

# Novel Magnetic Chitosan Hydrogel Film, Cross-Linked with Glyoxal as an Efficient Adsorbent for Removal of Toxic Cr(VI) from Water

Maryam Mirabedini<sup>1</sup> · M. Z. Kassaei<sup>1</sup> · Samira Poorsadeghi<sup>1</sup>

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**Abstract** A novel magnetic chitosan hydrogel film, cross-linked with glyoxal (Fe<sub>3</sub>O<sub>4</sub>NPs/CS/glyoxal), has been synthesized and used as an easily reusable adsorbent for 80–90 % removal of toxic Cr(VI) from water. A *pseudo*-second-order kinetic (with correlation coefficient  $R^2 > 0.99$ ) is observed at room temperature. Characterization of the adsorbent is carried out by X-ray diffraction, scanning electron microscopy, and Fourier transform infrared spectroscopy. The adsorption isotherm is well fitted in the Langmuir equation at different temperatures [ $R^2 > 0.99$ , and  $0 < (R_L) < 1$ ]. So, our adsorbent, with the novelty of using glyoxal, and the ease of separation may be considered in Cr(VI) wastewater treatment technology.

**Keywords** Water treatment · Chromium · Chitosan · Adsorption · Hydrogel · Glyoxal

## 1 Introduction

Heavy metals (Hg, Cd, Pb, As, and Cr) keep on having their harmful effects on the environment and human health [1]. Among them, Cr is a highly toxic element found in water. It is generated by mining, leather tanning, cement, dyes, electroplating, steel, metal alloys, photographic materials, and metal corrosion inhibition [2, 3]. The Cr(VI) has been considered more hazardous to public health than Cr(III) by reason of its mutagenic and carcinogenic properties [4]. According to “the US Environmental Protection Agency (EPA),” the

maximum allowed limit for the total Cr in drinking water is  $100 \mu\text{g L}^{-1}$  [5]. As a result, removal of Cr(VI) from natural waters and wastewater streams has a great environmental significance. A wide range of physical and chemical processes are available for the removal of chromium from wastewater such as cyanide treatment [6], electro-chemical precipitation [7], reverse osmosis (RO) [8, 9], ion exchange (IE) [10, 11], and adsorption [12, 13]. Among these methods, the latter is one of the most economically favorable and is considered as a technically easy method [14].

Efficiency of the removal process depends on the choice of the adsorbent. A variety of materials have been reported as adsorbents for the removal of Cr(VI) from aqueous solution, such as rice bran [15, 16], treated saw dust [17], hydrated titanium(IV) oxide [18], polypyrrole–polyaniline nanofibers [19, 20], ureolytic mixed culture [21], fertilizer industry waste [22], and cross-linked xanthated chitosan [23]. Chitosan (CS) is the deacetylated form of chitin that is a linear polymer of acetylamino-D-glucose. CS is biocompatible and harmless to live species. It is hydrophilic and biodegradable with a good appetite for chemical derivatization. CS has a lot of amino and hydroxyl groups that can chelate heavy metal ions. It appears as a very capable starting material for chelating resins [24]. However, pure CS materials have some obvious disadvantages that include poor chemical resistance, low mechanical strength, and difficult recovery [25]. In addition, many metals are preferentially adsorbed in acidic media which may dissolve CS. To overcome such problems, some cross-linking agents such as glutaraldehyde [26], epichlorohydrin (ECH) [27, 28], and ethyleneglycol diglycidyl ether [29] are used to improve mechanical and chemical properties of the resulted composite and prevent its dissolution in acidic solutions. Undesirably, the adsorption capacity for cross-linked CS turns out lower than free CS, because the NH<sub>2</sub> is often cross-linked [30, 31].

✉ M. Z. Kassaei  
kassaeem@modares.ac.ir

<sup>1</sup> Department of Chemistry, College of Sciences, Tarbiat Modares University, Tehran, Iran

The traditional methods of separating adsorbent from solution include filtration, sedimentation, and centrifugation [32]. Magnetic separation technology is a kind of rapid, inexpensive, and efficient method. Magnetic CS can be prepared via combination of CS and magnetic nanoparticles. It can be simply removed from the reaction medium via an external magnet [33].

Recently Tran Dai Lam and coworkers have improved the removal of Cr(VI) from aqueous solution with maximum adsorption capacity of  $55.80 \text{ mg g}^{-1}$  in optimal adsorption conditions [28]. This is done by insertion of ECH in magnetic chitosan nanoparticles. However, rather expensive ECH is a highly reactive, flammable liquid. Due to the high vapor pressure, measures must be taken to ensure that vapor levels do not become hazardous especially at large scales [34,35]. Moreover, in contact with water, ECH hydrolyzes to a carcinogen found in food: 3 monochloropropane-1,2-diol or 3-chloropropane-1,2-diol. The latter is carcinogenic and highly suspected to be genotoxic in organisms. It has male antifertility effects and is a member of chemical contaminants known as chloropropanols [36–38]. In this work, we have excluded ECH in our modified magnetic chitosan hydrogel film, cross-linked with glyoxal ( $\text{Fe}_3\text{O}_4$  NPs/CS/glyoxal), and used it as an easily reusable adsorbent for removal of toxic Cr(VI) from water.

## 2 Materials and Methods

### 2.1 Materials

All reagents are of analytical grade and used as received without further purification. Chemicals purchased from “Acros Organics Company” include:  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , glyoxal,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{CH}_3\text{COOH}$ , HCl, NaOH, and chitosan (CS, degree of deacetylation =  $82 \pm 2\%$ ,  $M_w = 100,000$ – $300,000 \text{ g mol}^{-1}$ ).

