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Removal of highly toxic Cd(II) metal ions from aqueous medium using magnetic nanocomposite: adsorption kinetics, isotherm and thermodynamics

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ABSTRACT

In this research, trisodium citrate (TSC) based magnetite (Fe_3O_4) nanocomposite was developed (Fe_3O_4@TSC) and applied as an efficient adsorbent for removal of Cd(II) from aqueous medium. The influence of experimental factors such as pH of the solution, amount of Fe_3O_4@TSC, temperature, contact time and initial Cd(II) concentration were studied. The results exhibited that the optimum pH value, equilibrium time and temperature were 7.6, 60 min and 298 K, respectively. The adsorption isotherm and kinetics were followed to the Langmuir isotherm and pseudo-second-order model, respectively. The maximum monolayer adsorption capacity was 312.5 mg/g at 298 K. The adsorption of Cd(II) on Fe_3O_4@TSC was exothermic in nature and spontaneous process based on negative values of $\Delta H°$ and $\Delta G°$. The type of interactions between electropositive Cd(II) and the carboxylic group was electrostatic interactions.

Keywords: Magnetic; Nanocomposite; Isotherm; Kinetics; Toxic Cd(II)

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1. Introduction

Water contaminated by heavy metal is a serious issue for living beings on earth [1–5]. It is well-known that with the fast growth of the industry, heavy metal pollution caused serious environmental problems [6–8]. Heavy metals such as Cr(V), Pb(II), Cd(II), Hg(II) and As(III) are highly toxic to the human body and these metals can damage liver, kidney and cardiovascular system [9–11]. Among above these heavy metals, Cd(II) is considered as one of the most hazardous heavy metal ions to human health and could not be degraded by microbial and accrued in human beings, animals, and plants via food chain. Cd(II) in wastewater is widely released from the battery industry, electroplating manufacturer, pesticides, phosphate fertilizers, and pigments [12–17]. Nowadays, several methods have been utilized to remove Cd(II) from polluted water, such as electrochemical treatment, photocatalysis, chemical precipitation, biological treatment reverse osmosis, adsorption, and ion exchange, etc. [18–23]. Among these methods, adsorption is known as the best method for the exclusion of heavy metals even at low concentrations and it has many advantages such as economical, simple, easy operation, regeneration, effective and cheap [24–26]. Researchers have

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developed many adsorbents for removal of Cd(II) from wastewater such as hydrochar [27], nanomagnetic walnut shell-rice [28], activated sludge [29], calcined MgZnFe-CO_3 [30], iron-reducing bacteria [31], straw cellulose hydrogel beads [32], magnetic graphene oxide [33]. Fe_3O_4 nanoparticles have many characteristics such as cost-effective adsorbent, as high surface area and high saturation magnetization. It is easy to separate the adsorbents from wastewater or aqueous solution by using an external magnetic field [34]. Many adsorbents have been synthesized by researchers such as Fe_3O_4@PDA [35], Fe_3O_4@AMCA-MIL53(Al) [26]. Magnetite nanoparticles tend to agglomerate owing to strong magnetic attraction among particles and high energy surface [36]. To diminish the agglomeration and increase the stability of magnetite, Fe_3O_4 was modified by trisodium citrate (TSC).

In the present work, magnetic nanocomposite (Fe_3O_4@TSC) was applied as an efficient adsorbent for the removal of Cd(II) from aqueous medium. The influence of experimental parameters such as solution pH, amount of Fe_3O_4@TSC, temperature, contact time, and initial Cd(II) concentration was performed. The kinetic, isotherm and thermodynamic were also investigated.

2. Experimental section

2.1. Materials and methods

$FeCl_3·6H_2O$, $FeCl_2·6H_2O$, TSC solution was obtained from Sigma-Aldrich, U.S.A. Sodium hydroxide and $Cd(NO_3)_2$ $4H_2O$ were purchased from BDH, England and HCl and HNO_3 from Merck, Germany. Our adsorbent Fe_3O_4@TSC was prepared via the same method as described in the earlier study [25].

