



Chemical modification of silica gel surface with a carbothioamide Schiff base for removal of Cr(III) ions from wastewater samples

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ABSTRACT

In this study, a low-cost adsorbent was synthesized to efficiently remove Cr(III) ions from aqueous solutions and wastewater. First, 3-chloropropyl-trimethoxy silane (CPTS) was modified on silica gel (Si). Then, (E)-2-(1-(3-methyl-3-phenyl cyclobutyl)-2-morpholino ethylidene) hydrazine carbothioamide (PMH) Schiff base was immobilized on the Si-CPTS compound, and the Si-CPTS-PMH adsorbent was synthesized. The newly synthesized adsorbent was characterized through using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy. Several experiments using batch method were conducted to investigate the maximum adsorption capacity of Cr(III) ions on Si-CPTS-PMH adsorbent. The effect of several factors including pH, contact time and amount of adsorbent, temperature and concentration on the adsorption of Cr(III) ions were investigated. To illuminate the adsorption mechanism, Langmuir, Freundlich and Dubinin–Radushkevich (D–R) adsorption isotherms and thermodynamic calculations (ΔG° , ΔS° and ΔH°) were used. The optimum values obtained from this study were 6, 150 min, 0.025 g, 20 mg/L and 323.15 K for pH, interaction time, adsorbent amount, concentration and temperature, respectively. As a result, the newly synthesized support material can be used for the removal of Cr(III) ions both in industrial wastewater and aqueous solutions.

Keywords: Adsorption; Chromium; Surface treatments; Functional adsorbent material; Silica gel; Immobilization

1. Introduction

Pollution from heavy metals, which influences the environment and living organisms due to the toxicological importance, has been a growing interest for the near decades [1]. High concentrations of heavy metals are presented in industrial wastewaters; therefore, purification process is required prior to realising wastewater containing heavy metals into the environment. Outside mining and metal industries, there are a large number of industrial wastes that lead to heavy metal discharges [1–4].

The main industrial sources of chromium wastewaters that are harmful to environment and also all living things in the nature are steel manufacturing, paint, pigments and metal processing [4–6]. In the natural environment, chromium from heavy metals is presented in two stable oxidation states such as Cr(III) and Cr(VI) [7] that the Cr(III) [8,9] ion form is more harmless than the Cr(VI) form [10,11]. The presence of low levels of Cr(III) ions [12–14] in the environment is necessary for plant and animal metabolism. However, Cr(VI) ions [4,6,15,16] are toxic to plants, animals and bacteria.

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In addition, prolonged contact with Cr(III) ions at high concentrations may cause allergic skin reactions, cancer and DNA damage [17].

Several methods have been developed for separation and purification processes over the years, including membrane adsorption [18,19], precipitation [20–22], photocatalyst, electrodialysis, ultrafiltration chemical precipitation, reverse osmosis, ion exchange [23,24] and phyto-regulation, etc. Among them, the adsorption method was the most suitable one because of the low cost and easy application and the high percentage of separation [3].

Silica gel has been used as a solid support especially in recent years due to its thermal and chemical properties, mechanical stability [25], high selectivity by covalent adsorption and two different functional groups (Si–O–Si and Si–OH) [26,27]. As a result, the presence of Si–O–Si (siloxane) or Si–OH (silanol) molecules in the silica gel structure results in the formation of the reaction on the silica gel and the modification of the silica [28]. Briefly, in this process, the organic reagents comprising of the desired organic functional groups or the synthesized organic molecules are linked to the direct supports [29] and the obtained modified silica adsorbent [30–32] is used to remove chromium heavy metals from industrial wastewater and aqueous solutions by adsorption method.

There are many studies on the removal of Cr(III) ions [33–36]. Unlike these studies, we expanded the surface area of silica gel, which is used as a support agent, by CPTS and Schiff base (PMH) synthesized to form an effective adsorbent with utilizing the stable structure of silica gel (not soluble in water and many acids, not easy swelling due to cross bonds, cheapness and repeatability of experiments). For the first time, modification of CPTS onto silica gel and immobilization of Schiff base onto the resulting compound was performed.

Accordingly, in this work, we first synthesized a Schiff base derivative and this compound was chemically immobilized to silica gel surface. Second, we examined the applicability of the adsorbent material obtained for the removal of Cr(III) ions from aqueous solutions and wastewater. Finally, Dubinin–Radushkevich (D–R) [37], Freundlich [38] and Langmuir [38,39] isotherm models from adsorption isotherm parameters were also calculated from the maximum

adsorption capacities. The values of the free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) from the thermodynamic parameters were also calculated from the experimental results related to the adsorption amounts at different temperatures.

2. Materials and methods

2.1. Materials

All solvents and chemicals were analytical grade and used without any purification. Chemicals used in experiment and characteristics are tabulated (Table 1).

pH of chromium solutions was adjusted with the dilute sodium hydroxide and nitric acid solutions. Industrial wastewater samples containing Cr(III) ion were obtained from the production car motor vehicles in Konya/Turkey.

2.2. Instrument

The tools and apparatus used in this study are given in Table 2.

2.3. Preparation of Si-CPTS-PMH adsorbent

First, 70.0 g of the silica gel was transferred to a round bottom flask and 120 mL of hydrochloric acid (HCl) (37%) was added [40]. The reaction mixture was stirred at 150°C for 72 h under reflux and then filtration process was carried out under vacuum. The obtained hydrolyzed silica gel was completely washed three times with distilled water to remove hydrochloric acid from the mixture. The resulting hydrolyzed silica gel was allowed to dry for 24 h in a vacuum oven set at 180°C [40,41]. The obtained hydrolyzed silica gel structure (hydrolysis of silica gel structure) is shown in Fig. 1.

