7.4 and temperature 300 K. Studies on thermodynamic parameters reveal that the adsorption process is endothermic and spontaneous. Furthermore, the adsorption process was shown a positive response with an increasing temperature from 290 to 320 K.

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| Temperature | \( \Delta G^\circ \) | \( \Delta H^\circ \) | \( \Delta S^\circ \) |
|-------------|---------------------|---------------------|---------------------|
| K           | kJ mol\(^{-1}\)     | kJ mol\(^{-1}\)     | kJ mol\(^{-1}\) K\(^{-1}\) |
| 290         | -0.458              |                     |                     |
| 300         | -1.165              | 41.75               | 0.145               |
| 310         | -2.595              |                     |                     |
| 320         | -4.025              |                     |                     |

Table 3. Thermodynamic parameters for the adsorption of RhB onto L-Ser capped Fe\(_3\)O\(_4\) NPs.
Disclosure statement

No potential conflict of interest was reported by the authors.

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