2.2. Batch adsorption experiment

The batch adsorption tests were performed by adding 10 mg of Fe_3O_4@TSC into 25 mL of 10 mg/L Cd(II) solutions. The solution was shaken at 100 rpm and 298 K for 24 h. Then, the solitons were isolated via an external magnetic field. The concentration of Cd(II) which was left in the solution phase was determined by atomic absorption spectroscopy. The q_e (mg/g) and % adsorption were calculated by the following equations:

$$q_e = \left(C_0 - C_e\right)\frac{V}{m} \tag{1}$$

$$\%\text{Adsorption} = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

The influence of various factors on the adsorption of Cd(II) on Fe_3O_4@TSC such as pH (2.6 – 9.15), equilibrium time (1 – 240 min), amount of Fe_3O_4@TSC (0.01 – 0.05 mg), temperature (25°C–55°C), initial concentration of Cd(II) (10–250 mg/L) were investigated. The experiment of desorption study was carried out by the following procedure: 10 mg of Fe_3O_4@TSC was added into a conical flask containing 25 mL of 10 mg/L Cd(II) solutions. The solution was shaken at 100 rpm and 298 K for 24 h. Then the soliton was separated by using an external magnetic field. After 60 min, the sample was washed three times with D.I. water to remove any Cd(II) ions which were loosely attached to the conical flask or to the adsorbent itself. Then, the saturated Fe_3O_4@TSC was eluted by using two eluents (HNO_3 and HCl) at different concentrations. The % desorption of Cd(II) ions was calculated by the following equation:

$$\%\text{ Desorption} = \frac{\begin{array}{c}\text{Concentration of Cd}\left(\text{II}\right)\\ \text{desorbed by the eluent}\end{array}}{\begin{array}{c}\text{Initial concentration of Cd}\left(\text{II}\right)\\ \text{adsorbed on the adsorbent}\end{array}} \times 100 \tag{3}$$

3. Results and discussion

3.1. Adsorption studies

The effect of pH on Cd(II) adsorption was carried out in the range of 2.6–9.15 (conditions: contact time – 24 h; temperature – 298 K; C_0 – 10 mg/L; agitation speed – 100 rpm; adsorbent dosage – 10 mg). The results are given in Fig. 1a which showed that when the pH was enhanced from 2.66 to 7.63, the adsorption capacity was enhanced from 5.1 to 24.24 mg/g. The maximum adsorption capacity was noted at pH 7.63 which indicated that the pH of the solution had a considerable impact on the adsorption capacity of Cd(II) using Fe_3O_4@TSC nanocomposite. At low pH, the carboxylic groups were protonated and the surface of Fe_3O_4@TSC nanocomposite became positively charged, which formed a repulsive force between electropositive Cd(II) ions and Fe_3O_4@TSC nanocomposite [37,38]. H_3O^+ can also compete with Cd(II) ions resulting in low removal efficiency. When the pH was raised, the degree of deprotonation of carboxylic groups was gradually increased which led to an increase in the adsorption capacity due to the more electrostatic attraction between Cd(II) and Fe_3O_4@TSC nanocomposite. After pH 7.63, the adsorption of Cd(II) ions was reduced due to the formation of metal hydroxides [37].

Various amounts of Fe_3O_4@TSC nanocomposite (0.01–0.05 g) was added to 25 mL of 10 mg/L Cd(II) solutions in order to test the influence of adsorbent dosage (conditions: contact time – 60 min; temperature – 298 K; agitation speed – 100 rpm; C_0 – 10 mg/L; pH – 7.63). It is clear from Fig. 1b that with the increase of the amount of Fe_3O_4@TSC nanocomposite from 0.01 to 0.05 g, the q_e was decreased from 23.5 to 4.8 mg/g which might be due to the aggregation of Fe_3O_4@TSC particles [25,39].