Second, the preparation of Si-CPTS was carried out with the following three steps. In the first step of the Si-CPTS modification process, 30 g of hydrolyzed silica gel was added to 100 mL of dry toluene. 15 mL of CPTS (3-chloropropyltriethoxysilane) was then added to the resulting solution and the mixture was refluxed at 110°C for 72 h under nitrogen atmosphere [42,43]. In the second step, the resulting Si-CPTS was washed with toluene, ethyl alcohol and diethyl ether,

Table 1
Chemicals used in experimental studies and their properties

Chemical name	Chemical formula	Product specification	Brand
Silica gel	SiO ₂	High-purity grade, pore size 60 Å, 70–230 mesh	Sigma-Aldrich
3-Chloropropyltrimethoxysilane	C ₆ H ₁₅ ClO ₃ Si	≥97%	Merck
Toluene	C ₇ H ₈	Anhydrous, 99.8%	Sigma-Aldrich
Chromium(III) nitrate nonahydrate	Cr(NO ₃) ₃ ·9H ₂ O	99%	Sigma-Aldrich
Sodium hydroxide	NaOH	BioXtra, ≥98% acidimetric	Sigma-Aldrich
Methanol	CH ₃ OH	Anhydrous, 99.8%	Sigma-Aldrich
Nitric acid	HNO ₃	90%	Sigma-Aldrich
Ethanol	CH ₃ CH ₂ OH	Absolute, reag. ISO, reag. Ph. Eur., ≥99.8% (GC), liquid (clear, colorless)	Sigma-Aldrich
Diethyl ether	(C ₂ H ₅) ₂ O	Anhydrous, ≥99.0%	Merck
Hydrochloric acid	HCl	37%	Merck
Diethyl ether	C ₄ H ₁₀ O	Anhydrous, ACS reagent, ≥99.0%	Sigma-Aldrich

Table 2
Name, purpose, characteristics and brand of instruments used in experimental studies

Used tools name	Purpose, features and brand
pH meter	pH values of the samples were adjusted by an Orion ion meter with combined pH electrode.
FTIR	Infrared spectra were measured in the range 650–4,000 cm ⁻¹ by FT-IR spectrometer (ATR; 21°C temperature and 1 atm pressure, Perkin Elmer Spectrum 100 FT-IR Spectrometer).
AAS	Metal concentrations in the filtrated solution were determined using atomic absorption spectrometer (AAS) (28°C temperature, 1 atm pressure, Contr AA 300, Analytic Jena) at 357 nm wavelength.
Thermostatic shaker	Thermostatic shaker (A Heidolph Unimax 2010) was used for the sorption studies.
Ultrapure water	All aqueous solutions were prepared with ultrapure water obtained from a water purification system (Millipore Milli-Q Plus).
SEM	Functionalized silica gel was characterized by scanning electron microscope (SEM) (by applying 05 kV electron acceleration voltage).

respectively. In the third step, obtained Si-CPTS was dried in vacuum oven at 50°C for 48 h [44,45]. The possible structure of the obtained Si-CPTS is given in Fig. 1.

Finally, 10 g of modified Si-CPTS was stirred with (E)-2-(1-(3-methyl-3-phenyl cyclobutyl)-2-morpholino ethylidene) hydrazine carbothioamide (PMH) of solution (33 mL) dissolved in dry toluene and the mixture (Si-CPTS-PMH) was stirred at 150°C under reflux and nitrogen atmosphere for 48 h [44–46]. The mixture was filtered under vacuum, washed with acetone and distilled water. The resulting Si-CPTS-PMH adsorbent was allowed to dry in a vacuum oven at 75°C for 72 h. The probable structure of the obtained Si-CPTS-PMH is depicted in Fig. 1.

2.4. Adsorption experiments

In order to evaluate sorption conducts of Cr(III) ions in industrial wastewater and aqueous solutions on obtained Si-CPTS-PMH adsorbent, the adsorption experiment studies were done by mixing Si-CPTS-PMH adsorbent (between 10 and 75 mg) with Cr(III) solution (10 mg/L) in a conical flask and followed then by shaking for 24 h at pH 6.0 and room temperature. The same procedure was also applied to Cr(III) ions in industrial wastewater. The effects of dose, temperature, concentration and pH on the sorption capacity of Cr(III) ions in standard aqueous solution (Cr(III)) and industrial wastewater (Cr wastewater) were also investigated. pH of solutions containing Cr(III) ions in standard aqueous solution (Cr(III)) and industrial wastewater (Cr wastewater) was adjusted using dilute nitric acid or sodium hydroxide. Adsorption isotherms of Cr(III) ions in standard aqueous solution and industrial wastewater were carried out by changing the concentration of Cr(III) ions from 8.0 to 40.0 mg/L at different temperatures (20°C–50°C ± 1°C) at pH 6.0. Adsorption kinetics was investigated by analyzing the residual chromium aqueous solution (Cr(III)) and industrial wastewater (Cr wastewater) concentration at specific intervals until equilibrium was attained [47]. The remainder chromium metal concentrations in the solution were gauged by atomic absorption spectroscopy (AAS) and the sorbent quantity of the Cr(III) cations was computed by Eq. (1) below.

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

Here V is the volume of aqueous phase (L), W is the dry weight of Si-CPTS-PMH adsorbent (g), C_0 and C_e are the inception and balance concentrations of the Cr(III) ions in aqueous phase (mmol L⁻¹), q is the quantity of chromium metal ion sorbent onto unit quantity of Si-CPTS-PMH adsorbent (mmol g⁻¹) [39].

