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Review

Citric acid coated magnetic nanoparticles: Synthesis, characterization and application in removal of Cd(II) ions from aqueous solution

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ABSTRACT

Citric acid coated magnetite nanoparticles (Fe_3O_4-Cit) have been synthesized for the removal of cadmium from aqueous solutions. As-prepared Fe_3O_4-Cit was characterized by using Fourier transform infrared spectroscopy (FT-IR), X-ray diffractometer (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and through the determination of pH_{zpc}. Several factors effecting the adsorption of Cd(II) ions on the surface of Fe_3O_4-Cit such as pH, temperature and contact time were investigated. The Cd(II) ions adsorption equilibrium on the Fe_3O_4-Cit were obtained by 35 min at the optimized pH 5. Kinetic study shows the Cd(II) adsorption onto Fe_3O_4-Cit follow the pseudo-second order kinetic model with $R^2 > 0.997$ at 308 K. The adsorption data was satisfactorily explained by Langmuir and Freundlich isotherm models. The experimental data found to be suitable linearity with Langmuir isotherm having maximum adsorption capacity (q_m) values in mg g^{-1} 10.81, 11.45 and 12.56 at the 298 K, 303 K and 308 K, respectively. The correlation coefficient $R^2 = 0.997$ fully supports the favorability of Langmuir isotherm in adsorption process. The negative values of ΔG°, −5.68, −6.31 and −6.95 kJ mol^{-1} throughout the temperature at 298 K, 303 K and 308 K are indicating the feasibility of adsorption process on to Fe_3O_4-Cit was spontaneous in nature.

Contents

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1. Introduction

Heavy metals in aquatic environment are of serious concern due to significant threats to human health and the ecological system. Heavy metals like chromium (Cr), copper (Cu), cadmium (Cd), nickel (Ni) and lead (Pb) are occurs in aquatic system from effluent discharge of different industry such as tannery, chemical manufacturing, smelting, metal plating, mining, alloy manufacturing, and lead storage battery [1,2]. The uninterrupted releases of heavy metals in the aquatic environment are considered to be non-biodegradable and long term persistent in nature [3]. Presence of heavy metals in aquatic bodies causes significant health problems to the aquatic community [4]. They can be accumulated in living tissues, causing various diseases and disorders in excess amount beyond their permissible limits.

Among the other metals, Cd(II) presence in effluent of different industries has been considered as one of the most harmful metal due to its known toxicity to human, which includes nausea, vomiting, diarrhea, loss of calcium from bones, damage of bone marrow, reduction of red blood cells, hypertension, kidney failure, chest pain and loss of sense [5]. Therefore, it is necessary to take considerable effort for developing effective treatment methods for removal of Cd(II) ions from wastewater before its discharge into the near water bodies.

Several physico-chemical methods such as precipitation [6], floatation [7], ion exchange [8], membrane process [9] and adsorption [10] have been used for the removal of Cd(II) from aqueous solutions. Most of them have their own drawbacks because of high operating cost, sludge generation and laborious techniques.

Among these used techniques adsorption methods is considered most effective and suitable for cadmium removal [11]. A variety of natural and industrials waste materials have been developed as potential adsorbent for the removal of heavy metals from wastewater. Many kinds of adsorbents such as clay, zeolites, waste biomass [12] agricultural waste biomass, biopolymers, considered low cost and easily available in nature have more efficiency for metals removals from wastewater. Whereas industrial waste such as fly ash, blast furnace sludge, waste slurry, battery industry waste and biogas residual slurry have been utilized for the removal of metal ions from industrial wastewater [13].

The nanosized magnetic materials have great potential to adsorb metal like Cd(II) ion due to their high surface area and unique advantage of easy separation under external magnetic field. Furthermore an increasing number of studies have been focused on surface modification of magnetic nanomaterial for high adsorption capacity, fast adsorption–desorption kinetics and easy separation and regeneration [14]. Considering these characteristics, magnetic particles have attracted much attention toward surface modification by coating of different surface stabilizer like chitosan, humic acid and diethylenetriaamine [15]. Functional group including carboxylate, phosphate and sulfur of stabilizer is known to bind to the surface of Fe_3O_4 and provide high surface area, selectivity and stability of functionalized Fe_3O_4 [16]. These functionalized magnetic nanoparticles were found to be cost-effective, chemically stable and environmental friendly in nature compared to bare Fe_3O_4 nanoparticles.

In the present work, Fe_3O_4-Cit nanoadsorbent was developed by colloidal process keeping in mind to explore its feasibility as adsorbent for the removal of Cd(II) ions. The batch adsorption performance of adsorbent was determined by optimize operational parameter like pH, temperature, adsorbent dose, and contact time. For predicting the mechanisms and performance of adsorbent, the adsorption isotherm model (i.e. Langmuir, Freundlich), kinetics (i.e. psuedo first and pseudo second order) and thermodynamics studies were applied on experimental data.

2. Materials and methods

2.1. Materials

All chemicals and reagents used were of analytical grade without any further purification. Ferric chloride ($FeCl_3{\cdot}6H_2O$), ferrous sulfate ($FeSO_4{\cdot}7H_2O$), ammonium hydroxide, sodium hydroxide (NaOH), sodium chloride (NaCl) and citric acid ($C_6H_8O_7$) were purchased from the Aldrich (Sigma–Aldrich, Steinem, Germany). Double-distilled deionized water was used for preparing solutions.