The impact of contact time on the Cd(II) adsorption on Fe_3O_4@TSC was carried out in the time range of 1–240 min by keeping all other factors constant: (temperature – 298 K; agitation speed – 100 rpm; C_0 – 10 mg/L; pH – 7.63; dose – 10 mg). Fig. 2a displays that the adsorption capacity was raised gradually from 15.1 to 21.95 mg/g with an increase in the time until the equilibrium was achieved. In the beginning, the adsorption of Cd(II) onto Fe_3O_4@TSC was fast. The removal efficiency of Cd(II) was rapidly reached 74.6% just within 5 min. The saturation capacity was reached around 60 min with a maximum adsorption capacity of 21.87 mg/g. At equilibrium time, the % adsorption was 93%

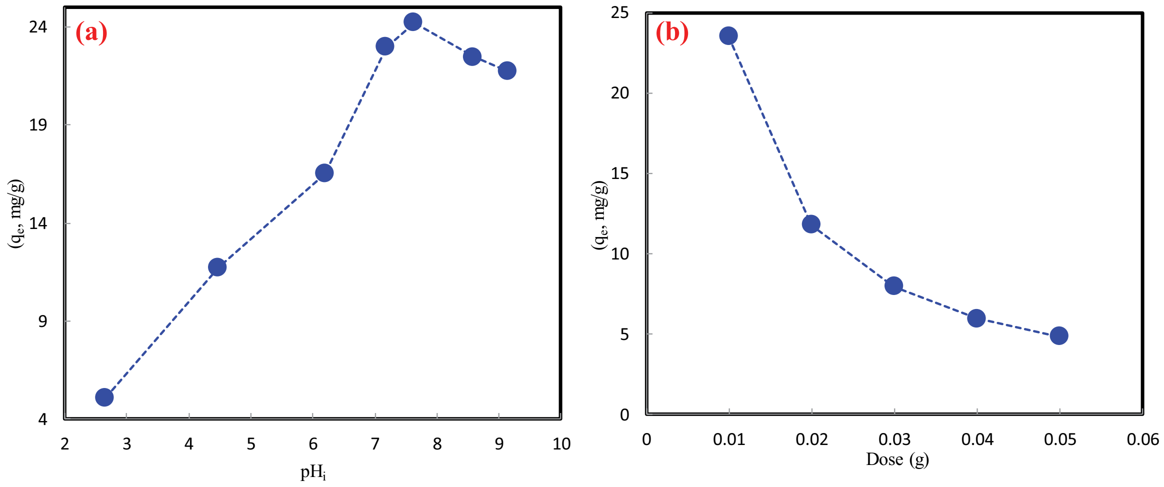

Fig. 1. (a) Effect of pH and (b) adsorbent dose on the adsorption of Cd(II) using Fe_3O_4@TSC nanocomposite.