3. Result and discussion

3.1. Characterization

3.1.1. FTIR analysis and scanning electron micrographs

Infrared spectra of pure silica gel, Si-CPTS and Si-CPTS-PMH (Fig. 2a) showed a weak IR band at ~1,628 cm⁻¹ and a strong wider band at 3,387 cm⁻¹ which were associated with the existence of the O–H bond stretching vibration of Si–OH group and the adsorbent water [48]. The intense band related to Si–O–Si stretching vibration was located at 1,041 cm⁻¹, and the peak around 789 cm⁻¹ was due to Si–O–Si symmetrical stretching [49]. O–H stretching vibration of the silica gel was observed at 3,387 cm⁻¹. After CPTS modification on the silica gel surface, O–H stretching vibration of Si-CPTS was observed at 3,441 cm⁻¹. The frequencies of the CH₂ stretching vibrations for Si-CPTS were observed at 2,946–2,830 cm⁻¹. In the Si-CPTS's spectrum, there is an absorption band located at 695 cm⁻¹, which is attributed to the C–Cl stretching vibration from the Si-CPTS [50]. Si-CPTS will be used instead of silylant agent (CPTS). Due to the presence of –OH groups present in the structure of the silica–Schiff base complexes, the formation of a wide –OH peak at 3,356 cm⁻¹ shows that Si-CPTS-PMH adsorbent was obtained. It was also observed that there were two new typical bands at 1,438 and 1,388 cm⁻¹, corresponding to C=N and C=C vibrations, respectively. These results indicated that the immobilization of (E)-2-(1-(3-methyl-3-phenylcyclobutyl)-2-morpholino ethylidene) hydrazine carbothioamide (PMH) onto the silica surface was achieved.

Silica gel, Si-CPTS and Si-CPTS-PMH were also investigated by using scanning electron micrographs (SEM). As seen in Fig. 2b, the SEM image of pure silica gel appears to be in a very smooth morphology [44] while SEM image of Si-CPTS (Fig. 2b) shows a rough morphology after synthesizing CPTS onto pure silica gel surface. SEM image of Si-CPTS-PMH (Fig. 2b) demonstrates a very rough morphology after immobilization of PMH to the Si-CPTS surface. The presence of

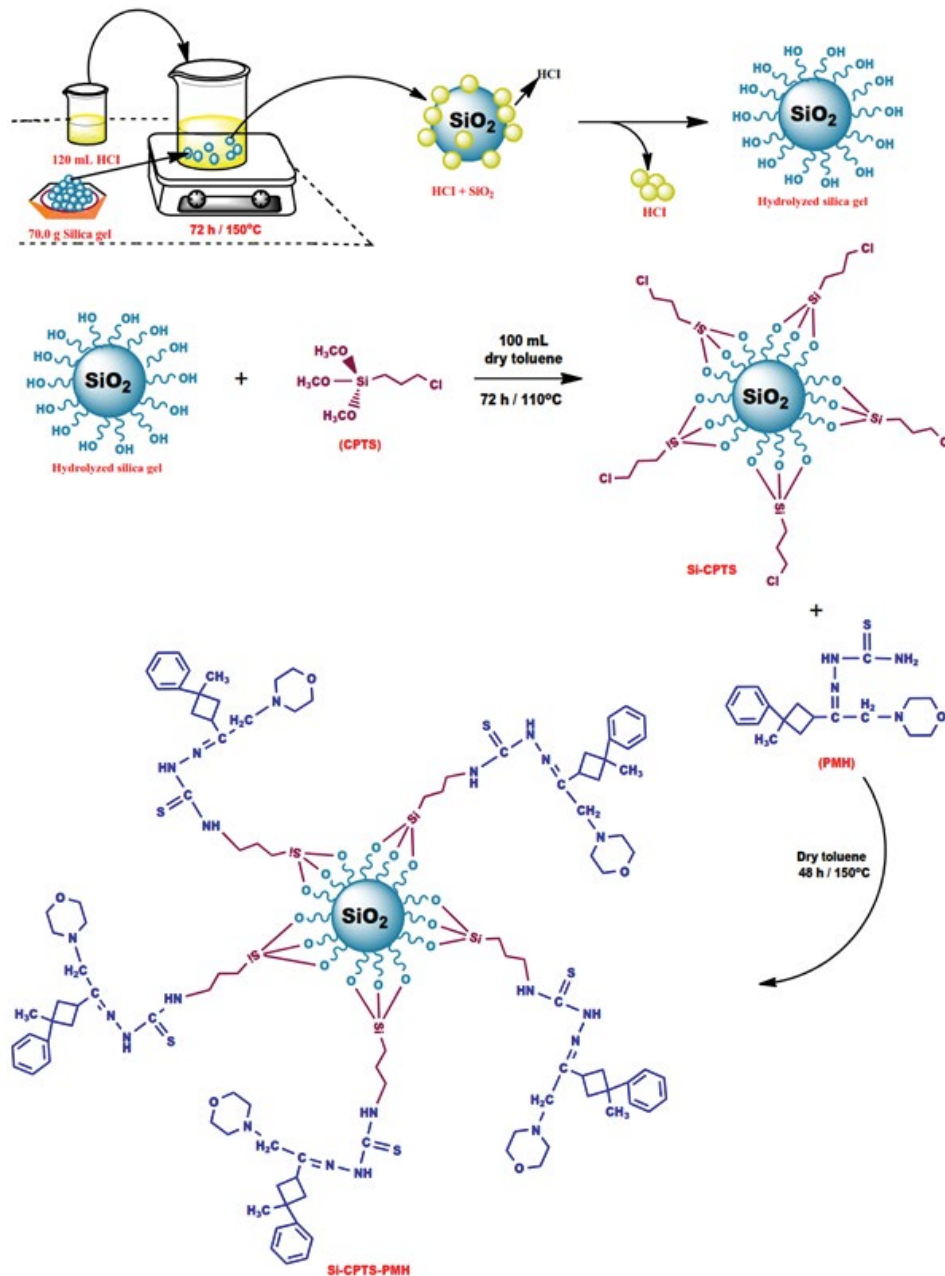


Fig. 1. Probable structures of the obtained hydrolysis of silica gel, Si-CPTS and Si-CPTS-PMH.

bound particles on silica gel surface confirms that the PMH was immobilized to the silica gel surface.