### 2.2 Synthesis of the Adsorbent

#### 2.2.1 Preparation of the $\text{Fe}_3\text{O}_4$ Nanoparticles

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  are dissolved in a molar ratio of 2:1 in 100 mL deionized  $\text{H}_2\text{O}$  under magnetic stirring. Subsequently, 3 M NaOH is added dropwise to the reaction mixture until pH reaches 12 at  $90^\circ\text{C}$ . After continuous stirring and aging for 2 h, a black precipitate separates. This mixture is repeatedly washed by distilled water and then dried at  $60^\circ\text{C}$  for 12 h [39].

#### 2.2.2 Preparation of $\text{Fe}_3\text{O}_4$ NPs/CS/Glyoxal

$\text{Fe}_3\text{O}_4$  nanoparticles (50 mg) are sonicated for 2 h in the CS solution (50 mg CS in 5 mL acetic acid: 2% v/v), at room

temperature. Then,  $22 \mu\text{L}$  glyoxal is added. After sonicating for another 1 h, the final solution is neutralized with 0.1 M NaOH (300 mL). To change the gel into the form of a film, the latter is dried overnight in the oven at  $60^\circ\text{C}$ . To remove the unreacted CS and glyoxal from the film, it is washed three times with acetic acid and two times with distilled water. Finally, it is dried overnight in the oven at  $60^\circ\text{C}$ .

#### 2.2.3 Adsorption Experiments

Batch experiments are carried out with 0.05 g of  $\text{Fe}_3\text{O}_4$  NPs/CS/glyoxal hydrogel in a 50 mL solution containing a specified concentration of Cr(VI). The pH is adjusted using 0.1 M solutions of NaOH and HCl. The experiments are conducted at different temperatures of 25, 35, and  $45^\circ\text{C}$ . Adsorption isotherms of Cr(VI) over  $\text{Fe}_3\text{O}_4$  NPs/CS/glyoxal hydrogel are measured at these temperatures. Such sorption isotherms are plots of the equilibrium adsorption capacity ( $q_e$ ) (according to Eq. 1) vs. the equilibrium concentration of the residual Cr(VI) in the solution ( $C_e$ ) [40]:

$$q_e = \frac{(C_0 - C_e) V}{W} \quad (1)$$

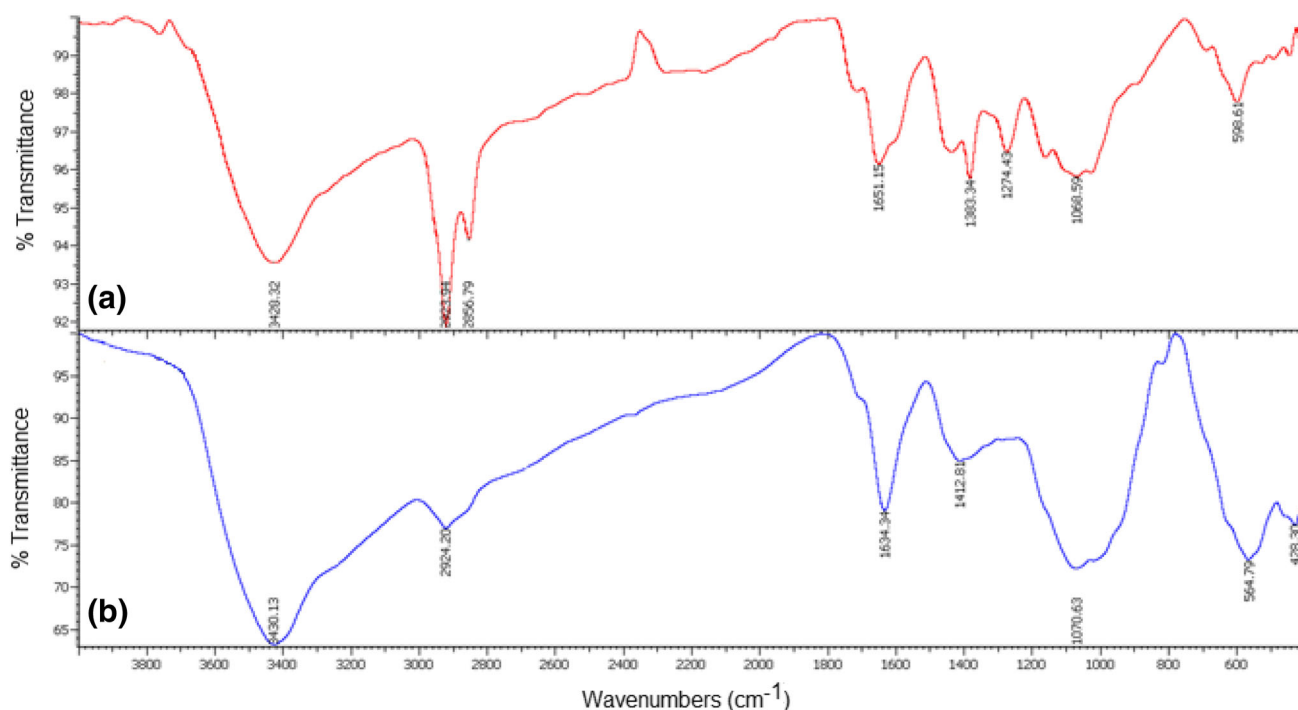
Here,  $q_e$  is the amount of metal ions adsorbed per weight unit of the adsorbent after equilibrium ( $\text{mg g}^{-1}$ ),  $C_0$  and  $C_e$  are the initial and equilibrium liquid phase solute concentrations ( $\text{mg L}^{-1}$ ), respectively.  $V$  is the liquid phase volume (L), and  $W$  is the amount of the adsorbent (g). Residual concentrations of Cr(VI) are determined with an inductively coupled plasma optical emission spectrometer (ICP-OES).