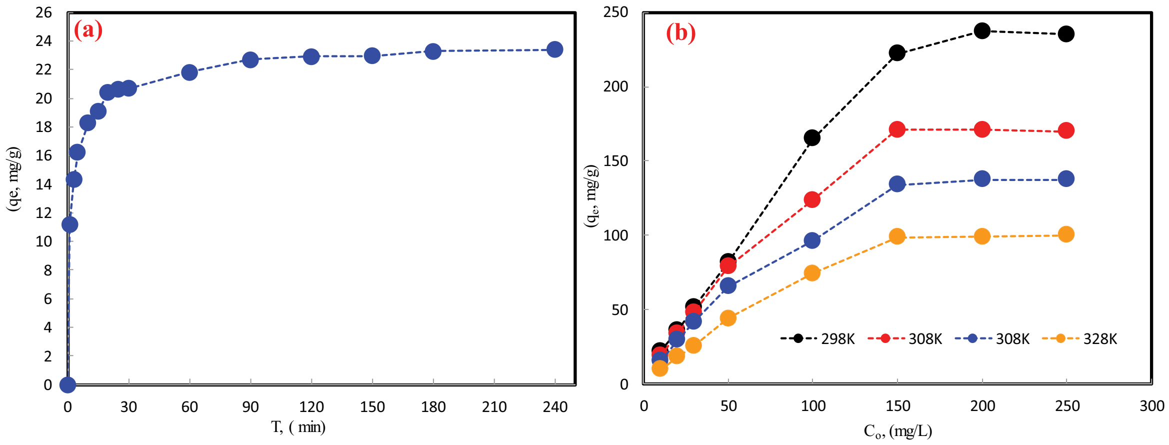

Fig. 2. (a) Effect of contact time and (b) initial concentration for adsorption of Cd(II) onto Fe_3O_4@TSC nanocomposite.

for Cd(II) metal ion, thus, the equilibrium time was kept 60 min for all experiments.

The impact of initial Cd(II) concentration on adsorption capacity was studied at varied concentration (10–250 mg/L) at various temperature (25°C, 35°C, 45°C and 55°C) with following conditions (time – 60 min; pH – 7.63; dose – 10 mg). As can be seen in Fig. 2b, an increase in the initial Cd(II) concentration from 10 to 250 mg/L resulted the increase in the adsorption capacity from (22 to 235 mg/g), (18.5 to 170 mg/g), (15.2 to 137.5 mg/g), (9.5 to 100 mg/g) at temperature 25°, 35°, 45° and 55°, respectively. The results also showed that with increasing the temperature from 25° to 55°, the adsorption capacity was decreased from 22 to 9.5 mg/g which indicating the exothermic nature of the adsorption procedure.

3.2. Adsorption modeling

3.2.1. Adsorption isotherms

To describe the adsorption behavior of Fe_3O_4@TSC towards Cd(II) adsorption, two adsorption models namely Langmuir [40] and Freundlich [41] were used. The nonlinear form of Langmuir and Freundlich models (Fig. 3a) can be given as:

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

$$q_e = K_F C_e^{1/n} \tag{5}$$

where q_e, (mg/g) is the adsorption capacity at equilibrium, q_m (mg/g) is the maximum adsorption capacity, C_e is the Cd(II) concentration (mg/L) in the solution. K_L is the Langmuir constant (L/mg), n is the intensity of adsorption and K_F is Freundlich constant [42]. The dimensionless constant (R_L) was also calculated using the following equation [43] to predict the type of adsorption process.

$$R_L = \frac{1}{1 + K_L C_0} \tag{6}$$

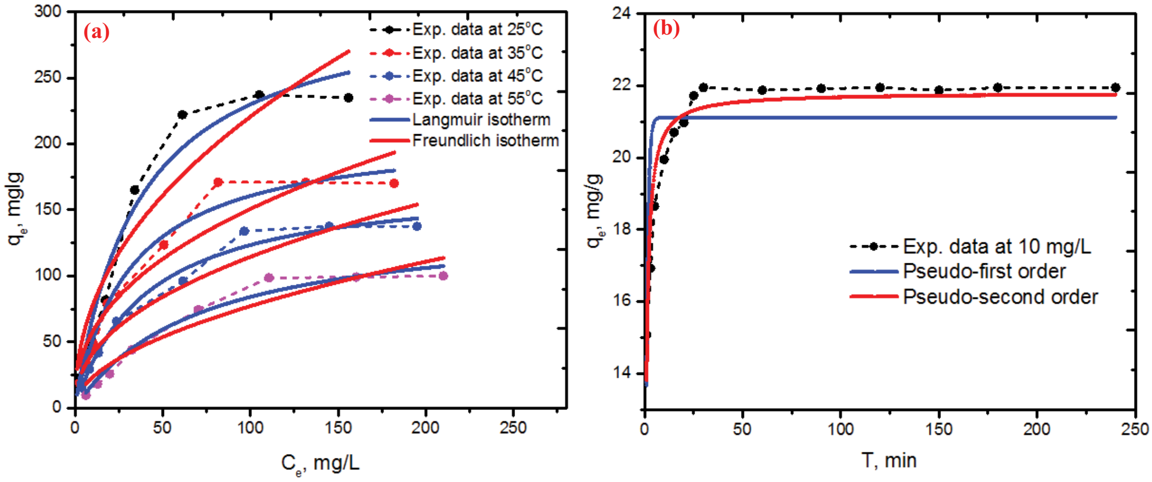

Fig. 3. (a) Non-linear adsorption isotherm and (b) Non-linear kinetic study of Cd(II) adsorption using Fe_3O_4@TSC nanocomposite.