3.2. Adsorption studies and mechanism

In this section, adsorption studies were performed in five different experiments. In our first experiment, the effect of sorbent amount on adsorption was investigated. Fig. 3a demonstrates the influence of Si-CPTS-PMH adsorbent amount on sorption of Cr(III) ions in industrial wastewater and aqueous solution. 0.001, 0.015, 0.025, 0.050 and 0.075 g of Si-CPTS-PMH adsorbents were, respectively, obtained in

50 mL beakers. Aqueous solution containing 10 mL of Cr(III) ion was, respectively, added there and stirred for 24 h in a magnetic stirrer. The same procedure was applied in industrial wastewater solutions. As seen in Fig. 3a, the optimum adsorption mass of Si-CPTS-PMH adsorbent was found to be 0.025 g for Cr(III) in industrial wastewater and aqueous solutions [51].

In the second experiment, the influence of contact duration was evaluated and Fig. 3b demonstrates the influence of the contact duration of adsorption of Cr(III) ions in industrial wastewater and aqueous solution onto Si-CPTS-PMH adsorbent. The influence of contact duration on Si-CPTS-PMH

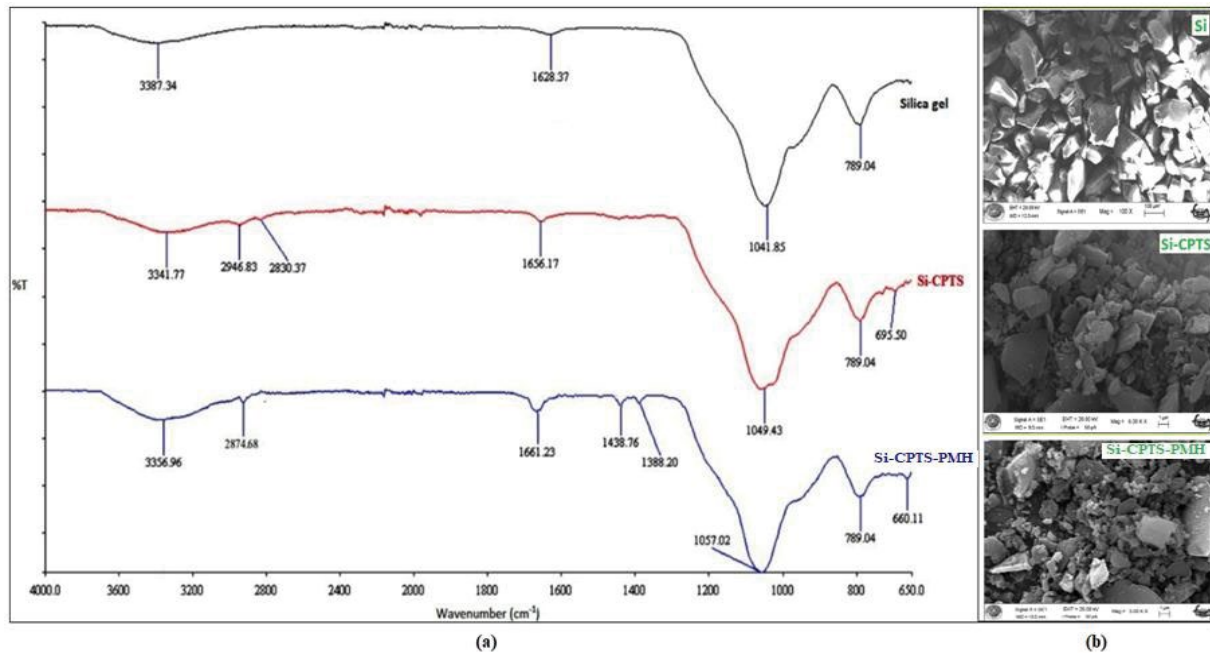


Fig. 2. FTIR spectra of activated Si, Si-CPTS and Si-CPTS-PMH (a), SEM images of Si, Si-CPTS and Si-CPTS-PMH (b).

absorbent was also investigated at six diverse contact times (between 30 and 180 min) at the room temperature with pH 6.0. As seen from Fig. 3b, the contact times were increased up to 150 min for the sorption on Si-CPTS-PMH adsorbent of Cr(III) ions in industrial wastewater and aqueous solutions and then were remained constant [52].

In the third experiment, a pH study involving that 0.025 g of adsorbent Si-CPTS-PMH was severally shuffled with the existence of 10 mL of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ aqueous solutions and 10 mL of industrial wastewater solutions was performed. The adsorption effects of Cr(III) ions at different pHs on Si-CPTS-PMH absorbance were also investigated at six different pHs (2.0, 3.0, 4.0, 5.0, 6.0 and 7.0) at the room temperature and same concentrations. As a result of the study, the graph in Fig. 3c was obtained using the data obtained from the sorption effect of Cr(III) ions at different pHs by the Si-CPTS-PMH adsorbent. As seen from Fig. 3c, the sorption of Si-CPTS-PMH adsorbent at low pH values (2.0–4.0) was generally observed to be low for Cr(III) ions in aqueous solutions and industrial wastewater solutions. Si-CPTS-PMH adsorbent exhibited a low affinity for Cr(III) ions at pHs lower than 5.0 for Cr(III) ions in industrial wastewater solutions (Cr (wastewater)). For Cr(III) ions in aqueous solutions of the Si-CPTS-PMH adsorbent, it exhibited a low affinity against Cr(III) ions at pHs lower than 4.0. The pH values for maximum sorption of Cr(III) ions in aqueous solution and industrial wastewater onto Si-CPTS-PMH adsorbent surface were found as 6.0. The optimum pH level for all other experiment study is 6.0 [53].