2.2. Preparation of Fe_3O_4-Cit

The previously reported method was applied for synthesis of bare Fe_3O_4 magnetic nanoparticles [17] and functionalized by citric acid coating. Briefly, 6.1 g of $FeCl_3{\cdot}6H_2O$ and 4.2 g of $FeSO_4{\cdot}7H_2O$ were dissolved in 100 mL distilled water and heated at 90 °C then afterwards 10 mL of ammonium hydroxide (25%) and 0.5 g of citric acid dissolved in 50 mL of distilled water was added. The mixture was stirred at 90 °C for 30 min and then cooled to room temperature. The light brown precipitate was collected after centrifugation of colloidal solution at 10,000 rpm and it was washed with acetone.

2.3. Characterization of Fe_3O_4-Cit

The surface functional groups of Fe_3O_4-Cit was determined by FTIR (Thermo-Scientific, Nicole 6700). SEM study was carried out using a scanning electron microscope (JEOL, JSM 6490 LV) at an electron acceleration voltage of 20 kV. TEM study was carried out with the help of transmission electron microscopy (Morgagni 268D, Fei Electron Optics). X-ray diffraction pattern was carried out with the help of X-ray diffractometer (XRD).

Solid addition methods were employed to calculate the point of zero charge of Fe_3O_4-Cit [18]. The 50 mL solution of 0.1 N KNO_3 was prepared in 150 mL conical flask and maintained its series of initial pH (pH_i) from 2 to 12 by adding either 0.1 N HCl or 0.1 N NaOH solutions. The adsorbent doses (0.5 g L^{-1}) were added to 50 mL 0.1 N KNO_3 solution and the suspension was allowed to stir for 40 min. The difference between the initial pH (pH_i) and final $pH_f - pH_i$ was plotted against pH_i to get zero point charge. The point of intersection of the resulting curve with the abscissa, at which $\Delta pH = 0$, has given the value of zero point charge (pH_{zpc}).

2.4. Adsorption procedure

Adsorption studies were carried out by batch experiment reported in literature [19,20]. The adsorption of Cd(II) ions by Fe_3O_4-Cit was performed at temperature 35 °C. The solution of 50 mL of desired concentration mg L^{-1} (25, 50, 75 and 100) of Cd(II) ion was prepared by adding $Cd(NO_3){\cdot}3H_2O$ in double distilled water. The pH of mixture was adjusted using 0.1 M HNO_3. The adsorbent (Fe_3O_4-Cit) 0.2 g L^{-1} was added in 50 mL metal concentration solution and mixture was shaken at desired time in an electrically thermo stated reciprocationg shaker at 120 rpm at

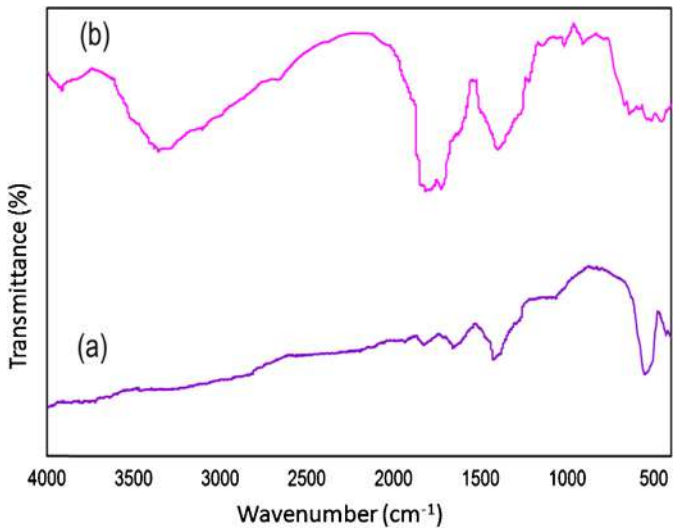

Fig. 1. FTIR spectra of magnetic nanoparticles (a) bare magnetic nanoparticles (Fe_3O_4), (b) citric acid coated magnetic nanoparticles (Fe_3O_4-Cit).

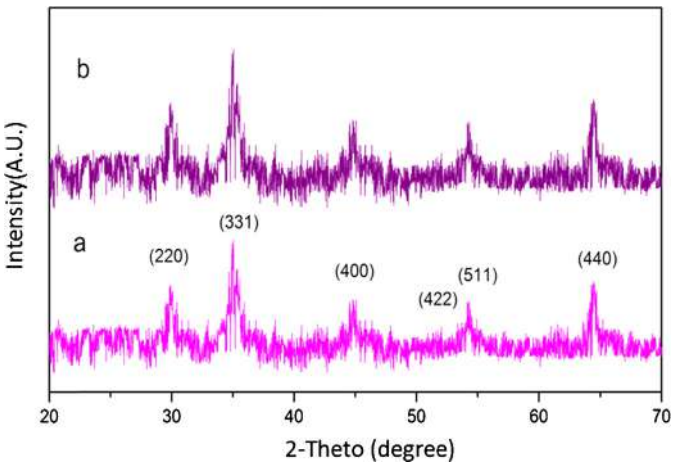

Fig. 2. XRD pattern of magnetic nanoparticles (a) bare magnetic nanoparticles (Fe_3O_4), (b) citric acid coated magnetic nanoparticles (Fe_3O_4-Cit).

