

Removal of hexavalent chromium by chemical modification of 4,4'-((1Z,11Z)-2,5,8,11-tetraazadodeca-1,8-diene-1,11-diyl)diphenol: kinetic and equilibrium modeling

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ABSTRACT

This study aimed to synthesize a new resin through immobilization of the 4,4'-((1Z,11Z)-2,5,8,11-tetraazadodeca-1,8-diene-1,11-diyl)diphenol (TRA) onto silica gel modified (Si-CPTS) with 3-chloropropyltrimethoxy silane (CPTS) and its application for the removal of chromium(VI) ions from aqueous solution as well as from industrial wastewater. The same applications were also made for industrial wastewater vapor. The objective purpose of this work was to investigate the influences of concentration, temperature, amount of metal ions, contact time and pH to sorption on the surface modified by TRA (Si-TRA). The newly synthesized Si-TRA is characterized with scanning electron microscope and elemental analysis and Cr(VI) heavy metal ions were used as sorbate. The sorption of Cr(VI) ion was evaluated by using batch methods. The value of adsorption of Cr(VI) ion was detected with an atomic absorption spectrometer. The maximum adsorption capacities and isotherm parameters were calculated from the Langmuir, Freundlich, and Dubinin–Radushkevich isotherm equations. Thermodynamic parameters such as free energy (ΔG°), entropy (ΔS°), and enthalpy (ΔH°) were also calculated from the sorption results. The modified structure used as adsorbent was successfully employed in the removal of Cr(VI) ions from the samples of industrial wastewater.

Key words | adsorption, chromium, immobilization, silica gel, wastewater

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INTRODUCTION

Contamination of water and wastewater by various heavy metals is a serious environmental problem. Metals are non-biodegradable and have a tendency for bioaccumulation and pose various health problems both in humans and animals. Among various heavy metals, Cr(VI) is one of the most important priority pollutants due to its vast applications in various industries, such as electroplating, alloying, leather tanning, textile dyeing, steel fabrication, and wood preservative treatment (Kowalshi 1994; Rao & Rehman 2010; Chen *et al.* 2011). On the other hand, hexavalent chromium poses various health problems, such as liver damage and pulmonary congestion (Chen *et al.* 2010) and is carcinogenic. According to SEPA, the maximum contamination level for Cr(VI) in domestic water supplies is 0.05 mg/L, and 0.1 mg/L for effluent discharge to inland surface water (Jain *et al.* 2010). Therefore, Cr(VI) must be removed from

wastewaters before their disposal to natural aquatic environments. Reverse osmosis, chemical precipitation, filtration, ion exchange, evaporation, caustic oxidation and reduction, membrane separation, and adsorption are well-known techniques used for the treatment of Cr containing effluents. Most of these techniques involve high cost, long operation time, incomplete metal removal, and sludge generation (Karthikeyan *et al.* 2005). Adsorption is one of the most promising techniques due to its low initial cost and simplicity of design (Sharma *et al.* 2010). Utilization of agricultural waste for the synthesis of adsorbent materials may solve the problems to some extent (Mussatto *et al.* 2010; Owlad *et al.* 2010; Zhang *et al.* 2010). Similarly, various low cost materials and agricultural wastes have been used for the removal of Cr(VI) from aqueous solutions (Garg *et al.* 2007; Khazaei *et al.* 2011). Research on the modification of low cost materials

for the enhancement of removal efficiency has also been carried out by various researchers.

Silica modified with both inorganic and organic functionalities has been used in areas such as metal ion preconcentration (Padilha *et al.* 1999), ion exchange (Espinola *et al.* 2000), biotechnology (Kallury *et al.* 1993), catalysis (Fisher *et al.* 1991), clean technology, and green chemistry (Clark & Macquiarrie 1998). The silica surface consists of two types of functional groups, siloxane (Si–O–Si) and silanol (Si–OH) (Akl *et al.* 2004; Antonio *et al.* 2004; Filha *et al.* 2006), which provide functionalization with different functional groups. Thus, silica modification can occur via the reaction of particular molecules with either siloxane or silanol (Cestari *et al.* 2001). Among the different adsorbents, silica gel immobilized with various organic compounds with metal chelating ability has immense importance (Zaporozhets *et al.* 1999; Kim & Yi 1999; Prado & Airoidi 2001). Modification of silica gels can be achieved via chemisorptions of the active species onto the silica surface. In this process, organic reagents or synthesized organic molecules containing the desired organic functional group are directly attached to the supports (Pyell & Stork 1992).

Silica gel provides good solid support for adsorption due to its thermal, chemical, and mechanical stability (Sales *et al.* 2004). It has a high surface area of 480–540 m²/g, and a relative micro pore size of 6 nm (Silva *et al.* 2006). The use of silica gel as support material has certain advantages such as high thermal stability and high resistance to organic solvents and no swelling. Binding to the surface of silica gel is easier than binding to the surface of the organic supports and is the most popular substrate for the study of the surface. The modified silica gels generally provide higher adsorption capacities than many other organic–inorganic structures used as support. Therefore, immobilized molecules are used for removal of metal ions from industrial wastewater (Soliman *et al.* 2001; Cui *et al.* 2007). Chemical immobilization with appropriate organic groups on silica gel is formed as a new surface and can be used as an adsorbent for removal of heavy metal ions.

The main effect of the immobilization of Schiff bases (TRA) on silica gel is to produce a new surface, which could be used as an adsorbent of heavy metal ions. The present study was designed to immobilize chemically Schiff bases (TRA) on the silica gel by using a batch method along check the capabilities of novel modified adsorbent for removal of Cr(VI) from aqueous solution.

MATERIALS AND METHODS

Materials

Silica gel (Merck Darmstadt Co., Darmstadt, Germany) with high surface area of 480–540 m²/g, micro pore size of 6 nm, 0.036–0.200 mm diameter, pore volume of 0.74–0.84 (cm³/g), and particle size of 70–180 µm was used in the study. 3-chloropropyltrimethoxy silane (CPTS) and K₂Cr₂O₇ were also purchased from Merck. A series of standard metal solution with appropriate dilution of the stock metal solution were prepared. The dilute NaOH and HNO₃ solutions were used for pH adjustments. All chemicals used in the study were analytical grade. Cr(VI) ion-containing industrial wastewater sample was obtained from the valve factory in Konya, Turkey.