R_L indicates the type of adsorption isotherm; if linear or irreversible when R_L is 1 or 0 respectively, if unfavorable when $R_L > 1$ or favorable when $0 < R_L < 1$.

Table 1 summarizes the Langmuir and Freundlich model parameters for Cd(II) adsorption onto Fe_3O_4@TSC. As can be seen from Table 1, the adsorption process was well fitted to the Langmuir model due to the better correlation coefficient (R^2) values of the Langmuir isotherm in comparison to the Freundlich isotherm. The maximum monolayer adsorption capacity was 312.5 mg/g at 298 K which was better as compared to the other adsorbent given in Table 2 [33,44–47]. The values of R_L were in the range of 0.758 to 0.876 which indicating the favorable adsorption process between the Fe_3O_4@TSC and Cd(II) [48]. The results also showed the values of K_F were reduced when the temperature was increased from 25° to 55° which also designated the exothermic nature of the adsorption procedure.

3.2.2. Adsorption kinetics

The nonlinear form of pseudo-first-order [49] and pseudo-second-order [50] (Fig. 3b) kinetic models which were used for this study can be given as:

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{7}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{8}$$

Table 1
Adsorption isotherm parameters for the Cd(II) adsorption onto Fe_3O_4@TSC nanocomposite

Temperature (K)	$q_{m,\text{exp.}}$ (mg/g)	Langmuir isotherm				Freundlich isotherm		
		$q_{m,\text{cal.}}$ (mg/g)	K_L (L/mg)	R_L	R^2	K_F (mg/g)(L/mg)$^{1/n}$	n	R^2
298	235	312.50	0.027	0.782	0.963	27.14	2.19	0.888
308	170	210.84	0.031	0.758	0.978	22.03	2.39	0.911
318	137.5	173.23	0.024	0.801	0.983	14.73	2.24	0.935
328	100	143.52	0.014	0.876	0.973	6.948	1.91	0.912

Table 2
Comparison of maximum adsorption capacities for Cd(II) using different adsorbents

Adsorbent	Conations	q_m (mg/g)	Reference
Magnetic graphene oxide	pH: 10; T: 25°C; dose: 100 mg; time: 360 min	128.2	[33]
P-MCS	pH: 6.1; T: 45°C; dose: 12 mg; time: 120 min	71.53	[44]
Fe_3O_4-GS	pH: 6–7; T: 25°C; dose: 8–10 mg; time: 120 min	27.83	[45]
Imprinted polymer	pH: 7; T: 25°C; dose: 10 mg; time: 80 min	107	[46]
Pleurotus ostreatus spent substrate	pH: 6; T: 25°C; dose: 1.0 g; time: 90 min	100	[47]
Fe_3O_4@TSC	pH: 7.63; T: 25°C; dose: 10 mg; time: 60 min	312.5	This study

Table 3
Adsorption kinetics parameters for the Cd(II) adsorption onto Fe_3O_4@TSC nanocomposite

C_0 (mg/L)	$q_{e,\text{exp.}}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
		$q_{e1,\text{cal.}}$ (mg/g)	k_1 (1/min)	R^2	$q_{e2,\text{cal.}}$ (mg/g)	k_2 (g/mg-min)	R^2
10	21.95	21.11	1.043	0.568	21.80	0.079	0.902

where k_1 and k_2 are rates constant for pseudo-first-order (1/min), and pseudo-second-order (g/mg min), respectively. Table 3 summarizes the kinetic parameters for Cd(II) adsorption using Fe_3O_4@TSC at various concentrations. The results displayed the R^2 for the pseudo-second-order model kinetic was greater than pseudo-first-order. The $q_{e,\text{cal.}}$ value for pseudo-second-order model ($q_{e,\text{cal.}}$ = 21.80 mg/g) was very closer to the $q_{e,\text{exp.}}$ value ($q_{e,\text{exp.}}$ = 21.95 mg/g) indicating that the pseudo-second-order model better described the adsorption process.