35 °C. The magnetic adsorbent was removed magnetically whereas the concentration of Cd(II) ions was measured by atomic adsorption spectroscopy (Ruilli-130). The samples were analyzed in triplicates and percentage removal and adsorption capacity at equilibrium (q_e) were calculated by using Eqs. (1) and (2), respectively [21,22].

$$\text{Removal}\,(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)}{W} \times V \quad (2)$$

where C_0 is the initial concentration of adsorbate (mg L^{-1}); C_e is concentration of adsorbate at equilibrium in (mg L^{-1}); V is volume of solution in (L) and W is mass of adsorbent (g).

3. Results and discussion

3.1. Characterization of adsorbent

The FTIR spectrum range (4000–400 cm^{-1}) of citric acid coated Fe_3O_4 dispersed in KBr revealed bands from the iron citrate spectrum. A large and intense band at 3450 cm^{-1} that could be assigned to the structural OH groups as well as to the traces of molecular water and citric acid. Whereas the 1700 cm^{-1} peak assignable to the C=O vibration (symmetric stretching) from the COOH group of citric-acid (CA) shifts to an intense band at about 1600 cm^{-1} for the Fe_3O_4 coated with citric acid (Fe_3O_4-Cit) revealing the binding of a CA radical to the magnetite surface showing in Fig. 1. The band at 1400 cm^{-1} to the asymmetric stretchings of CO from the COOH group can be assigned. The low-intensity bands between 400 and 600 cm^{-1} can be associated with the stretching and torsional vibration modes of the magnetite. The assignments are concordant with previous study [23] which described two broad band's at 580 and 400 cm^{-1} associated with magnetite (Fe_3O_4).

The XRD patterns of Fe_3O_4-Cit show the crystalline structure of nanoparticle as depicted in Fig. 2. For Fe_3O_4 the peak were obtained 30.2° (2 2 0), 35.6° (3 3 1), 43.2° (4 0 0) 53.4° (4 2 2) 57.2° (5 1 1), and 62.7° (4 4 0) at 2θ degree indicated the cubic spinal structure of magnetite [24]. The similar peaks were found for Fe_3O_4-Cit, which reveals that citric acid coating does not result in the phase change of bare Fe_3O_4 [25,26].

Fig. 3(a) and (b) reveals that monodispersed rough surface of Fe_3O_4-Cit was confirmed through the SEM analysis whereas the TEM analysis demonstrate the particles size in the range of 15–27 nm as shown in Fig. 4(a) and (b). The similar size of Fe_3O_4-Cit with Fe_3O_4 has valuable effect in equal aggregation of prepared material in solution [27].

3.2. Cd(II) adsorption

3.2.1. Effect of pH

In adsorption process pH plays a key role to determine the charge on the surface of adsorbent by their functional group and also determine the speciation of metal in solution [28]. The pH study of Cd(II) ions adsorption on the surface of Fe_3O_4-Cit was observed below the pH_{pzc} (6.3). It was observed that with an increase in initial pH of the solution from 2 to 5 at fixed initial metal ions concentration (50 ppm) and time 40 min, the adsorption capacity increased from 8.5 mg L^{-1} to 11.67 mg L^{-1} of Cd(II) aqueous solution. Whereas the adsorption percentage found constant at the pH 5 as shown in Fig. 5(a). Surface modified bare Fe_3O_4, means Fe_3O_4-Cit have more acidic surface groups and the surface area compare to bare material. In aqueous solution, the acidic surface group on the adsorbent undergoes ionization by producing H^+ ions [24]. These H^+ ions are directed toward the liquid phase leaving the carbon surface with negatively charged —COO— sites that are necessary for the adsorption process. With the increase in pH of the solution, the deprotonation of acidic functional groups strengthens and the attraction between adsorbent and metal ions increased the Cd(II) ions. At higher pH (>5) the predominance of OH^- ions in the solution creates a competition between negatively charged adsorbent surface and OH^- ions which resulted a decrease in the adsorption of Cd(II) ions [18].

3.2.2. Effect of temperature

The effect of temperature on the adsorption under optimized conditions is depicted in Fig. 5(b). It was observed that adsorption of Cd(II) increases 10.7–12.1 mg L^{-1} with increases in temperature from 293 K to 308 K and further decreases at the higher temperature. The decrease in the adsorption capacity with temperature was due to the weakening of the adsorptive forces between the active sites and the adsorbate species on the adsorbent surface [29,30].

3.2.3. Effect of contact time and removal percentage

The effect of contact time on the equilibrium of Cd(II) adsorption by Fe_3O_4-Cit is shown in Fig. 6(a). The removal efficiency increases from 10.6 mg L^{-1} to 12.05 mg L^{-1} with time in the first 40 min. Then the adsorption curve reached at equilibrium stage after that time. The Cd(II) adsorption equilibrium within few minutes reveals that