Instruments

Infrared spectra were obtained in the range of 650–4,000 cm^{−1} using a Perkin Elmer 100 Fourier transform infrared (FTIR) spectrometer (KBr pellets, 21 °C temperature and 1 atm pressure). The functionalized silica gel was characterized with scanning electron microscope (SEM). The pH values were monitored with Jenway 3010 model digital pH meter with glass and saturated calomel electrode, calibrated on the operational stage using standard buffer solution at 25 ± 1 °C. A Selecta-Ivmen 100D thermostatic shaker was used for the sorption experiments. The metal concentrations of the supernatant were determined by a flame atomic absorption spectrometer (AAS) (28 °C temperature, 1 atm pressure, ContrAA 300, Analytic Jena). All aqueous solutions were prepared with ultra-pure distilled water obtained from a water purification system (Millipore Milli-Q Plus).

Preparation of Si-TRA

Silica gel was converted into Si–OH. The immobilization of the CPTS onto silica gel was carried out by suspending the silica gel (15.0 g) in dry toluene (100 mL) and CPTS (9 mL). The mixture was refluxed for 72 hours and conditioned under vacuum conditions. In the next step, 10 g of Si-CPTS was treated with 25% TRA solution (33 mL) dissolved in toluene and stirred for 15 hours. After filtration of

the suspension, the residue was washed with water and ether and dried under vacuum at $40 \pm 1^\circ\text{C}$ for 72 hours to obtain Si-TRA. A schema of the target structure is given in Figure 1.

Sorption studies

0.1, 0.015, 0.025, 0.05, and 0.075 g adsorbent with 10 mL sorbate were shaken in a temperature controlled shaker incubator at $25 \pm 1^\circ\text{C}$ (30, 60, 90, 120, 150, 180 minutes) until equilibrium was reached (180 minutes). After extraction, the solid phase was separated by filtration. The residual metal concentration of the supernatant was measured using a flame AAS and the amount of cations sorbed was calculated using Equation (1).

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

where q is the amount of metal ion sorbed onto unit amount of the adsorbent (mol/L), C_0 and C_e are the initial and equilibrium concentrations of the metal ions in aqueous phase (mol/L), V is the volume of the aqueous phase (L), and W is the dry weight of the adsorbent (g).

pH studies

Twenty milligrams of Si-TRA was stirred with the presence of 10 mL of Cr(VI) and in wastewater solution in 10 mol/L concentration and studied to different pH values (2.0, 3.0, 4.0, 5.0, 6.0, 7.0). The mixture was shaken for 180 minutes at $25 \pm 1^\circ\text{C}$ (Cestari *et al.* 2001).

Effect of concentration

The sorption was investigated with batch method for aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$ and wastewater at $25 \pm 1^\circ\text{C}$. For these sorption measurements, 20 mg of modified silica gel was suspended in 10 mL of aqueous solution containing various amounts (0.01, 0.015, 0.025, 0.05, 0.075 g) of Cr(VI). These suspensions were shaken in concentrations between 8.0 and 40.0 ± 0.01 mol/L in a shaker thermostat for 180 minutes (Zhu *et al.* 2007). After equilibrium was

established, the amounts of metallic cations remaining in solution were determined with flame AAS.

Temperature studies

The experiments were carried out between 20 and $50 \pm 1^\circ\text{C}$ at optimum pH values for Cr(VI) aqueous solution and in wastewater. The amount of the adsorbed metal ion was calculated from the change in the metal concentrations in the aqueous solution (Sales & Airoidi 2005).

Sorption of evaporating Cr(VI) ion in industrial wastewater

One hundred milliliters of chromium industrial wastewater was added to a 250 mL beaker. One gram of Si-TRA compound was stuck on watch glass. Watch glass was closed over the beaker and the beaker was heated at 50°C as in Figure 2. A 5 mL sample was taken in the solution on days 3, 6, 9, 12, and 15. The initially dark yellow color of chromium wastewater solution changed with time. The color of the waste solution was a lighter yellow color at the end of 15 days (Figure 2). Meanwhile, it was observed that the surface of the white color Si-TRA pasted to the watch glass surface turned yellow. The samples were taken 3 days apart and were also measured with AAS.

RESULTS AND DISCUSSION

Characterization

On the basis of the elemental analysis (Çimen *et al.* 2014), the percentage amounts of carbon, nitrogen, and hydrogen are shown in Table 1.

The functionalized silica gel was characterized with FTIR and SEM. The infrared spectra of the prepared surface were compared with raw silica gel and this is shown in Figure 3(a).

OH stretching vibration in Si-CPTS was shifted to $2,907\text{ cm}^{-1}$ from $2,977\text{ cm}^{-1}$ (Si). A small decrease of OH stretching vibration in silanol was observed at 777 cm^{-1} . Hence, frequency of CH_2 stretching vibrations in Si-TRA