In the fourth experiment, adsorption amounts at different chromium concentrations were investigated. For adsorption measurements at AAS, 0.025 g of Si-CPTS-PMH adsorbent was added sequentially to Cr(III) solutions at concentrations of 8, 12, 20 and 40 mmol L⁻¹. The suspensions were shaken for 2 h at room temperature. The same procedure was applied

to industrial wastewater as well. After 2 h, the filtration was carried out and the quantities of chromium in aqueous solution and industrial wastewater were calculated by measuring with AAS [25]. Fig. 3d shows the influence of the adsorption attached to the chromium concentration [44,54]. Graphical curves for the industrial wastewater (Cr (wastewater)) and aqueous solution (Cr(III)) given in Fig. 3d demonstrated that the adsorption boosted with increasing chromium concentration and then attained fixed state values [55].

In the fifth experiment, adsorption amounts at different temperatures were investigated. Depending on the temperature, the chromium metal adsorption was carried out at pH 6.0 between at 20°C and 50°C ± 1°C for Cr(III) ions in industrial wastewater solution and aqueous solution, respectively. The quantities of adsorbed chromium were calculated from the alteration in chromium metal concentrations in industrial wastewater solution and aqueous solution. The effect of temperature on adsorption is reported in Fig. 3e. When looking at the adsorbed chrome curves in the industrial wastewater solution and aqueous solution in the graph, we observed that the quantity of sorption boosted with increasing temperature and then achieved fixed values. Fig. 3f shows the possible sorption mechanism of Cr(III) ions on Si-CPTS-PMH adsorbent surface. This sorption mechanism can be explained by an ion exchange process. However, it is thought that the Schiff base functional group's Si-CPTS-PMH adsorbent chelating effect also occurs during the adsorption process. It is possible to interpret that the hydroxyl groups in the Si-CPTS-PMH adsorbent and the surface coordination of the donor nitrogens are subject to the chemisorption of Cr(III) ions [56].

3.3. Adsorption isotherms

The analyses of adsorption isotherms (Dubinin–Radushkevich (D–R) isotherm, Freundlich isotherm and Langmuir