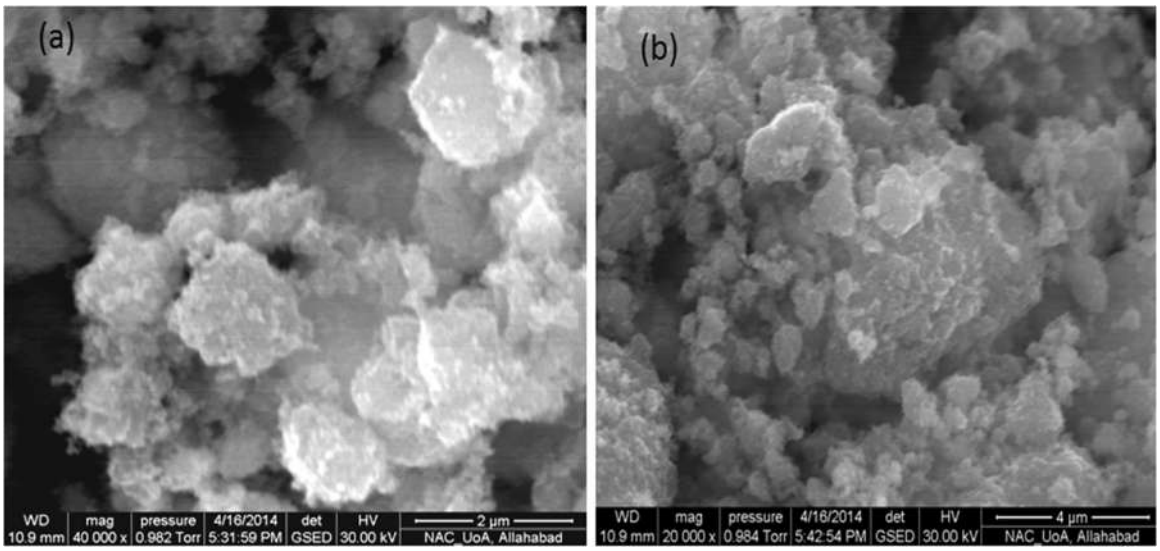

Fig. 3. SEM image of citric acid coated nanoparticles (Fe_3O_4-Cit).

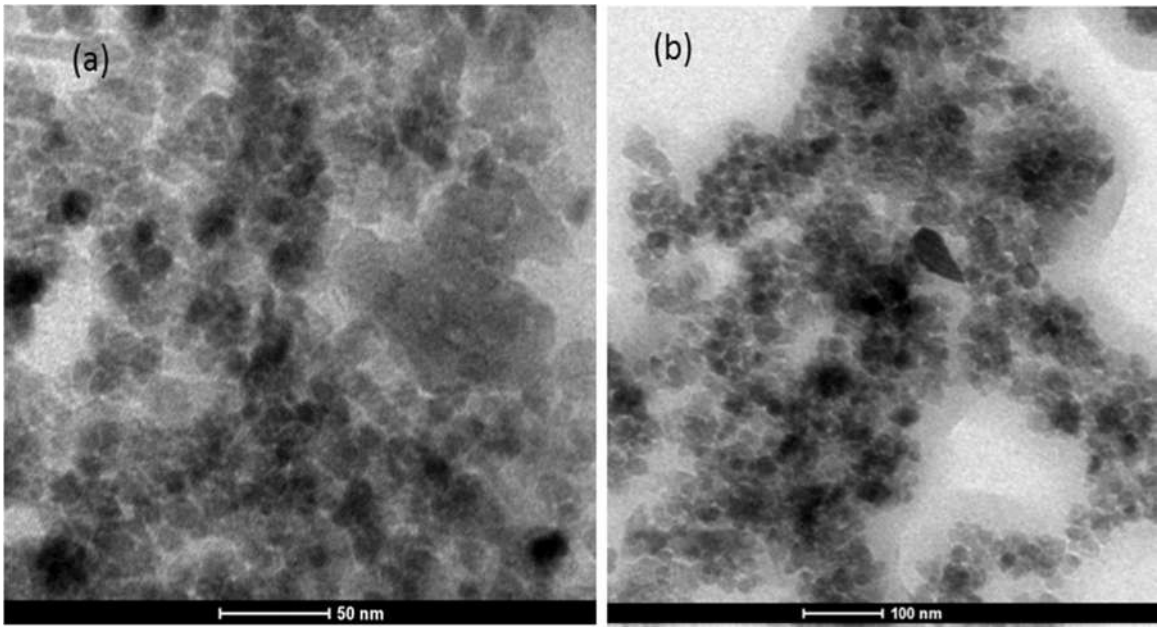

Fig. 4. TEM image of citric acid coated nanoparticles (Fe_3O_4-Cit).

reaching equilibrium in a short time is due to the absence of internal diffusion resistance [31,32]. The fast removal of Cd(II) ions 96% was observed when increasing the contact time 40 min as shown in Fig. 6(b). But after 40 min the Cd(II) ions adsorption percentage undergoes in decreasing order because after this time adsorptive sites of adsorbent blocked with adsorbent.

3.2.4. Adsorption isotherms

In adsorption system, equilibrium adsorption isotherm is a fundamental design to evaluate that how the metal ions are partitioned between adsorbent and liquid phase at equilibrium as a function of metal concentration. Keeping this view the linearized forms of Langmuir and Freundlich isotherm models were applied for the determination of Cd(II) adsorption onto the surface of Fe_3O_4-Cit. The Langmuir isotherm model is based on the assumption of homogeneity onto the surface of adsorbent with a finite number of identical sites and a constant adsorption potential. Langmuir isotherm model at nonlinear forms exists as following expression represented in Eq. (3) [33,34].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where C_e is metal concentration in aqueous phase in mg L^{-1} and q_e is the amount of Cd(II) ions adsorbed on per unit weight of Fe_3O_4-Cit in mg g^{-1} at equilibrium. The q_m is the maximum adsorption capacity (mg g^{-1}) reflected on a complete monolayer adsorption and K_L is the Langmuir constant (L mg^{-1}) related to adsorption energy. The Langmuir isotherm parameters can be obtained from its linearized form as represented in Eq. (4) [35].