#### 2.2.4 Characterization Methods

FT-IR spectra are recorded via PerkinElmer 597 and Nicolet 510P spectrophotometers. XRD patterns of  $\text{Fe}_3\text{O}_4$  NPs and the resulting film are obtained on Holland Philips Xpert XRD diffractometer (Cu  $K\alpha$ , radiation,  $\lambda = 0.154056 \text{ nm}$ ), at a scanning speed of  $2^\circ \text{ min}^{-1}$  from  $10^\circ$  to  $80^\circ$  ( $2\theta$ ). Morphology of the film is observed using a SEM of a Holland Philips XL30 microscope.

#### 2.2.5 Results and Discussion

$\text{Fe}_3\text{O}_4$  NPs/CS/glyoxal hydrogel is synthesized. After characterization via FT-IR, XRD, and SEM, it is applied for the first time, as an efficient adsorbent for the removal of Cr(VI) from water. Consequently, effects of pH, temperature, contact time, and initial Cr(VI) concentration on Cr(VI) removal are studied. Afterward, Langmuir isotherm, thermodynamic, and kinetic aspects of the adsorption process are considered. Finally, reusability of  $\text{Fe}_3\text{O}_4$  NPs/CS/glyoxal hydrogel is examined.



**Fig. 1** FT-IR spectra of CS (a), Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal hydrogel (b)

## 2.3 Characterization of the Adsorbent

### 2.3.1 FT-IR Analysis

The FT-IR spectrum of CS shows a broad band at 3428.32 cm<sup>-1</sup> (Fig. 1a). It corresponds to the stretching vibrations of N–H and O–H groups. Peaks appearing at 2856.79 and 2923.94 cm<sup>-1</sup> are characteristic of C–H stretching vibrations. The band at 1651.15 cm<sup>-1</sup> is assigned to N–H bending vibrations [41]. In FT-IR spectrum of Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal hydrogel, absorptions of CS appear along with a peak at 564.79 cm<sup>-1</sup> which corresponds to the stretching vibration of Fe–O groups (Fig. 1b). C–N bending vibration is shifted from 1383.34 to 1412.81 cm<sup>-1</sup>, due to its Schiff base reaction with the amine group of CS [42–44]. The band at 1634.34 cm<sup>-1</sup> is attributed to the C=N vibration of imine group as well as the bending vibration of unreacted N–H group [41, 42].

### 2.3.2 XRD Analysis

The crystalline phase of Fe<sub>3</sub>O<sub>4</sub> NPs and Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal hydrogel is probed by XRD (Fig. 2). Diffraction peaks of cubic magnetite Fe<sub>3</sub>O<sub>4</sub> nanoparticles at 2θ = 35.45°, 41.83°, 51.01°, 63.65°, 68.02°, and 75.02° correspond to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) lattice planes, respectively [45–47]. At the same time, it can be seen that the characteristic diffraction peaks of Fe<sub>3</sub>O<sub>4</sub> could be found in the pattern of Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal hydrogel. Diffraction

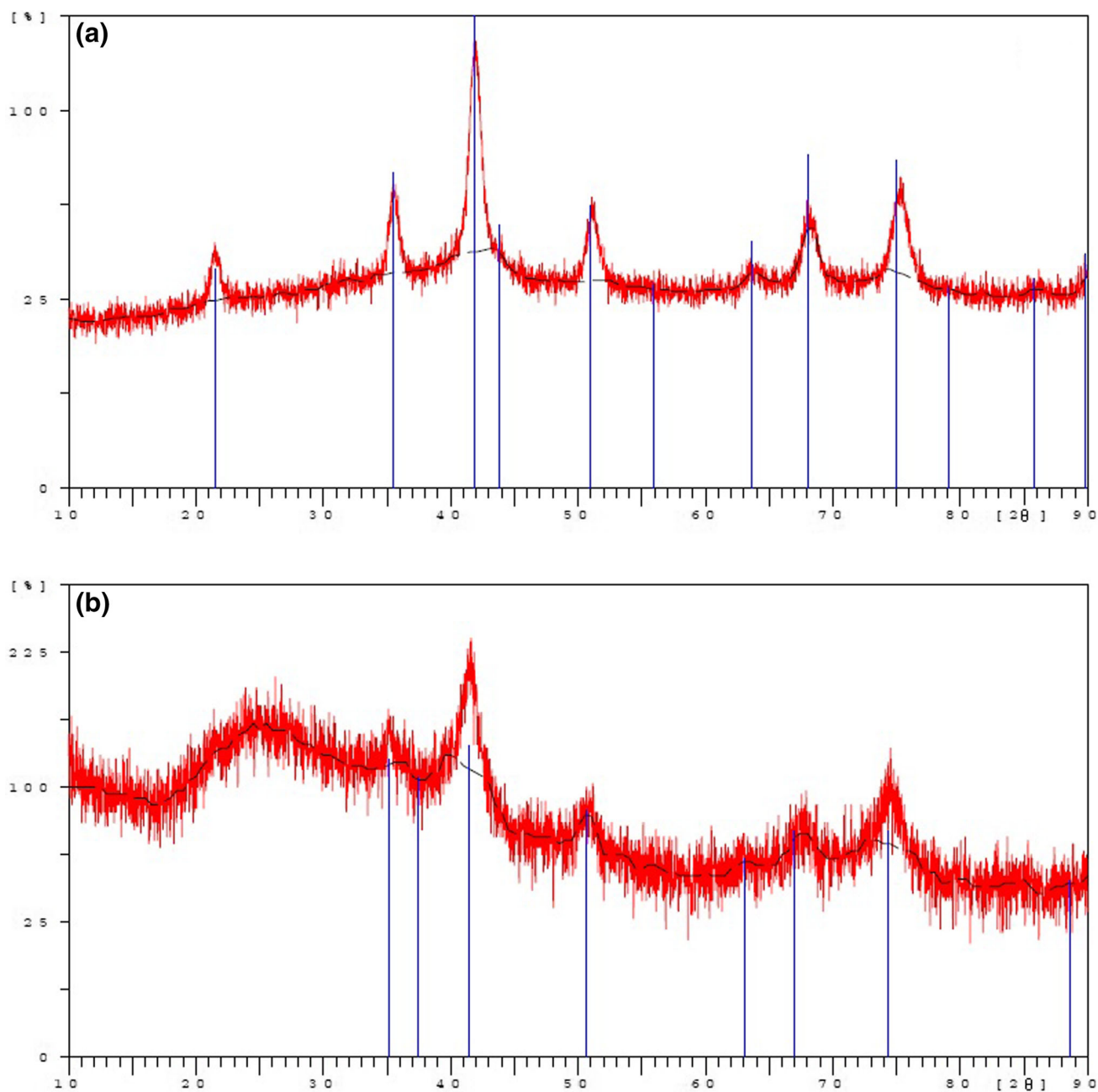
peaks between 2θ = 21°–28° are associated with chitosan. They are of amorphous nature pointing to its low crystallinity [48, 49].