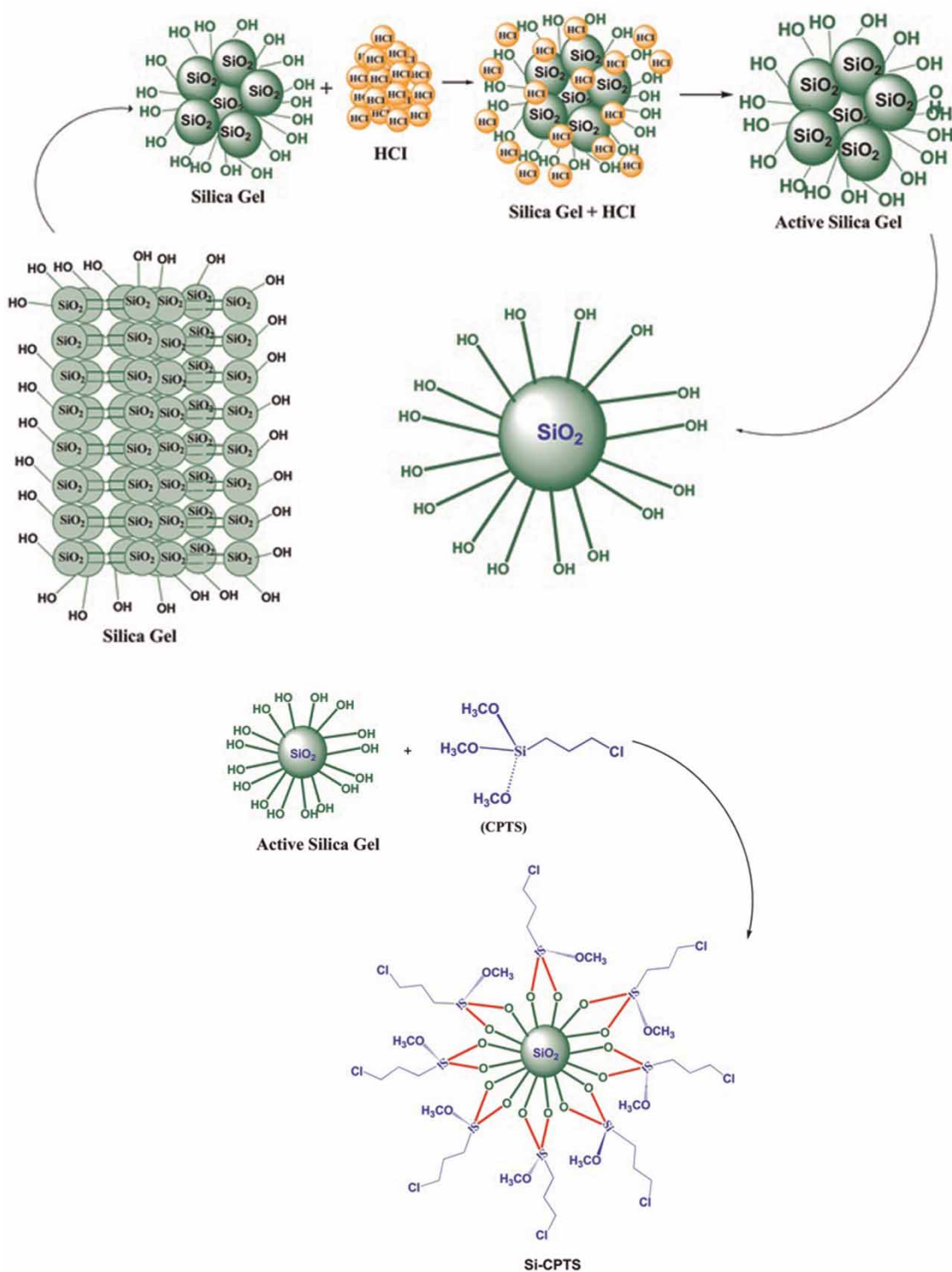


Figure 1 | Possible structure of silica gel bonded 4,4'-((12,11Z)-2,5,8,11-tetraazadodeca-1,8-diene-1,11-diyl)diphenol (TRA) molecules.