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{4}$$

The value of K_L, q_m and correlation coefficient (R^2) obtained from the Langmuir isotherm parameters was shown in Table 1, which demonstrate that the maximum adsorption capacity (q_m)

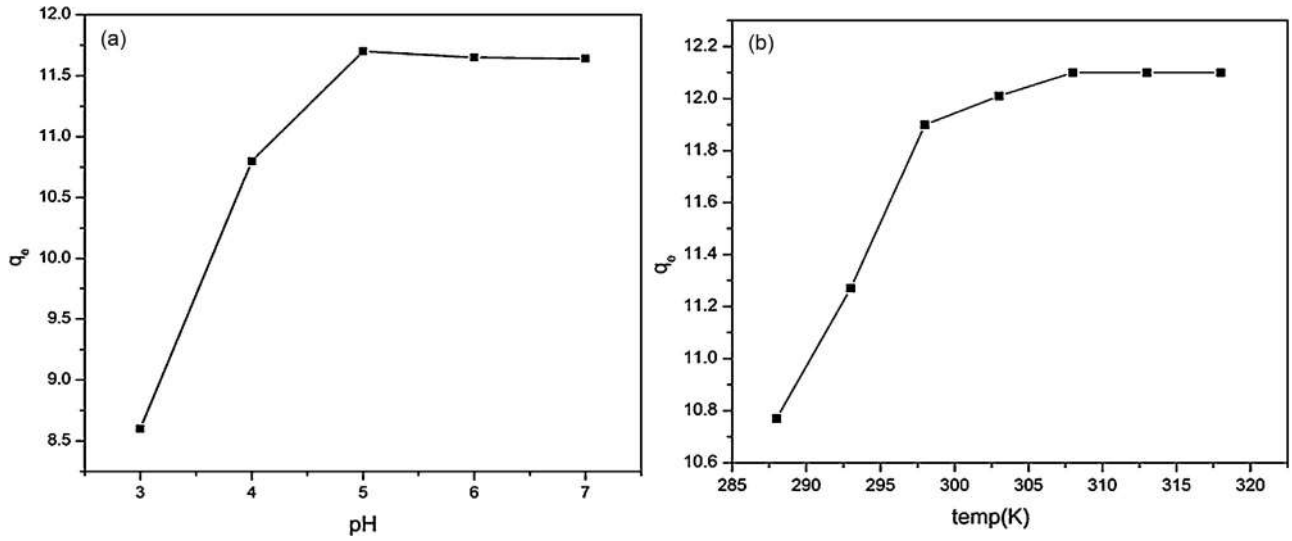

Fig. 5. Effect of pH (a) and effect of temperature, (b) on the adsorption of Cd(II) 25 mg L^{-1} on to 0.2 g adsorbent dose.

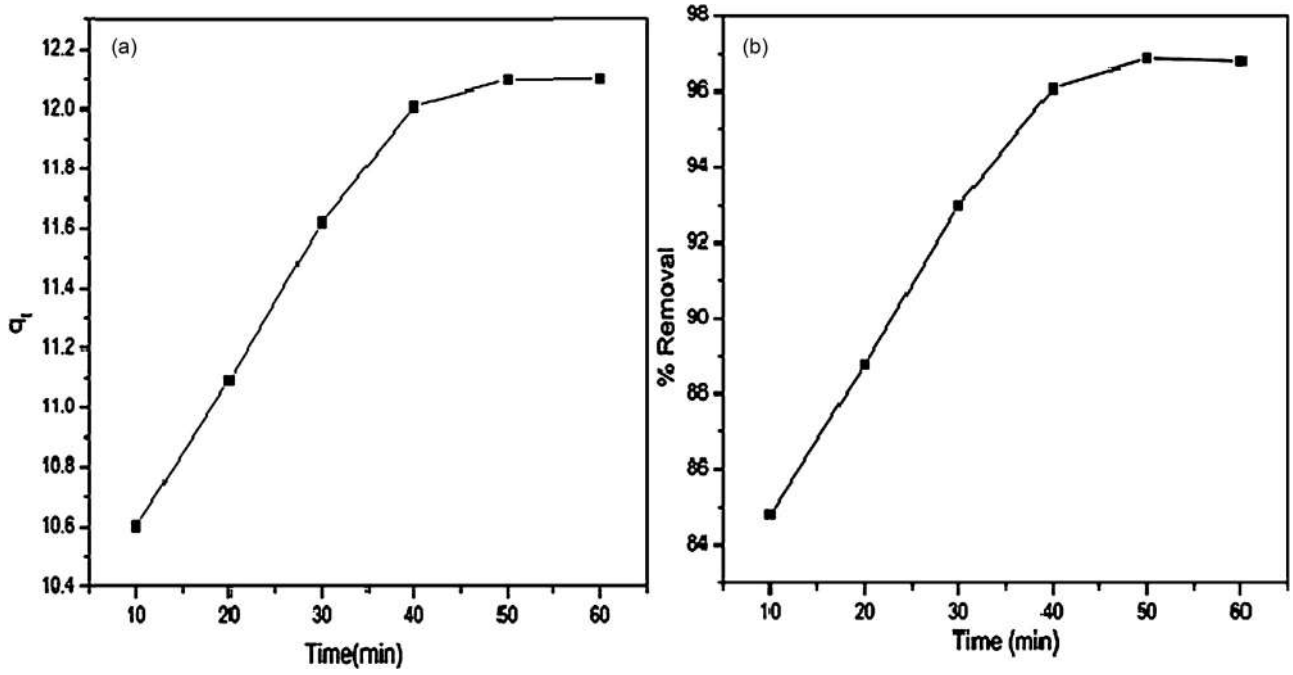

Fig. 6. Effect of contact time (a) percentage removal, (b) on the adsorption of Cd(II) 25 mg L^{-1} on to 0.2 adsorbent dose.