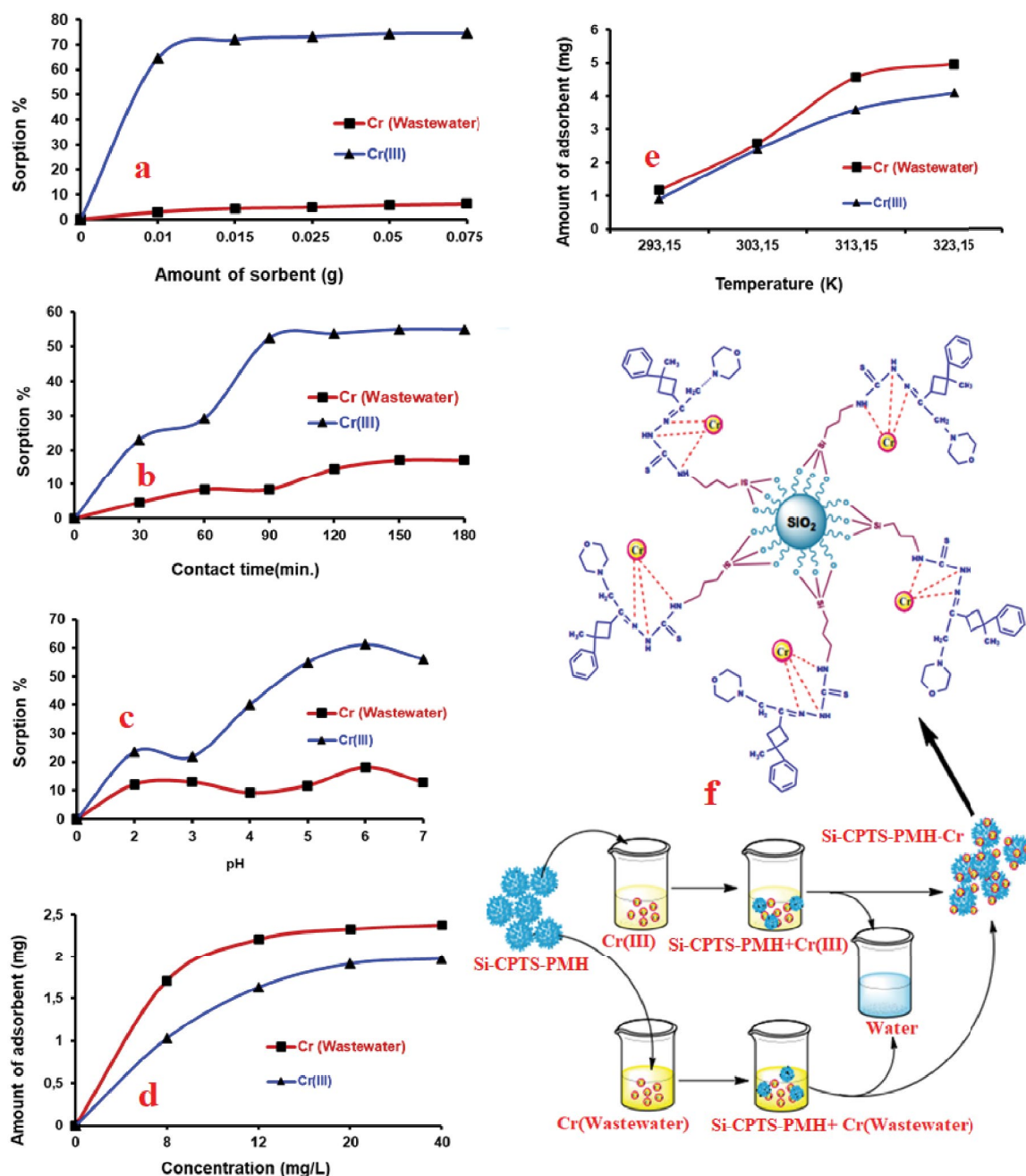


Fig. 3. Effect of the amount of Cr(III) and Cr (wastewater) ions on adsorption (a). The effect of the contact time on the adsorption of Cr(III) and Cr (wastewater) ions (b). The effect of pH on the adsorption of Cr(III) and Cr (wastewater) ions (c). The effect of the concentration on the adsorption of Cr(III) and Cr (wastewater) ions (d). The effect of temperature on the adsorption of Cr(III) and Cr (wastewater) ions (e). The estimated perspective of Si-CPTS-PMH-Cr ions combination (f).

isotherm) were carried out using the experimental data obtained for the effect of different Cr(III) concentrations on the adsorption capacity (using the experiment done in Fig. 3d). Fig. 4 depicts D-R, Freundlich and Langmuir adsorption isotherms graphs and parameters for Cr(III) ions in industrial wastewater (Cr wastewater) and aqueous solutions (Cr(III)).

The Langmuir isotherm model assumes that the adsorption is confined to a single-layered of matter on the surface

and that adsorbed substances do not move on the solid surface. Eq. (2) and explanation for the Langmuir isotherm model are given below.

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{q_0 b} \quad (2)$$

where q_e and q_0 are equilibrium and maximum adsorption capacity (mmol g^{-1}), respectively [57], q_e is the amount of

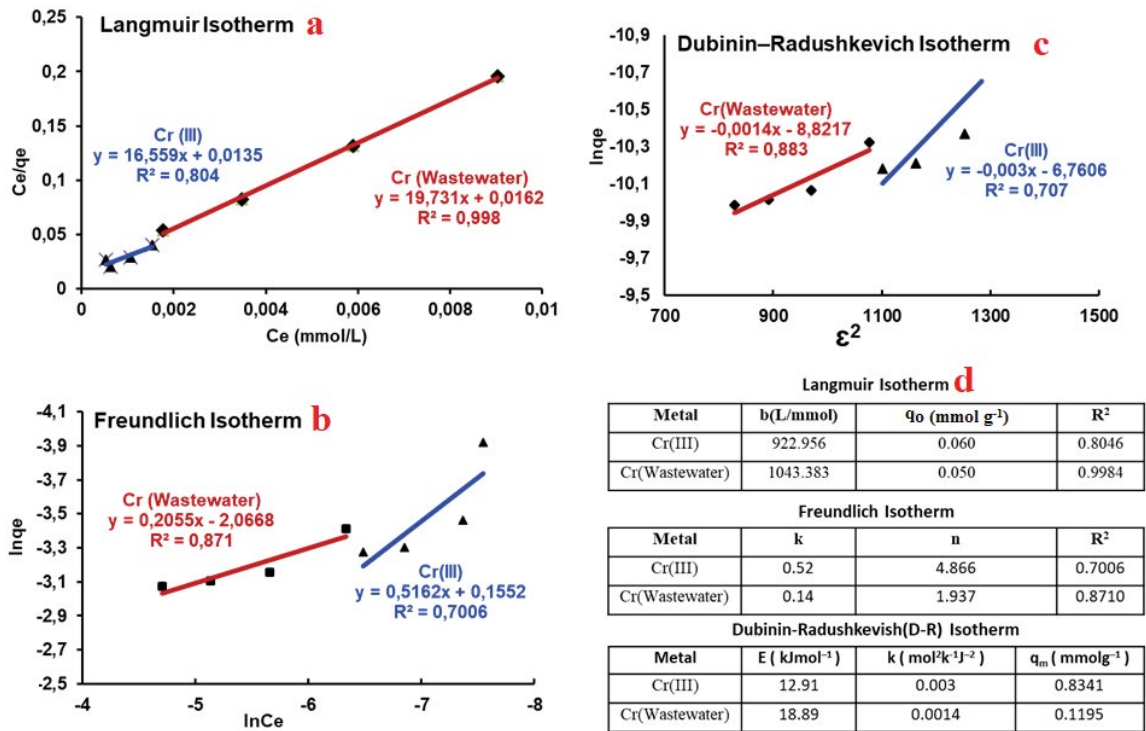


Fig. 4. Langmuir isotherms of Cr(III) and Cr (wastewater) removal by Si-CPTS-PMH at room temperature (pH 6.0 and contact time of 2 h) (a). Freundlich isotherms of Cr(III) and Cr (wastewater) removal by Si-PMH at room temperature (pH 6.0 and contact time of 2 h) (b). D–R isotherms of Cr(III) and Cr(wastewater) removal by Si-CPTS-PMH at room temperature (pH 6.0 and contact time of 2 h) (c). The parameters of Langmuir, Freundlich and D–R adsorption isotherms (d).

solute sorbent (mmol g^{-1}), C_e is the equilibrium ion concentration in the chromium solution (mmol dm^{-3}), q_0 is the Langmuir constant and the maximum surface density at monolayer coverage (mg g^{-1}), b is the Langmuir adsorption constant and represents the energy of sorption and changes with temperature ($\text{dm}^3 \text{mmol}^{-1}$) [58,59].