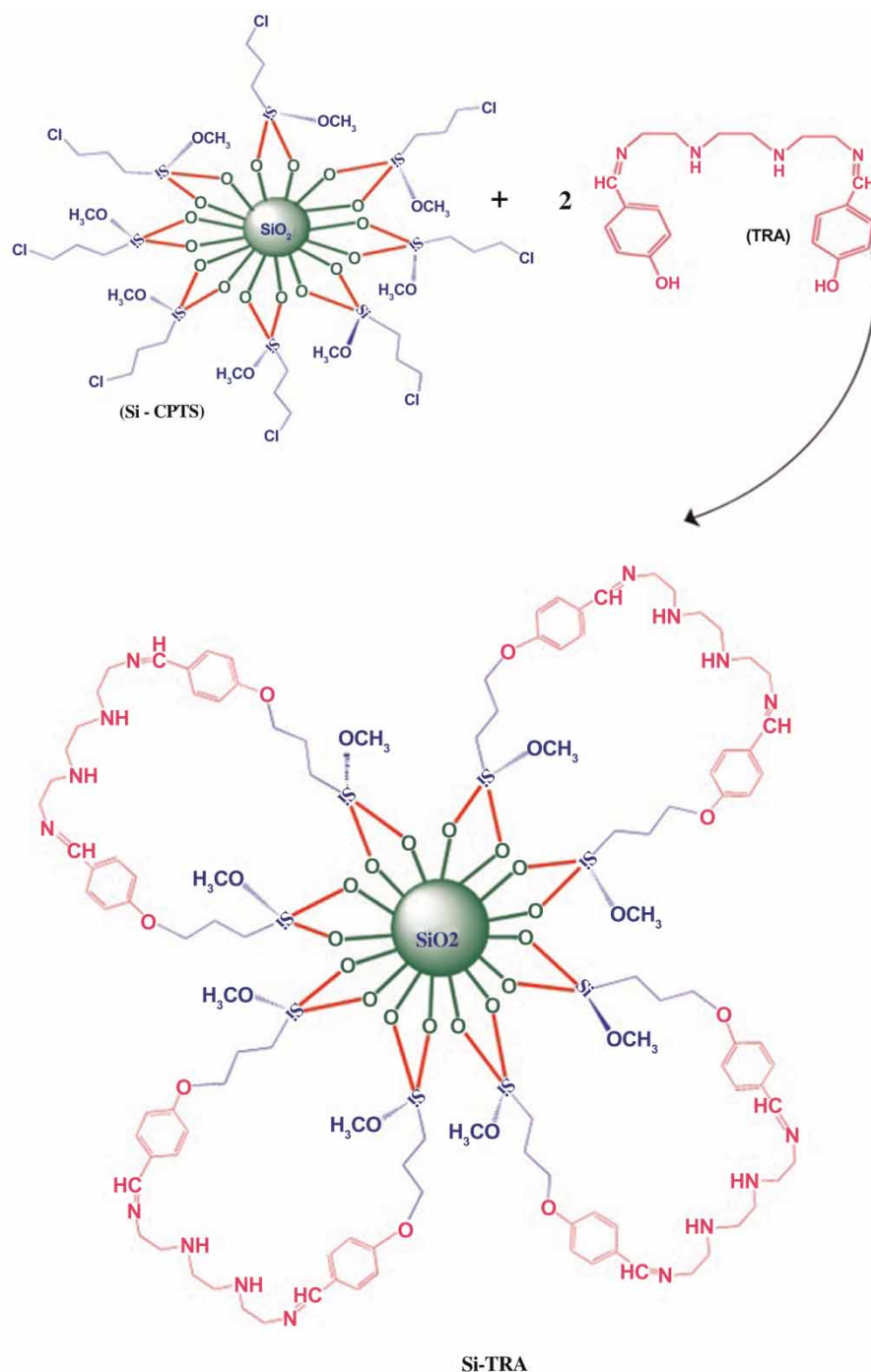


Figure 1 | continued.

were observed at $2,907\text{--}2,977\text{ cm}^{-1}$ (Figure 3(a)); spectrum of Si-TRA has a broad --OH peak at $3,100\text{ cm}^{-1}$ due to the --OH groups which are in the structure of silica-based organic compounds (Kursunlu *et al.* 2009). Stretching of

$\text{C}=\text{N}$ group observed at $1,638\text{ cm}^{-1}$ showed primer amine group of Si-CPTS, TRA, and organic substances. The peak at $1,244\text{--}1,170\text{ cm}^{-1}$ was bending of --C--OH . The peaks at $1,434\text{--}1\text{ cm}^{-1}$, 500 cm^{-1} and $2,837\text{ cm}^{-1}$ were interpreted

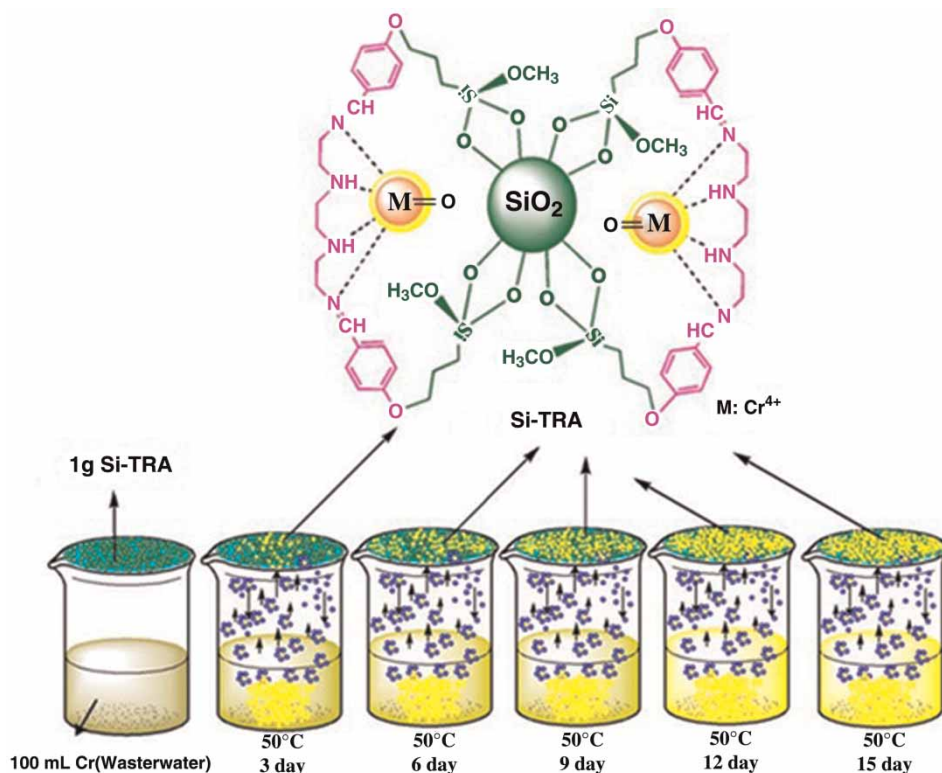


Figure 2 | Sorption diagram of evaporating Cr(VI) in industrial wastewater ions.

Table 1 | Percentages (%) of hydrogen (H), carbon (C), and nitrogen (N) for the matrices SiO₂, Si-CPTS, and Si-TRA

Surface	Nitrogen (%)	Carbon (%)	Hydrogen (%)	Carbon (mmol g ⁻¹)
SiO ₂	0	0	0	–
Si-Cl	0	7.22	0.84	1.21
Si-TRA	5.07	34.29	2.31	1.07

as stretching of C = C and C-H in the benzene ring, respectively (Kursunlu *et al.* 2009).

The infrared spectra of the prepared surface (Si-TRA) were compared with wastewater vapor treated Si-TRA-Cr(VI) and is shown in Figure 3(b). Although small shifts were observed in other peaks, C = N stretching vibration in Si-TRA was shifted from 1,638 to 1,630 cm⁻¹ (Si-TRA-Cr(VI)) by complex formation. The peak at 1,244–1,238 cm⁻¹ belongs to bending of –C-OH or C-O. COH makes a connection with metals and this shift occurs because of the C-O- bond metal. Interaction between the metal-donor atom concerns most of these two bonds;

therefore, these two bonds are the most affected. The peak at around 1,000 cm⁻¹ and 1,400–1,600 cm⁻¹ was stressed Si-O and aromatic C = C, respectively (Kursunlu *et al.* 2009; Ozmen *et al.* 2010).