was found to be 10.81 mg g^{-1}, 11.45 mg g^{-1}, 12.56 mg g^{-1} at different temperatures 298 K, 303 K and 308 K represented in Fig. 7(a). A high values of correlation coefficient (R^2) to be 0.997 at 298 K, 0.993 at 303 K and 0.991 at 308 K indicate that the applicability of Langmuir isotherm best fitted for linearity of different concentration solution of metal and also assumed a monolayer coverage and uniform activity distribution on the adsorbent surface [36,37].

Table 1
Langmuir and Freundlich isotherm parameters for the adsorption of Cd(II) from aqueous solution by Fe_3O_4-Cit.

Temp. (K)	Langmuir model			Freundlich model		
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	N	K_F	R^2
298	10.81	4.07	0.997	2.51	11.34	0.993
303	11.45	3.86	0.993	2.51	11.84	0.992
308	12.56	3.47	0.991	2.82	13.01	0.991

The Freundlich isotherm is a an empirical equation based on highly heterogeneity surface adsorption applied to experimental data for determination of Freundlich constant K_F (multilayer adsorption) and the exponent n (adsorption intensity) shown in Table 1. The value of K_F and n was calculated through the intercept and slope obtained by plot of ln q_e versus ln C_e as shown in Fig. 7(b) The linear form of the Freundlich isotherm is given by Eq. (5) [38].

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

The value of Freundlich parameter n was found to be 2.52, 2.51, and 2.82 at temperatures 298 K, 303 K and 308 K respectively have more indication of significant adsorption onto the adsorbent [30]. The correlation coefficient R^2 = 0.993 at 298 K, 0.992 at 305 K and 0.991 at 308 K may support the favorability of Freundlich model. The comparative values of correlation coefficient of both model reveal that the correlation coefficient values of Langmuir is higher

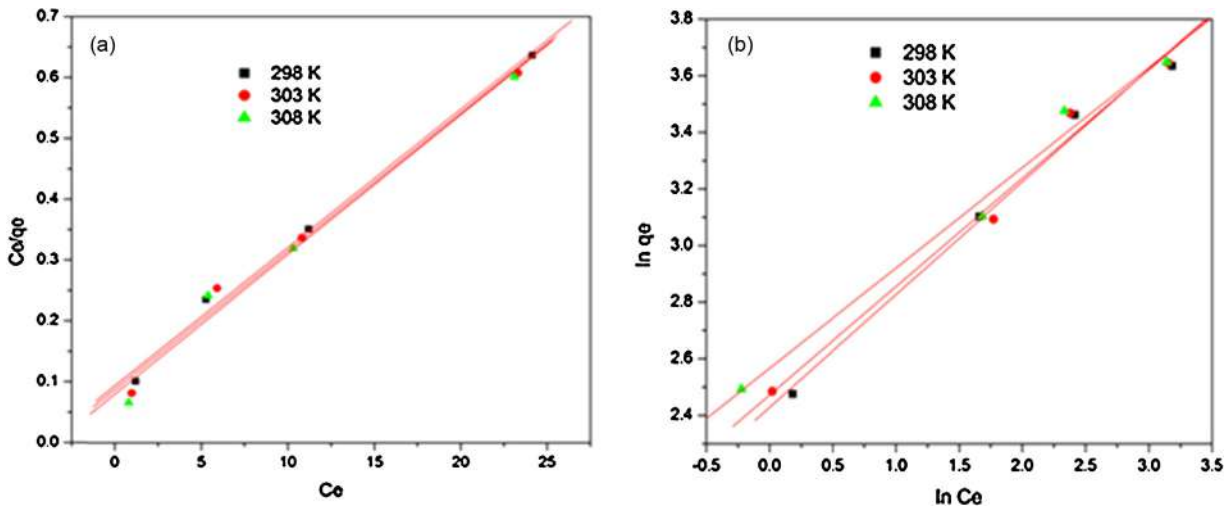

Fig. 7. Graphical representation of linear fit of isotherm model (a) Langmuir isotherm, (b) and Freundlich isotherm for the adsorption of the different eqilibrium concentration solution od Cd(II) ion onto 0.2 g adsorbent dose.

then Freundlich thus it is clear that Freundlich model is not suitable of linear fit for different concentration of Cd(II) metal ions [39].

3.2.5. Adsorption kinetics

In adsorption process the kinetic parameters are very important for determination of rate of adsorption. The Lagergren form of Pseudo first [40] and Pseudo second order [41] kinetics were applied for testing experimental data expressed in Eqs. (6) and (7).

$$\ln(q_e - q_t) = \ln q_t - k_1 t \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the metal uptake per unit weight of adsorbent (mg g^{-1}) at equilibrium and metal uptake per unit weight of adsorbent (mg g^{-1}) at time t, (min), respectively. k_1 (min^{-1}) and k_2 (gm g^{-1} min^{-1}) are the rate constant of pseudo first-order and second order respectively. The obtained value of slope and intercept were utilized for determination of k_1, and k_2.