### 2.3.3 SEM Analysis

Portions of CS appear as beautiful pieces of a puzzle in the corresponding SEM images (Fig. 3a, b). There is a big difference in the surface morphology and roughness between chitosan and magnetic hydrogel film. Our SEM images of Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal hydrogel film appear similar to those reported for Fe<sub>3</sub>O<sub>4</sub> NPs/CS by Alzahrani [50]. In both sets of images, magnetic nanoparticles appear as small seeds spread out on the surface of CS (Fig. 3c, d).

## 3 Effect of Initial pH on the Adsorption Process

Solution pH is the most important variable affecting the adsorption characteristics. The surface charge and the protonation degree of the adsorbent are significantly affected by pH of the solution. Cr(VI) exists with different ionic forms in the solution. The most toxic is Cr(VI) in the form of chromate (CrO<sub>4</sub><sup>2-</sup>), dichromate (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>), and hydrogen chromate (HCrO<sub>4</sub><sup>-</sup>). Their concentrations depend on the solution pH and total chromate content [51, 52]. Adsorption process is investigated at pH 2.0–8.0. The maximum capacity of Cr(VI) absorption takes place at pH 4.0 (Fig. 4). Cr(VI) exists predominantly as HCrO<sub>4</sub><sup>-</sup> in aqueous solution with lower pH,



**Fig. 2** XRD patterns of Fe<sub>3</sub>O<sub>4</sub> NPs (a), and Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal hydrogel (b)

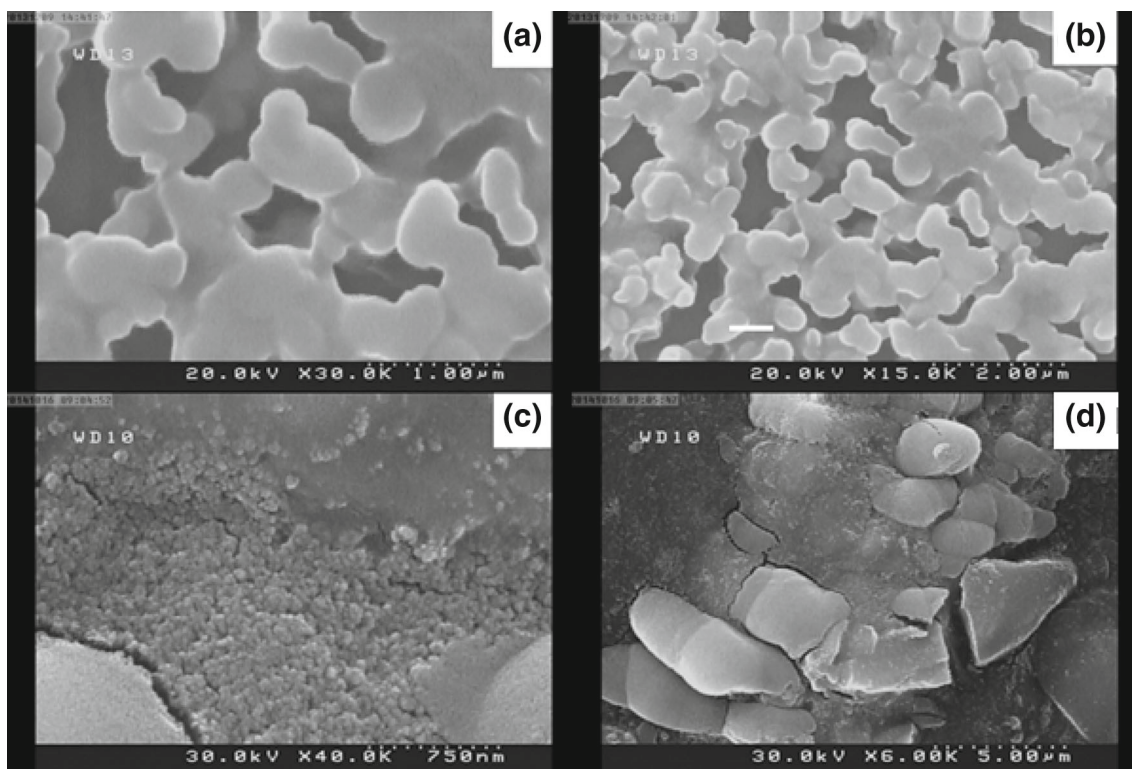
and the amino groups ( $-\text{NH}_2$ ) of magnetic CS nanoparticles appear in protonated cationic form ( $-\text{NH}_3^+$ ) in acidic solution. This results in the stronger attraction for negatively charged ions [53,54]. Electrostatic interaction between the sorbent and  $\text{HCrO}_4^-$  ions also contributes to the high chromium removal. However, a strong competition for adsorption sites between  $[\text{H}_2\text{CrO}_4]$  and protons occurs at pH values lower than 4. Decreasing of the adsorption capacity at higher pH may be explained by the dual competition between  $[\text{CrO}_4^{2-}]$  and  $[\text{OH}^-]$  [55].