Since the sorption is a surface phenomenon, the rate and degree of sorption is mainly dependent on the surface functional groups, pore size, and surface area of the sorbent. Therefore, SEM is known as one of the most widely used surface diagnostic tools (Memon *et al.* 2008) and for that reason SEM micrographs were obtained (by applying 0.5 kV electron acceleration voltage) to observe the surface morphology of pure silica gel and Si-TRA. The SEM micrograph of pure silica gel (Figure 4(a)) shows a very smooth morphology whereas after the immobilization of TRA onto the surface of pure silica gel (Figure 4(b)) and TRA Schiff base (Figure 4(c)) it shows an irregular morphology covered with foreign material, i.e., TRA. The presence of attached particles, i.e., TRA on the surface of silica gel, confirms the immobilization.

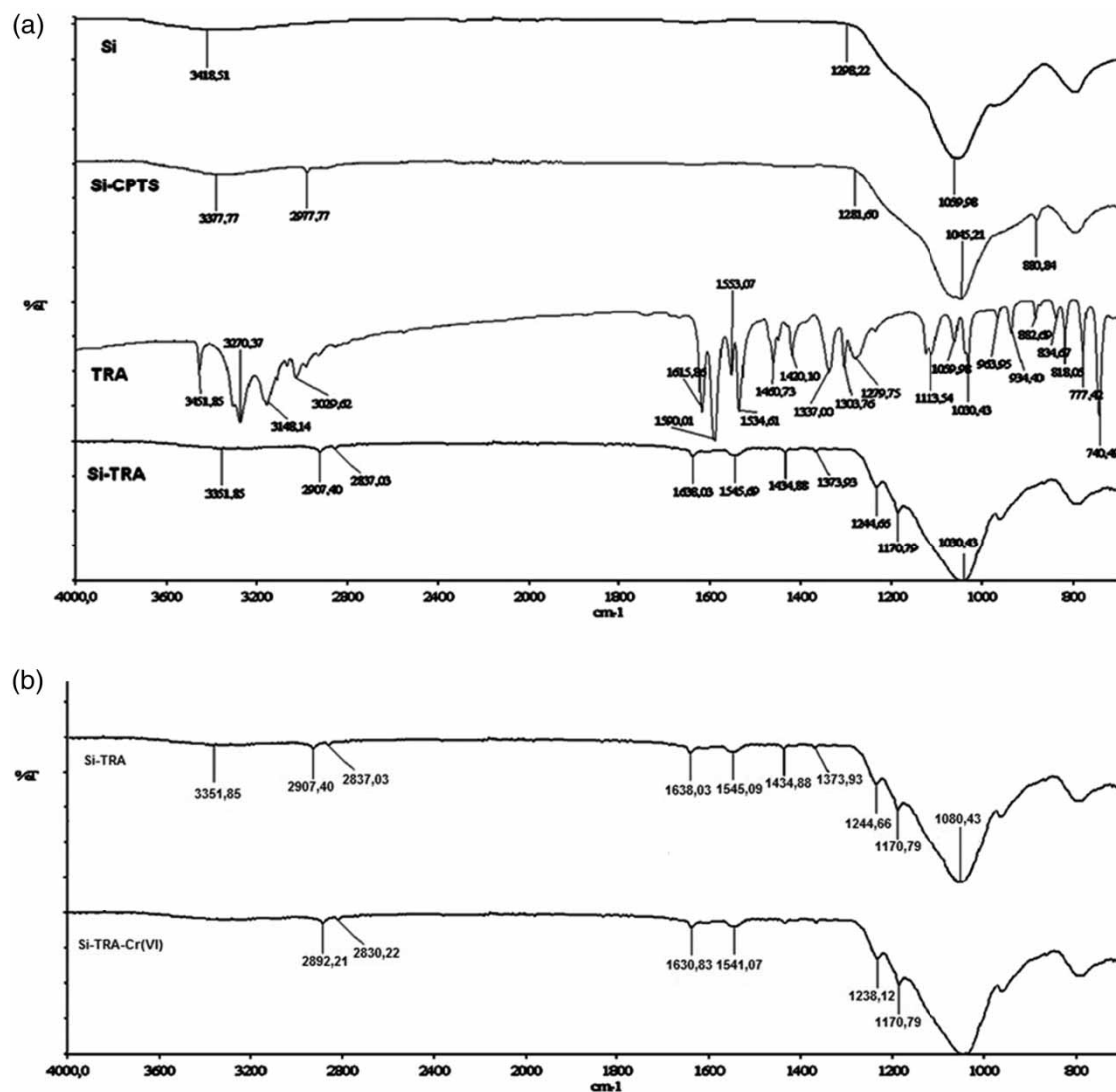


Figure 3 | (a) FTIR spectra of Si, Si-CPTS, TRA and Si-TRA. (b) FTIR spectra of Si-TRA and Si-TRA(Cr(VI)).

Adsorption studies

Effect of adsorption

Figure 5(a) shows the effect of the amount of sorbent on the sorption of Cr(VI) in aqueous solution and in industrial wastewater. The adsorption change depends on the increase of the amount of adsorbent. When the amount of adsorbent is increased, the total amount of adsorbing metal ions increased. The maximum amount of adsorbent for Cr(VI) in aqueous solution and

in industrial wastewater ions was found to be 0.075 g. The excess of the metal ion might be adsorbed with the adsorbent owing to the increase of the active surface.

Effect of contact time

Figure 5(b) shows the effect of the contact time on the adsorption for Cr(VI) in aqueous solution and in industrial wastewater. As expected, the contact time increased with the amount of adsorption for the studied metal ions.