In the first order kinetics the value of k_1, and q_e was calculated from the plot of $\log(q_e - q_t)$ versus time t shown in Fig. 8(a). The correlation coefficient (R^2) values were 0.996 at 298 K, 0.989 at 303 K and 0.985 at 308 K obtained at different metal ion concentration equilibria. It is found that the calculated (cal.) value of q_e from the first order kinetics model was dramatically lower than the experimental (exp.) value presented in Table 2. The result, which was consistent with the 2 mg g^{-1} adsorbate, was reported by previous study [42].

In the second order kinetics, the value of K_2, q_e and correlation coefficient R^2 are listed in Table 2. The plot t/q_t versus t was used to calculate the k_2 and q_e, showed good agreement with experimental data depicted in Fig. 8(b). It revealed the high values of correlation coefficient (R^2) 0.996 at 298 K and 0.997 at 303 K and 0.998 at 308 K, which is higher than R^2 values of pseudo first order at different temperature. Similar trends have been reported by previous studies of Cd(II) ions form aqueous solution by other adsorbent [43,44]. The higher values of R^2 of pseudo second order and [45] applicability of Langmuir isotherm indicated that the process to be chemisorptions in nature [36,46]. The linear fit of pseudo second order kinetics model on experimental value of different equilibrium concentration of metal solution suggested the multi-step process involving sorption on the external surface and diffusion into the interior of adsorbent. This model also suggested the process to be chemo-sorption through valency force by sharing or by exchange of electron between Fe_3O_4-Cit adsorbents and Cd(II) ions [47,48].

3.2.6. Adsorption thermodynamics

In the present study the effect of temperature on adsorption experiment was carried out at the temperature 298 K, 303 K and 308 K. The optimized pH 5 and adsorbent dose 0.2 g L^{-1} and equilibrium contact time 40 min were applied to the different Cd(II) ions concentration aqueous solution 25 ppm, 50 ppm, 75 ppm and 100 ppm respectively. Due to the effect of temperature the value of adsorption increases or decreases may be due to strengthening or weakening of adsorptive force between the active site of adsorbent and adsorbate species [49].

The thermodynamics parameter viz. change in Gibbs free energy (ΔG) (kJ mol^{-1}), standard enthalpy change (ΔH) (kJ mol^{-1}) and the standard entropy change (ΔS) (J k^{-1} mol^{-1}) have significant role in determining the feasibility, spontaneity and heat change of the adsorption process with respect to temperature. These parameters have been calculated using the following Eqs. (8)–(11) [50,51].

$$\Delta G^\circ = -RT \ln K_d \tag{8}$$

$$K_d = \frac{q_e}{C_e} \tag{9}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{10}$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{11}$$

where R is the universal gas constant (8.314 J mol^{-1} K), T is the absolute temperature in Kelvin, K_d is distribution coefficient, q_e (mg g^{-1}) is the equilibrium concentration of Cd(II) ions adsorbed onto Fe_3O_4-Cit and C_e (mg L^{-1}) is the remained concentration of Cd(II) ions in the solution. The value of ΔH° and ΔS° were calculated with the slope and intercept of the plot and other thermodynamic parameter at three temperature studies are listed in Table 3. The positive value of ΔS° is an indication of increased randomness at the adsorbent-adsorbate interface during the adsorption of Cd(II) at different temperature. The negative value of ΔG° in kJ mol^{-1} (−5.68, −6.31 and −6.95) at all temperature found which confirms the feasibility of the metal ion adsorption on to adsorbent surface was spontaneous in behavior [52]. While the positive value of the ΔH (+73.13 kJ mol^{-1}) indicating the endothermic nature of the adsorption process, and the high positive value of ΔH indicates that the adsorption process may be likely due to strong interactions