#### 4 Adsorption Isotherms

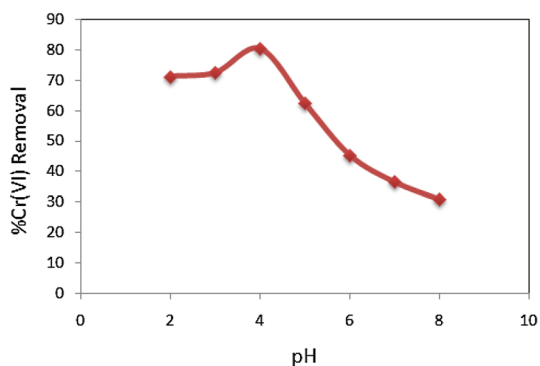
Equilibrium experimental data is effectively fitted to the Langmuir isotherm whose equation can be expressed as [56]:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (2)$$

Here,  $q_e$  is the amount of solution adsorbed per unit mass of the adsorbent ( $\text{mg g}^{-1}$ ),  $C_e$  is the solute equilibrium concentration ( $\text{mg L}^{-1}$ ),  $q_m$  is the maximum adsorbate amount



**Fig. 3** SEM images of CS (a, b), Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal hydrogel film (c, d)

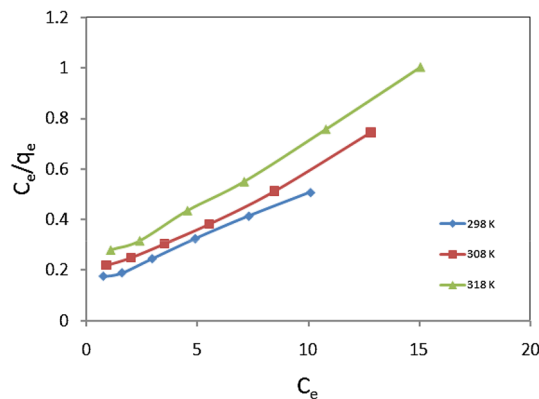


**Fig. 4** Influence of initial pH on removal of Cr(VI) (metal concentration = 15 mgL<sup>-1</sup>, adsorbent dose = 0.05 g, volume = 50 mL, contact time = 110 min, temperature = 25 °C)

(mg g<sup>-1</sup>) that forms a complete monolayer on the surface, and *b* is the Langmuir constant related to adsorption heat (L mg<sup>-1</sup>). When *C<sub>e</sub>/q<sub>e</sub>* is plotted against *C<sub>e</sub>* and the data are regressed linearly, the *q<sub>m</sub>* and *b* constants may be calculated from the slope and the intercept. The essential characteristics of the Langmuir isotherm can be described by a separation factor, which is described as [23,56]:

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

Here, *b* is the Langmuir constant (L mg<sup>-1</sup>), and *C<sub>0</sub>* is the initial Cr(VI) concentration (mg L<sup>-1</sup>). The value of *R<sub>L</sub>* points to



**Fig. 5** Langmuir isotherm for the adsorption Cr(VI) ions on Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal at 25°, 35°, and 45 °C (the range of *C<sub>0</sub>* = 5 – 30 mgL<sup>-1</sup>; adsorbent dose = 0.05 g; volume = 50 mL; pH 4.0 and contact time = 110 min)

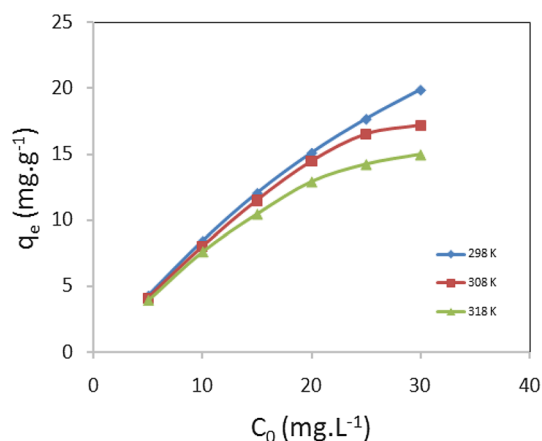
the shape of Langmuir isotherm and the nature of the adsorption process. It is considered as a favorable process when its value falls within a range of 0–1 [57].

The experimental data fit well with Langmuir isotherm (*R*<sup>2</sup> > 0.99), confirming that the adsorption process is monolayer and the values of *R<sub>L</sub>* are favorable (Fig. 5; Table 1). The adsorption isotherms of Cr(VI) on the Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal hydrogel at different temperatures (25°, 35°, and 45 °C) and pH 4.0 appear instructive (Fig. 6).