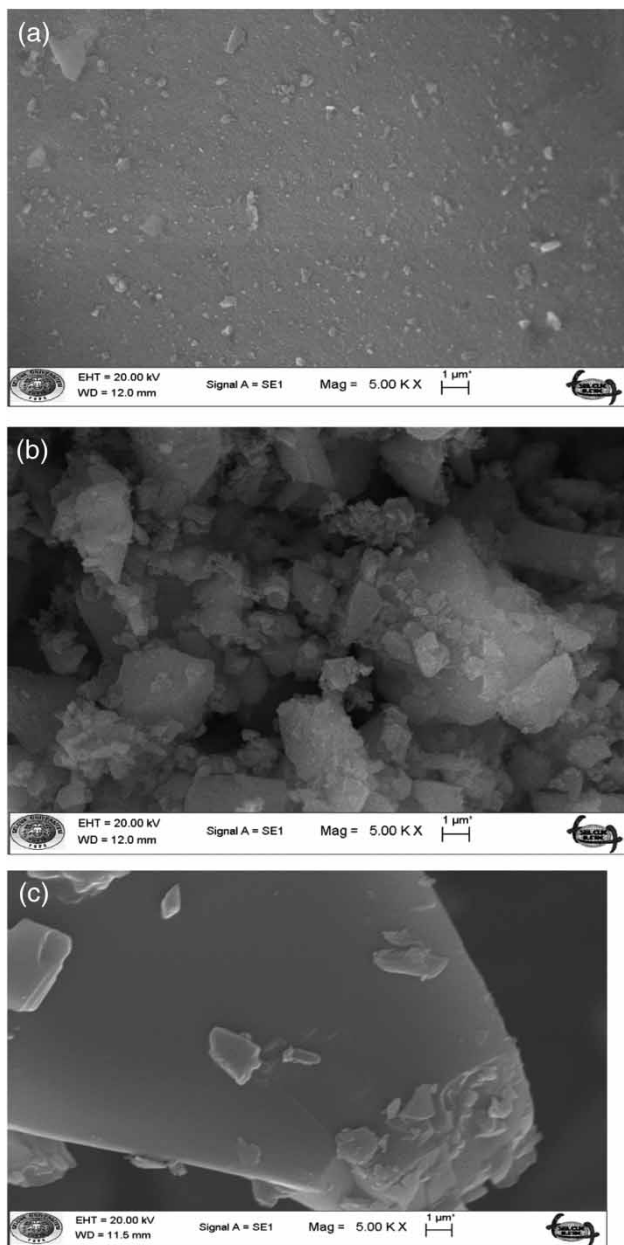


Figure 4 | SEM images of Si (a), Si-TRA (b) and TRA (c).

Effect of pH

The effect of pH on the sorption studied for Cr(VI) in aqueous solution and in industrial wastewater ions is shown in Figure 5(c). According to results, the adsorption of Cr(VI) in aqueous solution and in industrial wastewater ions decreased at a low pH. The competition of H_3O^+

ions with the metal ions was enhanced due to the increased concentration of H_3O^+ ions in the medium (Ngeontae *et al.* 2007). The pH for maximum sorption of Cr(VI) in aqueous solution and in industrial wastewater ions was found to be 5.

Effect of concentration

Figure 5(d) shows that the adsorption effect depends on the concentration of metal ions. The curves of the graph show that the adsorption increases with the increasing concentration of metal ions and reaches steady-state values.

Effect of temperature

Figure 5(e) exhibits the effect of temperature on the adsorption. The amount of adsorption increased with temperature. Depending on the endothermic nature of the sorption, the thermodynamic parameter values also changed with increasing temperature.

Sorption of evaporating Cr(VI) ion

Figure 5(f) shows the percentage adsorption of Cr(VI) ions in industrial wastewater by the Si-TRA compound. According to experimental results, Cr(VI) ions in solution were absorbed by water vapor onto the Si-TRA compound. Sorption (%) is in line with the results found by the batch method but sorption time is longer (15 days).

Isotherm studies

The experimental measurements were evaluated with the Langmuir isotherm, Freundlich isotherm, and Dubinin-Radushkevich (D-R) isotherm. The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases and as follows (Equation (2)):

$$\frac{c_e}{q_e} = \frac{c_e}{q_o} + \frac{1}{q_o b} \quad (2)$$

where q_e is the amount of solute sorbed on the surface of the sorbent (mol/L), C_e is the equilibrium ion concentration in the solution (mol/L), q_o is the maximum surface density at monolayer coverage, and b is the Langmuir adsorption