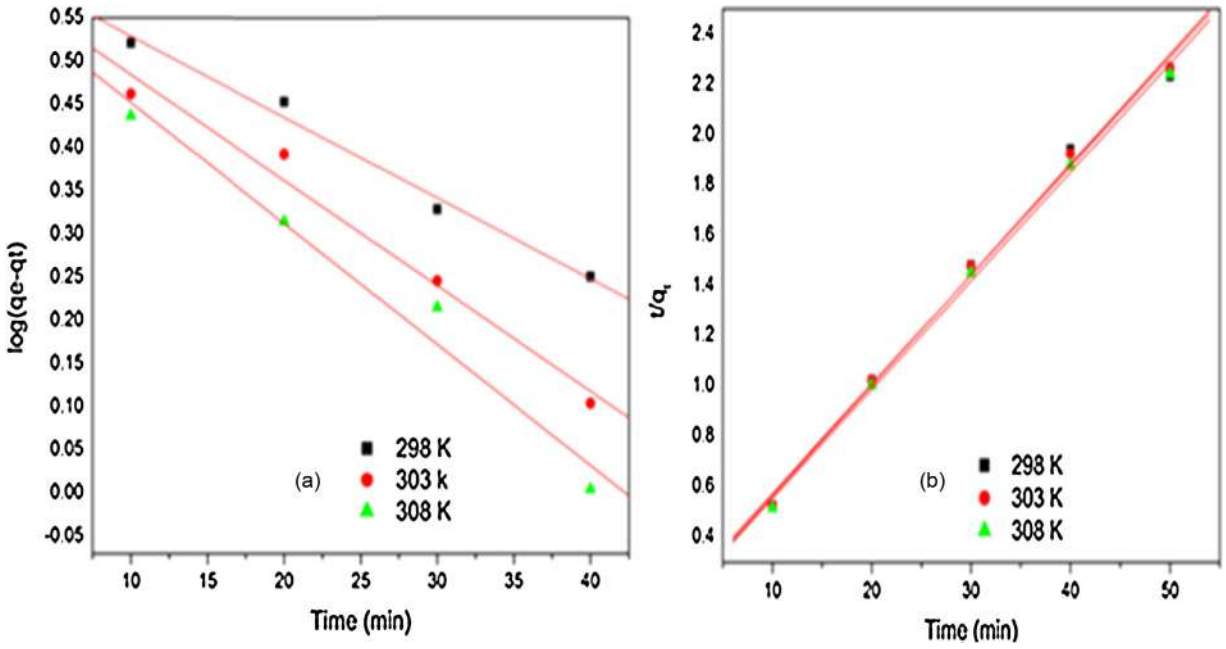

Fig. 8. Graphical representation of linear fit of kinetics model (a) pseudo first order, (b) pseudo second order for the adsorption of different equilibrium concentration solution of Cd(II) ion onto 0.2 g adsorbent dose.

Table 2
Pseudo first and second order kinetics data of Cd(II) adsorption by Fe_3O_4-Cit at different temperature.

Temp. (K)	Pseudo fist-order			Pseudo second-order		
	k_1 (min^{-1})	q_e·cal ($mg\,g^{-1}$)	R^2	k_2 ($g\,mg^{-1}\,min^{-1}$)	q_e·cal ($mg\,g^{-1}$)	R^2
298	0.021	4.19	0.996	0.013	23.04	0.996
303	0.028	4.02	0.989	0.015	22.75	0.997
308	0.032	3.91	0.985	0.015	22.08	0.999

Table 3
Thermodynamics parameters for Cd(II) Adsorption onto adsorbent at different temperature.

Temp. (K)	ΔG° ($KJ\,mol^{-1}$)	ΔH° ($KJ\,mol^{-1}$)	ΔS° ($J\,K^{-1}\,mol^{-1}$)
298	−5.68	73.13	289.92
303	−6.31		
308	−6.95		

Table 4
Desorption studies of Cd(II) containing Fe_3O_4-Cit ion different concentration of acidic solution.

Concentration of HCl(M)	Percentage desorption of Cd (II)
0.01	23.76
0.025	28.67
0.05	72.67
0.075	93.78
0.1	99.2
0.125	99.3
0.15	99.6
0.20	99.8

between the Cd(II) ion and the functional groups on the surface of the Fe_3O_4-Cit [49].

3.2.7. Desorption study

To understand desorption of metal loaded Fe_3O_4-Cit, the minerals acid of various concentration 0.001–0.20 M HCl was used as desorption media. In desorption study batch experimental technique was applied to evaluate the desorption performance of Fe_3O_4-Cit [53]. The result of experimental values is depicted in Table 4. The maximum value of desorption efficiency was observed 99.98% with 0.20 M HCl. It has been assumed that the hydrogen ions may be replacing the Cd(II) ions on the metal loaded adsorbent through the ion exchange process. After removing Fe_3O_4-Cit from HCl solution remaining concentration of Fe was determine by the atomic adsorption spectrophotometer (AAS). The remaining concentration of Fe, 0.0048% was obtained compare to the amount of Fe_3O_4-Cit. To detect the reusability of adsorption–desorption, eight times desorption were carried using same adsorbent. Finally observed no desorption capacity occurs after multi adsorption–desorption cycle. Thus, these results indicate that the Fe_3O_4-Cit has good reusability and suitability for removal of Cd(II) ions [45].

4. Conclusion

In the present study, citric acid coated magnetite nanoparticles (Fe_3O_4-Cit) have been synthesized and characterized by FT-IR, SEM, TEM and XRD analyses. Its adsorption capability for Cd(II) ion was investigated in aqueous solutions. The adsorption was carried out at pH 5 and 35 °C temperature of different initial concentration of Cd(II) ions, 25 $mg\,L^{-1}$, 50 $mg\,L^{-1}$, 75 $mg\,L^{-1}$, 100 $mg\,L^{-1}$ in aqueous solution. The removal percentage 96% was obtained on 0.2 $g\,L^{-1}$ adsorbent of 25 $mg\,L^{-1}$ aqueous solution at optimized temperature, pH and contact time. The adsorption data were satisfactorily correlated by Langmuir and Freundlich isotherm model. The experimental data have to suitable linearity with Langmuir isotherm with maximum adsorption capacity ($mg\,g^{-1}$) 10.81, 11.45 and 12.56 at

the 298 K, 303 K and 308 K respectively. The correlation coefficient $R^2 = 0.997$ fully support the favorability of Langmuir isotherm in adsorption process. The experimental data is giving best linear fit with pseudo second order with $R^2 = 0.999$ at optimize temperature 308 K. The negative value of ΔG°, −5.68, −6.31 and −6.95 kJ mol^{-1} at all temperatures also confirms the feasibility and spontaneity of the Cd(II) ions adsorption on to Fe_3O_4-Cit surface. As the synthesized nanoparticles have the ability to interact with a verity of compounds, the particles may also be utilized for the remediation of dye, PAHS, organic pollutant and treatment of wastewater at the industrial scale.

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