Si-CPTS-PMH adsorbent exhibited high adsorption capacity for Cr(III) ions in industrial wastewater and aqueous solutions. The plot of C_e/q_e vs. C_e for the adsorption gives a straight line of slope $1/b q_0$ and intercepts $1/q_0$ (Fig. 4a) [41]. Fig. 4d shows that correlation coefficients (R^2) and constants calculated for the Langmuir isotherm and also the constant b (mol dm^{-3}) value relates to the bond-term value [58]. These values in Fig. 4d were quite large for Cr(III) ions in industrial wastewater and aqueous solutions, suggesting a quite high thermodynamic stability for chelation of Cr(III) ions on the surface of Si-CPTS-PMH adsorbent. These results indicated that Cr(III) ion interacts more effectively with nitrogen groups.

The Freundlich isotherm is used to describe multi-layer adsorption and to determine adsorption on heterogeneous surfaces. The Freundlich adsorption isotherm equation can be written as below.

$$\ln q_e = \ln K_F + \frac{1}{n \ln C_e} \quad (3)$$

where q_e (mmol g^{-1}) is the equilibrium solute concentration on adsorbent, (namely, adsorption capacity of the adsorbent);

C_e is the equilibrium concentration (mmol dm^{-3}) of Cr(III) ions, K_F is the constant of the Freundlich isotherm (mmol g^{-1}), which represents the adsorption capacity, n is the heterogeneity factor (the adsorption intensity) which represents the bond deploy [53,60,61].

The plot of $\ln q_e$ vs. $\ln C_e$ in Fig. 4b shows a flat line for Cr(III) ions in industrial wastewater (Cr (wastewater) and aqueous solutions (Cr(III)). The sorption data follow the Freundlich isotherm as well. Fig. 4d provides K and n values belonging to Freundlich isotherm. The K_F constants and n values of the Freundlich isotherm can be calculated from the intercept and slope of the plot demonstrated in Fig. 4b. The K_F constant and n values of the Freundlich isotherm in Fig. 4d indicate that the Si-CPTS-PMH adsorbent is a measure of the intensity and capacity of adsorption, respectively [55]. It is the nature of the fractional value of $1/n$ ($0 < 1/n < 1$) indicating that the surface of Si-CPTS-PMH adsorbent is heterogeneous [58,62,63].

Equilibrium data of D-R isotherm can be applied to distinguish the difference between the physical or chemical adsorption types and the following equation is used [64].

$$\ln q_e = \ln q_m - k \epsilon^2 \quad (4)$$

where ϵ (Polanyi potential) is $[RT \ln(1 + (1/C))]$, q_e is the amount of solute adsorbent per unit weight of adsorbent (mol g^{-1}), k is a constant related to the adsorption energy ($\text{mol}^2(\text{kJ}^{-1})^{-1}$), q_m is the adsorption capacity (monolayer sorption capacity) (mol/g^{-1}) [58].

Fig. 4c shows the plot of $\ln q_e$ vs. ε^2 , from Eq. (4). Therefore, we can generate q_m values from the intersection points in Fig. 4c, and it is possible to generate k values from the slopes. The constant k is used to calculate the average free energy (E) (kJ mol^{-1}) and the average free energy (E) gives information about the sorption mechanism. E can be calculated using the following equation [65,66].

$$E = \frac{1}{(-2k)^{\frac{1}{2}}} \quad (5)$$

The mean free energy (E) values were calculated from Eq. (5) and are shown in Fig. 4d. If the greatness of the average free energy (E) is the range of 8 and 16 kJ mol^{-1} , the sorption mechanism continues by ion exchange, while for values in the range of 1–8 kJ mol^{-1} , the adsorption mechanism is a physical adsorption [67–71]. If the average free energy (E) is above 16 kJ mol^{-1} , it is chemical adsorption [70]. As shown in Fig. 4d, E values for Cr(III) ions in industrial wastewater and aqueous solutions were calculated as 12.91 and 18.89 kJ mol^{-1} , respectively. For this reason, it can be said that the sorption mechanism of Cr(III) ions in aqueous solutions on Si-CPTS-PMH adsorbent is an ion exchange process, the adsorption mechanism of Cr(III) ions in industrial wastewater is realized by chemical adsorption.

3.4. Thermodynamic studies

Thermodynamic parameters (free energy change [ΔG°], enthalpy change [ΔH°] and entropy change [ΔS°]) of Cr(III) ions sorption in industrial wastewater and aqueous solution on Si-CPTS-PMH adsorbent surface were evaluated using the following equations:

$$K_D = \left(C_0 - \frac{C_e}{C_e} \right) \times \frac{V}{W} \quad (6)$$

$$\log K_D = \frac{\Delta S^\circ}{2.303} R - \frac{\Delta H^\circ}{2.303RT} \quad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

where C_0 and C_e are initial and equilibrium Cr(III) ion concentrations in solutions (mg L^{-1}), V is the volume of Cr(III) ion containing solution (mL), W is the dry weight of the adsorbent (g), ΔG° is the change in free energy (kJ mol^{-1}), ΔH° is the change in enthalpy (kJ mol^{-1}), ΔS° is the change in entropy (J (mol K)^{-1}), T is temperature (K), R is the ideal gas constant

($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$), K_D is the distribution coefficient (equilibrium constant).