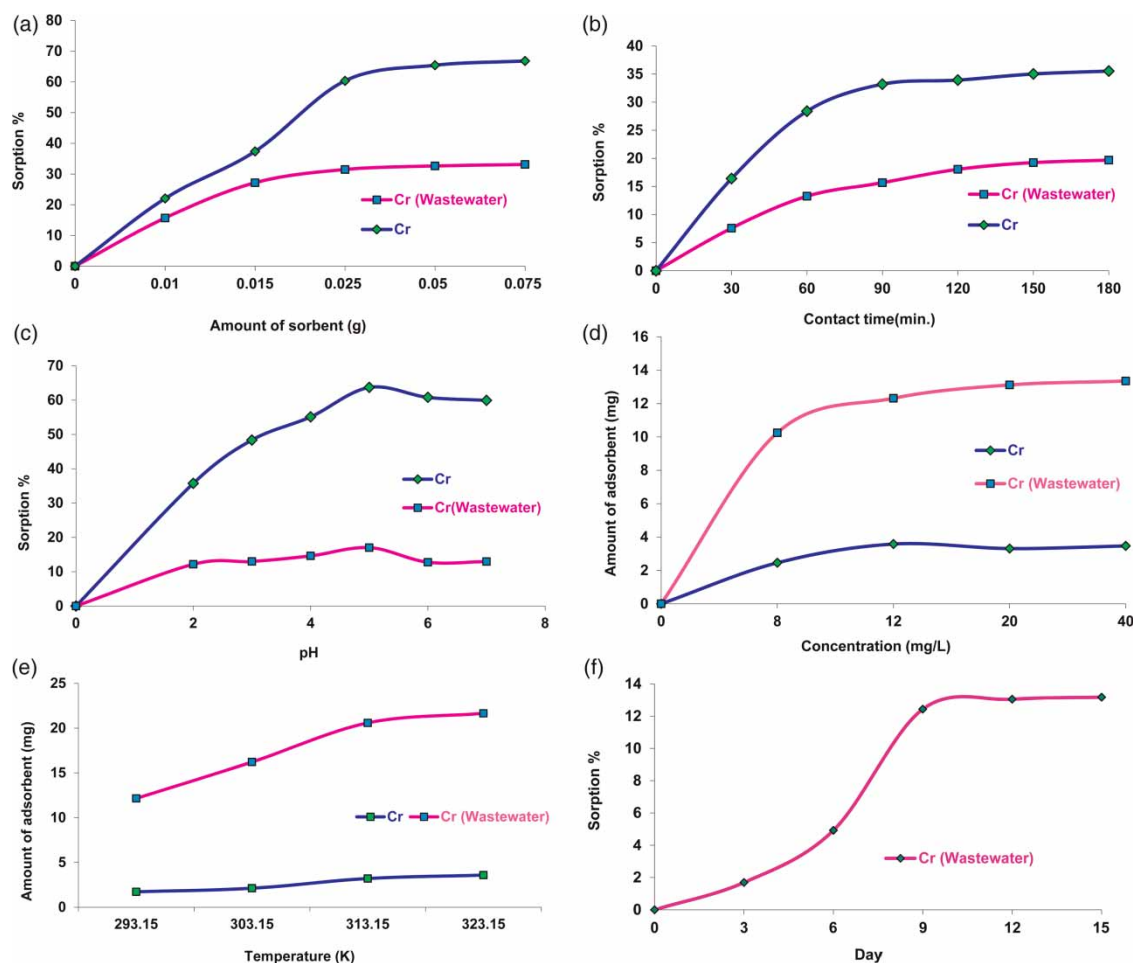


Figure 5 | (a) The effect of the amount of Cr(VI) in aqueous solution and in industrial wastewater ions on the amount of sorbent. (b) The effect of the contact time on the adsorption of Cr(VI) in aqueous solution and Cr(VI) in industrial wastewater ions. (c) The effect of pH on the sorption of pH of Cr(VI) in aqueous solution and in industrial wastewater ions. (d) The adsorption effect depend on concentration of Cr(VI) in aqueous solution and in industrial wastewater ions. (e) The effect of temperature on the adsorption of Cr(VI) and in industrial wastewater ions. (f) The effect of the contact time of evaporating Cr(VI) ions in industrial wastewater ions.

constant (mol/L). The plot of C_e/q_e versus C_e for the sorption gives a straight line of slope $1/bq_0$ and intercepts $1/q_0$ (Figure 6(a)).

The Freundlich isotherm is an empirical isotherm model which is used for adsorption on heterogeneous surfaces or surfaces supporting sites of varied affinities (Oo *et al.* 2009). The Freundlich isotherm can be written as Equation (3)

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

where q_e , C_e , and K_F are the equilibrium solute concentration on adsorbent (mol/L), the equilibrium concentration of the solute (mol/L), the Freundlich constant, respectively.

According to Equation (3), the plot of $\ln q_e$ versus $\ln C_e$ gives a straight line, and K_F and n values can be calculated from the intercept and slope of this straight line (Treybal 1980).

The values of $1/n$ for Si-AHAP are <1 which is an indication of high sorption intensity (Gubbuk 2011). The K_F values showed that immobilized silica gel has higher adsorption capacity for Cr(VI) in aqueous solution and in industrial wastewater (0.14 and 0.09 mol/L) (Vazquez *et al.* 2002). Values of $n > 1$ represent favorable adsorption conditions (Hameed *et al.* 2009). Values of K_F and n were calculated from the intercept and slope of the plot (Figure 6(b)) and are listed in Table 3.

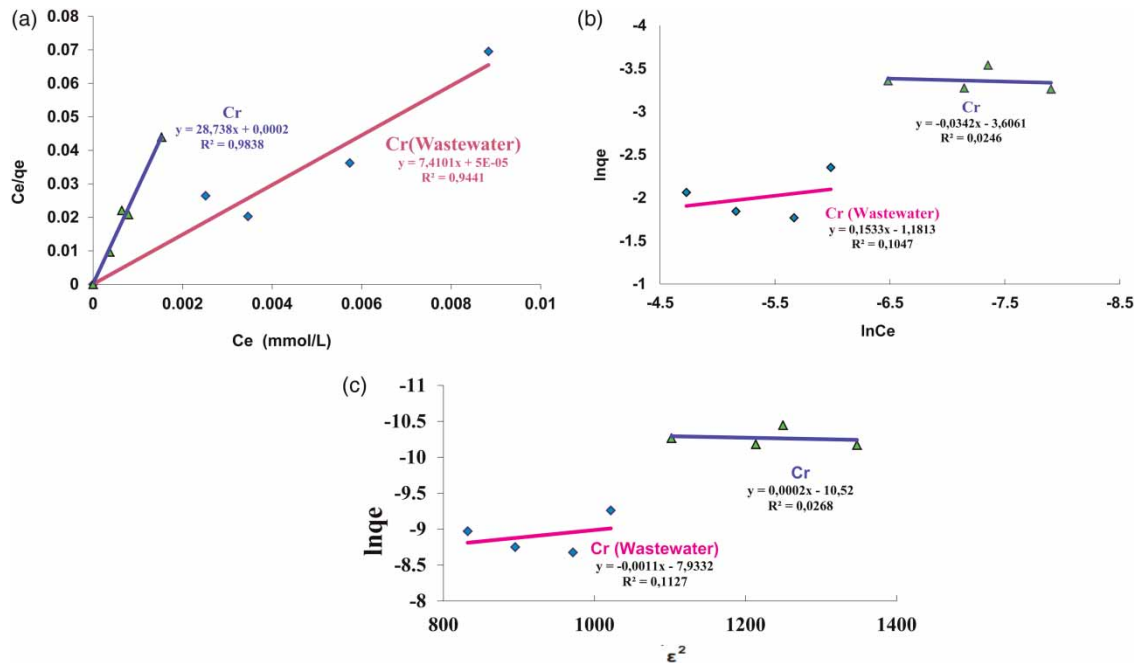


Figure 6 | (a) Langmuir isotherms of Cr(VI) in aqueous solution and in industrial wastewater removal by Si-TRA. (b) Freundlich isotherms of Cr(VI) in aqueous solution and in industrial wastewater ions removal by Si-TRA. (c) D-R isotherms of Cr(VI) in aqueous solution and in industrial wastewater ions removal by Si-TRA.