**Table 1** Value of the Langmuir constants for adsorption of Cr(VI) on Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal hydrogel

Temperature (K)	$q_m$ (mg g <sup>-1</sup> )	$b$	$R^2$	$R_L$
298	27.25	0.261	0.997	0.113
308	22.62	0.280	0.991	0.106
318	19.01	0.265	0.996	0.112

Volume = 50 mL; adsorbent dose = 0.05 g; initial concentrations = 5, 10, 15, 20, 25, and 30 mg L<sup>-1</sup>; pH 4.0; contact time = 110 min; temperature = 298, 308, 318 K

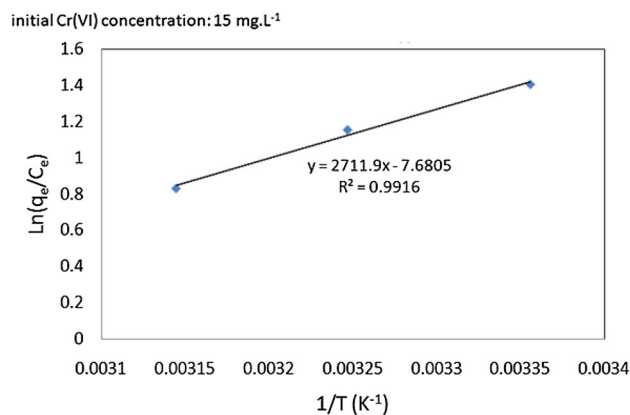
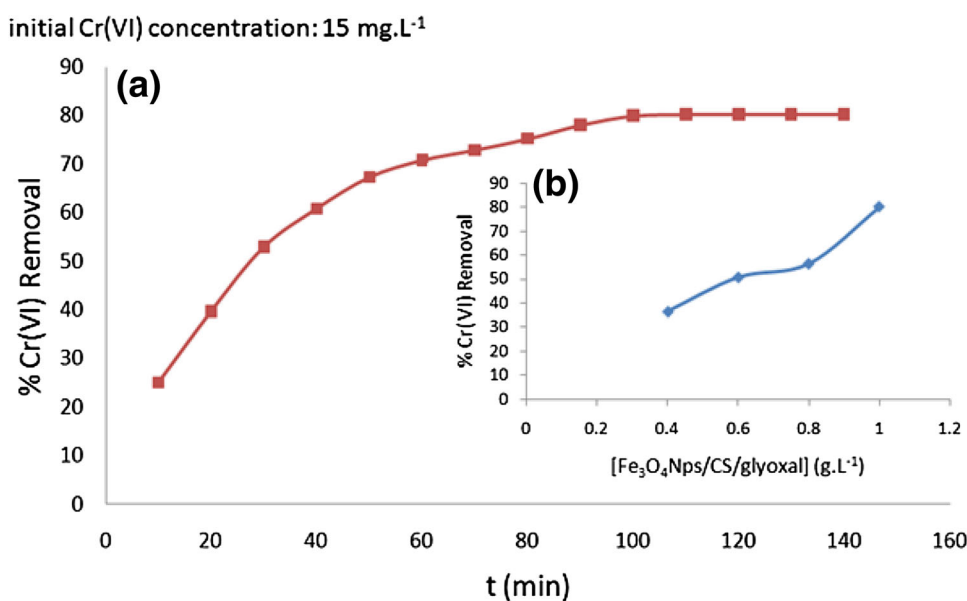


**Fig. 6** Adsorption isotherms of Cr(VI) onto Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal at 25°, 35°, and 45°C (the range of  $C_0 = 5\text{--}30\text{ mg L}^{-1}$ ; adsorbent dose = 0.05 g; volume = 50 mL; pH 4.0 and contact time = 110 min).

### 5 Effect of Adsorption Time and Adsorbent Dose

The effect of adsorption time on the removal efficiency is probed with initial adsorbent concentration of 15 mg L<sup>-1</sup> (Fig. 7a). As a result, Cr(VI) adsorption increases by increas-

**Fig. 7** Removal efficiency of Cr(VI) at 25 °C and pH 4 as functions of: **a** the contact time, at adsorbent dose = 0.05 g; **b** concentration of the adsorbent at contact time = 110 min



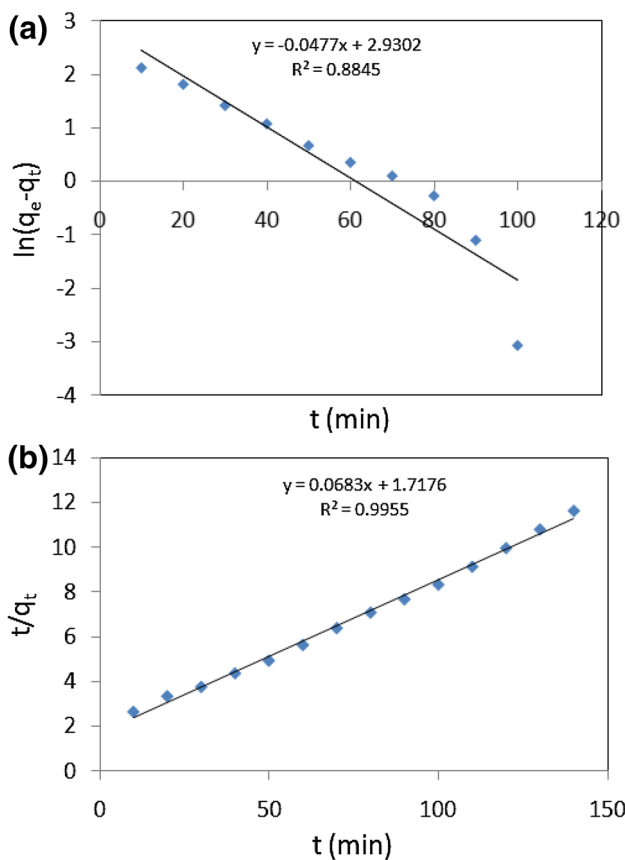
**Fig. 8** Thermodynamic plot of  $\ln(q_e/C_e)$  vs.  $1/T$

**Table 2** Thermodynamic data of Cr(VI) removal using Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal hydrogel

$T$ (K)	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )
298	-3.517	-22.546	-63.856
304	-3.134		
310	-2.751		
316	-2.368		

ing contact time. Specifically, in order to make sure that adsorption process may reach the equilibrium, the contact time is set at 110 min. The removal efficiency becomes 80.30 % for the 15 mg L<sup>-1</sup> initial Cr(VI) concentration.