The temperature affecting the adsorption of Cr(III) ions to the Si-CPTS-PMH adsorbent surface was investigated at 20°C, 30°C, 40°C and 50°C for Cr(III) ions in industrial wastewater and aqueous solutions at pH 6.0. Polyscience brand water tank was used for the temperature studies. From the results, $1/T$ and the distribution coefficient $\log K_D$ values were calculated and the graph in Fig. 5 showing the logarithmic plot value of the dispersion coefficient $\log K_D$ vs. $1/T$ was obtained. The entropy change (ΔS°) and enthalpy change (ΔH°) values for the adsorption of Cr(III) ions in industrial wastewater and aqueous solutions onto Si-CPTS-PMH adsorbent were estimated from Fig. 5. The free energy change (ΔG°) was also obtained using Eq. (7) and all the conclusions are shown in Table 3 [43].

As shown in Table 3, it is seen that ΔH° is positive for Cr(III) ions in industrial wastewater and aqueous solutions. These obtained values show the endothermic nature of adsorption. Adsorption is endothermic because a quantity of heat is consumed during the transfer of Cr(III) ions from the solution onto adsorbent (solid phase) [72]. Although there are no specific criterion for the enthalpy change (ΔH°) values that detect the type of adsorption, adsorption values between 20.0 and 418.4 kJ mol^{-1} indicate chemical reactions that occur during adsorption, and exhibit $\Delta H < 20.0 \text{ kJ mol}^{-1}$ physical reactions. Therefore, it can be interpreted as chemical adsorption since the enthalpy values for Cr(III) ions in aqueous solutions and industrial wastewater are +68.12 and 23.42 kJ mol^{-1} , respectively.

All free energy change (ΔG°) values for temperature interval 298–323 K were found to be negative values ranging from -9.59 to $-13.48 \text{ kJ mol}^{-1}$ and -8.29 to $-10.12 \text{ kJ mol}^{-1}$ for Cr(III) ions in industrial wastewater and aqueous solutions, respectively. The obtained negative valuations of the

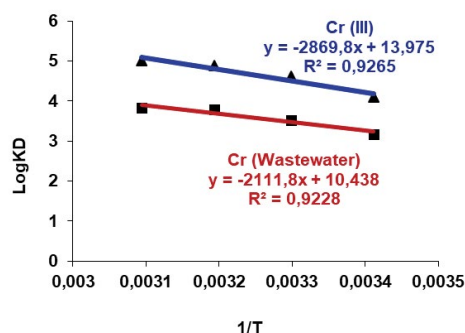


Fig. 5. Plots of $\log K_D$ vs. $1/T$ for Cr(III) and Cr (wastewater) removal by Si-CPTS-PMH.

Table 3

Thermodynamic parameters for adsorption of in Cr(III) and Cr(wastewater) ions on Si-CPTS-PMH

Metal	ΔH° (kJ mol^{-1})	ΔS° ($\text{J K}^{-1}\text{mol}^{-1}$)	$-\Delta G^\circ$ (kJ mol^{-1})			
			297	303	313	323
Cr(III)	54.94	221.45	9.97	11.64	12.74	13.43
Cr(Wastewater)	40.43	171.94	7.73	8.87	9.85	10.27

free energy change (ΔG°) here in indicate that the sorption of Cr(III) ions on the obtained Si-CPTS-PMH adsorbent is possible and spontaneous process. Also, free energy change (ΔG°) values became more negative with increasing temperature [73]. Therefore, higher temperature supported the Cr(III) ions adsorption onto Si-CPTS-PMH adsorbent.

The positive entropy change (ΔS°) values in Table 3 demonstrate the increment in indiscriminate at the solid–solution interface by the fixation of Cr(III) ions in industrial wastewater and aqueous solutions on the obtained Si-CPTS-PMH adsorbent throughout the adsorption. The Cr(III) ions were adsorbed on the modified Si-CPTS-PMH adsorbent surface and water molecules in advance bounded to the ions were released and dispersed in solution, resulting in an increase in ΔS° [69]. For Cr(III) ions in industrial wastewater and aqueous solutions, the entropy change (ΔS°) parameters were found as +265.09 and 108.20 kJ mol⁻¹ K⁻¹, respectively, and it externalizes the affinity of Si-CPTS-PMH adsorbent toward Cr(III) ions in aqueous solutions and industrial wastewater causing a slightly appropriate in distribution [74].

4. Conclusions

The preparation and characterization of Si-CPTS-PMH were successfully accomplished to provide both a more rigid structural feature and stabilization. Based on the adsorption experiments herein, the best Cr(III) removal was realized with the following parameters: pH = 6.0 with 0.025 g adsorbent at 323.15°C and concentration of 20 mg/L in 150 min contact duration. The sorption of Cr(III) ions on the obtained Si-CPTS-PMH adsorbent surface indicates the chemical structure of the adsorption process in our study. This situation was confirmed by Langmuir, Freundlich and D–R models of adsorption isotherms along with the ΔH° values obtained in thermodynamic studies. The enthalpy values for Cr(III) ions in aqueous solutions and industrial wastewater were +68.12 and +23.42 kJ mol⁻¹, respectively. For Cr(III) ions in industrial wastewater and aqueous solutions, the entropy change (ΔS°) parameters were found to be +265.09 and 108.20 kJ mol⁻¹ K⁻¹, respectively. All free energy change (ΔG°) values for temperature interval 298–323 K were found to be negative values between –9.59 and –13.48 kJ mol⁻¹ and between –8.29 and –10.12 kJ mol⁻¹ for Cr(III) ions in industrial wastewater and aqueous solutions, respectively. Thermodynamic studies showed that the adsorption process is possible with good affinity to adsorbent, endothermic in nature and spontaneously. Cumulatively, Si-CPTS-PMH adsorbent was shown to be an effective adsorbent for the removal of Cr(III) ions from aqueous solutions and wastewater.

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