3.2.3. Adsorption thermodynamics

The thermodynamic study for the adsorption of Cd(II) on Fe_3O_4@TSC was accomplished at four different temperatures (298, 308, 318, and 328 K). Entropy (ΔS°, J mol⁻¹ K⁻¹) and enthalpy (ΔH°, kJ mol⁻¹) were calculated by Van't Hoffs plot using Eq. (10) and ΔG° was calculated by Eq. (11).

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \times \frac{1}{T} \tag{9}$$

$$\Delta G^\circ = -RT \ln K_c \tag{10}$$

Table 4 summarizes the thermodynamic parameters for Cd(II) adsorption using Fe_3O_4@TSC at various concentrations. The results showed that the negative values of ΔG° indicated that the adsorption of Cd(II) on Fe_3O_4@TSC at various concentrations was spontaneous. A negative value of ΔH° recommended that Cd(II) adsorption on Fe_3O_4@TSC was an exothermic process. A negative value of ΔS° indicated the decreasing randomness at the solution (Cd(II)) and solid interface (Fe_3O_4@TSC) during the adsorption experimental.

3.3. Desorption study and mechanism of Cd(II) adsorption

To select the best eluent which can easily elute the Cd(II) ions from the surface of Fe_3O_4@TSC, two eluents (HNO_3 and HCl) were used at different concentrations. Fig. 4 displays that the best eluent for recovery of Cd(II) was 0.01 M HCl (90%) which might be the smaller size of Cl^- in comparison to the NO_3^-. The % desorption by using 0.01 M HNO_3 was only 75.9%. Fig. 5 shows the mechanism of Cd(II) adsorption on the surface of Fe_3O_4@TSC nanocomposite. As can be seen from Fig. 5, the adsorbent (Fe_3O_4@TSC) has two functional groups: carboxyl and hydroxyl groups. These functional

Table 4
Thermodynamics parameters for the Cd(II) adsorption onto Fe_3O_4@TSC nanocomposite

C_0 (mg/L)	(–) ΔH° (kJ/mol)	(–) ΔS° (J/mol-K)	(–) ΔG° (kJ/mol)			
			298 K	308 K	318 K	318 K
10	41.84	119.67	4.93	2.86	1.18	0.547
30	21.76	59.81	1.97	1.47	0.587	0.072
50	19.12	47.93	1.57	1.42	0.258	0.021