Also, the influence of adsorbent dose on the removal efficiency (% removal) of Cr(VI) is considered (Fig. 7b). The removal percent of Cr(VI) goes up from 36.56 to 80.30 % as the dosage of Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal is increased from 20.0 to 50.0 mg. Hence, more active sites become accessible with an increase in the adsorbent dose.



**Fig. 9** *Pseudo*-first-order (a) and *pseudo*-second-order (b) sorption kinetics of Cr(VI) onto Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal (volume = 50 mL, adsorbent dose = 0.05 g, initial concentration = 15 mg L<sup>-1</sup>, pH 4.0, temperature = 298 K)

### 6 Thermodynamic and Kinetic Studies

Thermodynamic considerations of an adsorption process are required to conclude whether the process is spontaneous or not. The experimental data obtained at different temperatures are used in calculating the thermodynamic parameters such as Gibbs free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ), and entropy change ( $\Delta S$ ). Thermodynamic parameters of the adsorption process, such as  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$ , can be obtained using the following equations [40]:

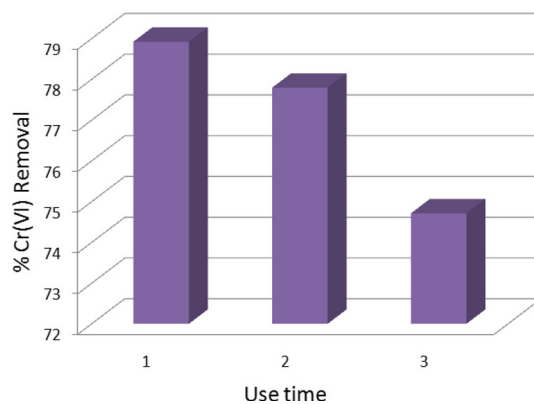
$$\Delta G = \Delta H - T \cdot \Delta S \tag{4}$$

$$\ln b = \ln \left( \frac{q_e}{C_e} \right) = - \frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{5}$$

**Table 3** Kinetic parameters are taken from Lagrangian models in the adsorption of Cr(VI) onto Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal

$q_{e,exp}$ (mg g <sup>-1</sup> )	Pseudo-first-order model			Pseudo-second-order model		
	$k_1$ (min <sup>-1</sup> )	$q_{e,cal}$ (mg g <sup>-1</sup> )	$R^2$	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$q_{e,cal}$ (mg g <sup>-1</sup> )	$R^2$
12.04	$4.77 \times 10^{-2}$	18.73	0.884	$2.71 \times 10^{-3}$	14.64	0.995

where  $q_{e,cal}$  and  $q_{e,exp}$  are the calculated and experimental quantities of Cr(VI) adsorbed (mg g<sup>-1</sup>)



**Fig. 10** Adsorption performance of Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal hydrogel in three cycles

Here,  $b$  is the Langmuir constant (L mol<sup>-1</sup>),  $T$  is the absolute temperature (K), and  $R$  is the ideal gas constant (8.31 J mol<sup>-1</sup> K<sup>-1</sup>).  $\Delta H$  and  $\Delta S$  are obtained from the slope and intercept of the plot  $\ln(q_e/C_e)$  vs.  $1/T$  (Fig. 8):