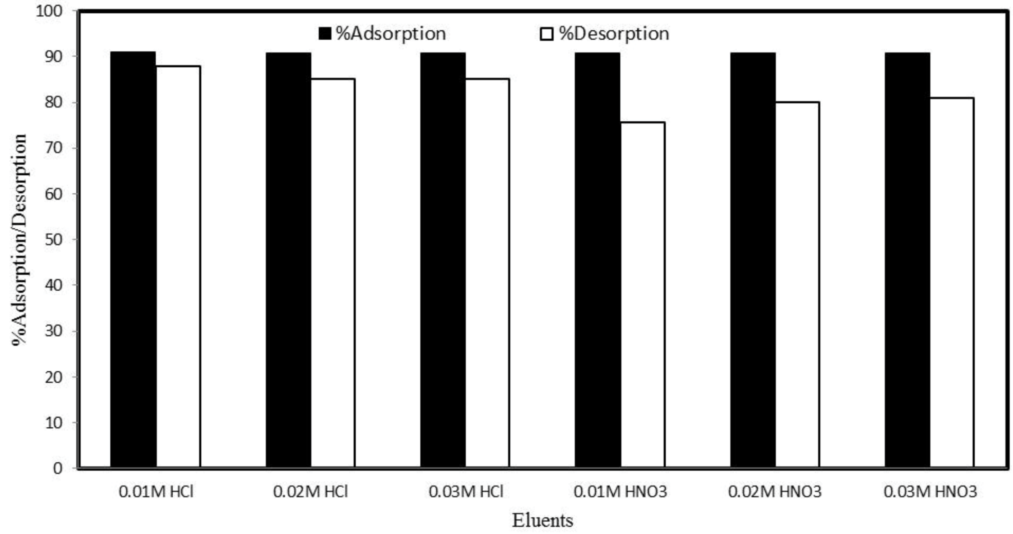

Fig. 4. Adsorption/desorption study.

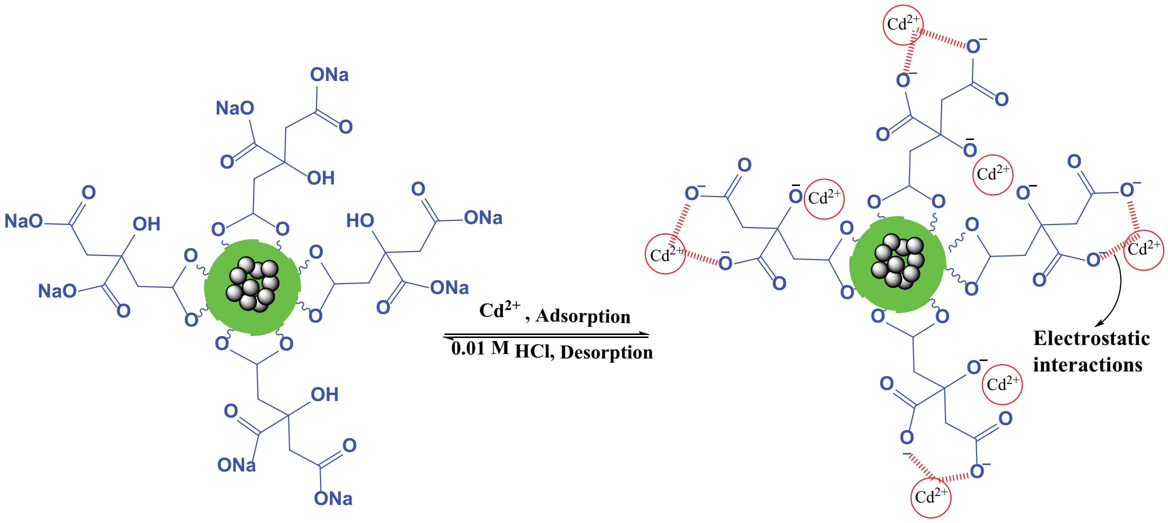

Fig. 5. Mechanism for the adsorption/desorption of Cd(II) ions using Fe_3O_4@TSC nanocomposite.

groups were interacted with electropositive Cd(II) by electrostatic interactions.

4. Conclusion

In conclusion, the present research describes the study on the adsorption performance of Fe_3O_4@TSC nanocomposite for Cd(II) from aqueous systems. The results revealed that the adsorption of Cd(II) on the surface of Fe_3O_4@TSC nanocomposite depends on some parameters such as solution pH, amount of adsorbent, contact time, temperature and initial Cd(II) concentration. The adsorption of Cd(II) onto Fe_3O_4@TSC nanocomposite was followed to the Langmuir isotherm model and the maximum monolayer adsorption capacity was 312.5 mg/g, at pH 7.63. From the thermodynamic study, it was observed that the adsorption process was exothermic in nature and spontaneous process. The type of adsorption mechanism was electrostatic interaction between Cd(II) ions and free carboxylic groups on the surface of Fe_3O_4@TSC. The % desorption by using 0.01 M HCl was 90%.

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