$$\Delta H = -22.546(\text{kJ mol}^{-1})$$

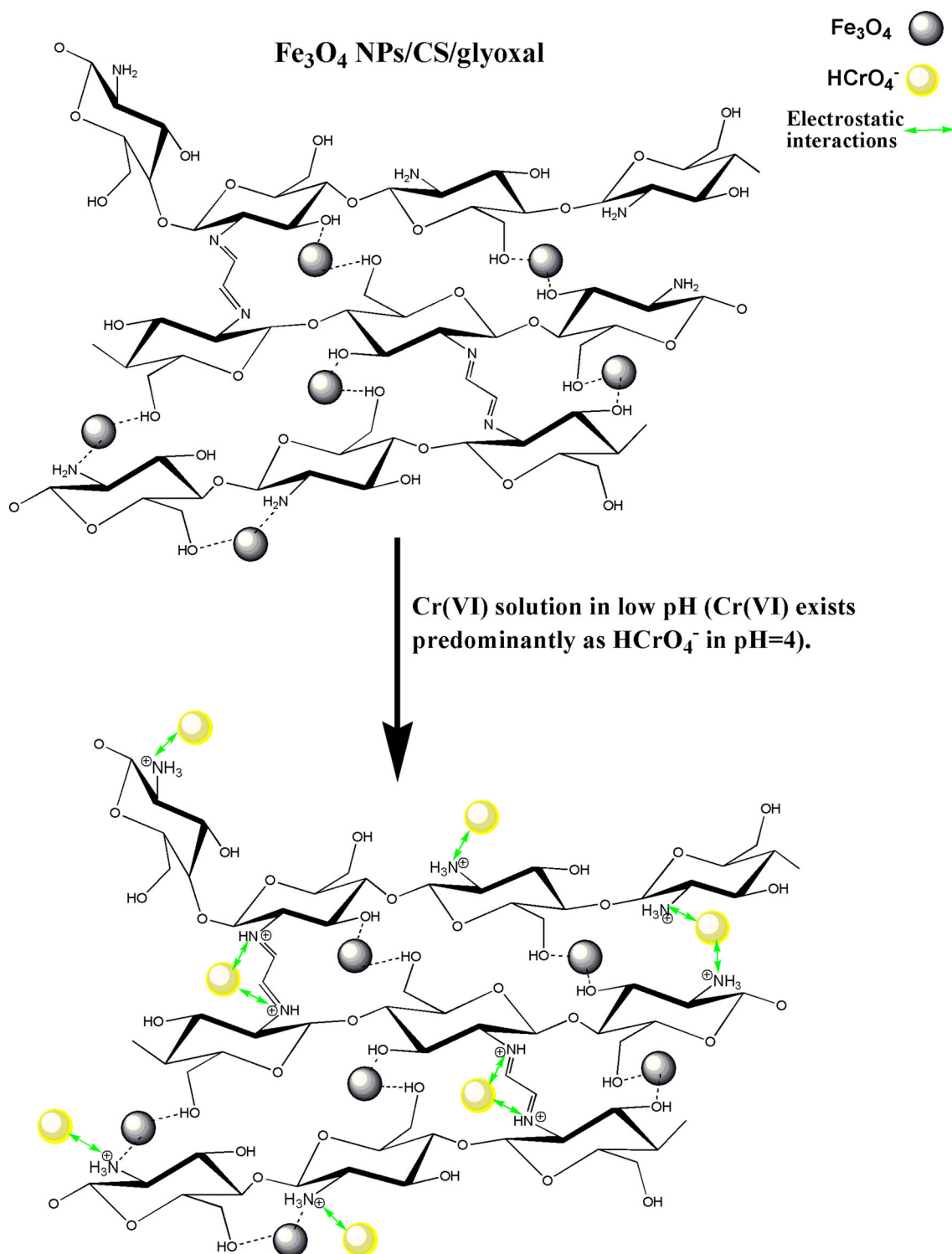
$$\text{and } \Delta S = -63.856(\text{J mol}^{-1} \text{K}^{-1}).$$

The negative values of  $\Delta G$  and  $\Delta H$  confirm the feasibility of the process and the exothermic spontaneous nature of the adsorption (Table 2). As a result, a lower temperature increases the adsorption as well as the  $q_m$ . A negative value of  $\Delta S$  points to decrease in the entropy as a result of the—adsorption of the Cr(VI) on Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal.

In order to study the controlling mechanism for the adsorption process, kinetic models are used to assess the experimental data. *Pseudo*-first-order and the *pseudo*-second-order kinetics are considered to the experimental data (Fig. 9). The *pseudo*-first-order rate expression of Lagergren is given as [58]:

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

Here,  $q_e$  and  $q_t$  (mg g<sup>-1</sup>) are the amounts of Cr(VI) adsorbed on the adsorbent at equilibrium and at time  $t$ , respectively, and  $k_1$  is the rate constant of first-order adsorption (min<sup>-1</sup>). The slopes and intercepts of plots of  $\ln(q_e - q_t)$  vs.  $t$  are used to determine the first-order rate constant  $k_1$  and  $q_e$ . The *pseudo*-second-order kinetic model is expressed as [58]:



**Scheme 1** Removal of Cr(VI) over Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal absorbent film in optimum condition (pH 4)

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t \quad (7)$$

Here,  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the rate constant of second-order adsorption. The slopes and intercepts of plots of  $t/q_t$  vs.  $t$  are

used to calculate the second-order rate constant  $k_2$  and  $q_e$ . The value of regression coefficient ( $R^2$ ) for *pseudo*-second-order model is close to 1 (0.995) for  $15 \text{ mg L}^{-1}$  initial Cr(VI) concentration (Table 3). The calculated value  $q_{e, \text{cal}}$  is close to the obtained  $q_{e, \text{exp}}$  value. Hence, the adsorption of Cr(VI) onto



Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal hydrogel could confirm the *pseudo*-second-order kinetic model.

## 7 Reusability of Fe<sub>3</sub>O<sub>4</sub> NPs/CS/Glyoxal Hydrogel

Reusability is customarily reported for adsorption ability during 3–5 adsorption cycles [59–61]. Our Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal hydrogel has demonstrated its adsorption ability during three adsorption cycles (Fig. 10). Hence, after three cycles, the Cr(VI) adsorption capacity decreases from initial 78.92 % to the final 74.71 %. This behavior indicates that the Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal hydrogel can be applied, at least three times, for efficient Cr(VI) adsorption, from aqueous solutions. Specifically, 0.1 M HCl solution is used as desorption agent. It does not harm our CS because of cross-linking strongly with glyoxal.

## 8 Conclusion

Here, we have excluded ECH in our modified magnetic chitosan (CS) hydrogel film, cross-linked with glyoxal (Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal), and used it as an easily reusable adsorbent for 80–90 % removal of toxic Cr(VI) from water. It appears as an efficient, economical, and relatively less toxic adsorbent whose removal efficiency is highly pH-dependent and the optimal adsorption occurs at pH 4, contact time = 110 min, and  $q_m = 27.25 \text{ mg g}^{-1}$ . The mechanism of adsorption included ionic interactions and electrostatic interactions between chromium cations and Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal hydrogel; thus, the adsorption was a physicochemical process (Scheme 1). Based on Langmuir model, the adsorption mechanism of Fe<sub>3</sub>O<sub>4</sub> NPs/CS/glyoxal hydrogel is a monolayer chemical adsorption process. Thermodynamically, the adsorption of Cr(VI) is spontaneous and exothermic. Kinetically, the adsorption under  $15 \text{ mg L}^{-1}$  initial concentration is fitted well with the *pseudo*-second-order kinetic model.

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