Table 2 | Isotherms' parameters for Cr(VI) in aqueous solution and in industrial wastewater by Si-TRA ($T = 298$ K)

Freundlich isotherm			Langmuir isotherm		D-R isotherm		
Metal	$1/n$	K_F	Q_0 (mmol)	b (Lmmol $^{-1}$)	k (mol 2 (kJ 2) $^{-1}$)	q_m (mmolg $^{-1}$)	E (kJmol $^{-1}$)
Cr	0.0342	0.149	0.034	29,681,31	0.0002	0.168	50.00
Cr (wastewater)	0.1533	0.090	0.134	947.62	0.0011	0.116	21.32

Table 3 | Thermodynamic parameters for sorption of Cr(VI) in aqueous solution and in industrial wastewater ions of Si-TRA (metal ion concentration 10 mol/L)

Metal	ΔH° (kJmol $^{-1}$)	ΔS° (kJ(molK) $^{-1}$)	$-\Delta G^\circ$ (kJmol $^{-1}$)			
			297	303	313	323
Cr	42.05	187.55	12.92	13.01	14.07	14.98
Cr (wastewater)	51.75	219.36	12.55	13.09	14.05	14.74

The D-R isotherm was chosen to estimate the adsorption energy. The model is expressed as Equation (4)

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

where ϵ (polanyi potential) is $[RT \ln(1 + (1/C))]$, q_e is the

amount of solute adsorbed per unit weight of adsorbent (mol/L), k is a constant related to the adsorption energy (mol 2 (kJ 2) $^{-1}$), and q_m is the adsorption capacity (mol/L). Hence by plotting $\ln q_e$ versus ϵ^2 it is possible to generate the value of q_m from the intercept, and the value of k from the slope (Figure 6(c)). The mean free energy (E), calculated

by the D-R isotherm, is presented in Table 2. The energy values were calculated using Equation (5)

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

The mean free energy was 50.00 kJmol^{-1} and 21.32 kJmol^{-1} for the Cr(VI) in aqueous solution and in industrial wastewater, respectively (Table 2). The adsorption of Cr(VI) in aqueous solution and in industrial wastewater occurs via chemical sorption. The energy adequate for the realization of the chemical sorption is between 8 and 16 kJmol^{-1} (Çimen *et al.* 2015).

Thermodynamic studies

The thermodynamic parameters such as enthalpy change (ΔH°), entropy change (ΔS°), and free energy change (ΔG°) are crucial and must be taken into consideration in order to determine the spontaneity of a process. The effect of temperature on the sorption for modified silica gel was investigated at temperatures ($20\text{--}50^\circ\text{C}$) under optimized conditions of pH values for each ion.

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

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

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

where K_D is the adsorption equilibrium constant, V is the volume of the aqueous phase (mL), and W is the dry weight of the sorbent (g) in Equation (6). ΔG° is the change in Gibbs free energy (kJmol^{-1}), ΔH° is the change in enthalpy (kJmol^{-1}), ΔS° is the change in entropy ($\text{J}(\text{molK})^{-1}$), T is the absolute temperature (K), and R is the gas constant ($8.314 \times 10^{-3} \text{ kJmol}^{-1}\text{K}^{-1}$). The enthalpy and entropy values for the sorption of metal ions onto Si-TRA were evaluated from the van't Hoff plots: $\log K_D$ versus $1/T$ in Equation (7). ΔG° was also calculated by using Equation (8) and results are listed in Table 2 (Sales & Airoidi 2005). Figure 7 shows the value of logarithmic plot of distribution coefficient K_D against $1/T$.

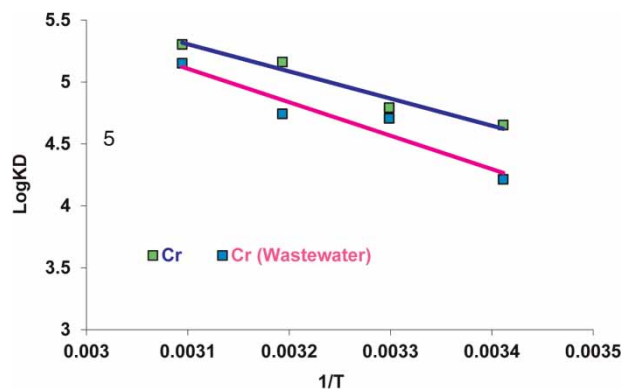


Figure 7 | Plots of $\log K_D$ versus $1/T$ for Cr(VI) in aqueous solution and in industrial wastewater removal by Si-TRA.

The positive value of ΔH° shown in Table 3 indicates the endothermic nature of adsorption, and the negative values of ΔG° for three cations indicate that adsorption onto the adsorbents is a feasible and spontaneous process and requires energy input from outside of the system. The sorbent used has a complexing capability, and so complex formation must be the predominant mechanism. Positive enthalpy values also support this argument. The values of ΔG° decreased with an increase in temperature, suggesting that the spontaneous nature of adsorption was inversely proportional to temperature. The positive value of entropy change (ΔS°) reflects the increased randomness at the solid-solution interface during sorption, and it also indicates the occurrence of ion replacement reactions. When the metal ion is coordinated with water molecules in solution, it binds to sorbent through coordinate covalent bond formation. Owing to the released water molecules, the degree of randomness increases the magnitude of ΔH° , related to the sorption energy indicating the type of binding mechanism involved, i.e., physical and/or chemical sorption. In physical sorption, the process is fast and usually reversible due to the small energy requirement. Energies of $4\text{--}8 \text{ kJmol}^{-1}$ are required by London, Van der Waals' interactions compared from 8 to 40 kJmol^{-1} for hydrogen bond. In contrast, the enthalpy associated with chemical sorption is about 40 kJ mol^{-1} and has been recognized as the transition boundary between both types of sorption processes (Cea *et al.* 2004). ΔH° values for Cr(VI) in aqueous solution (42.05 kJmol^{-1}) and in industrial wastewater (51.75 kJmol^{-1}) were recorded in the temperature range

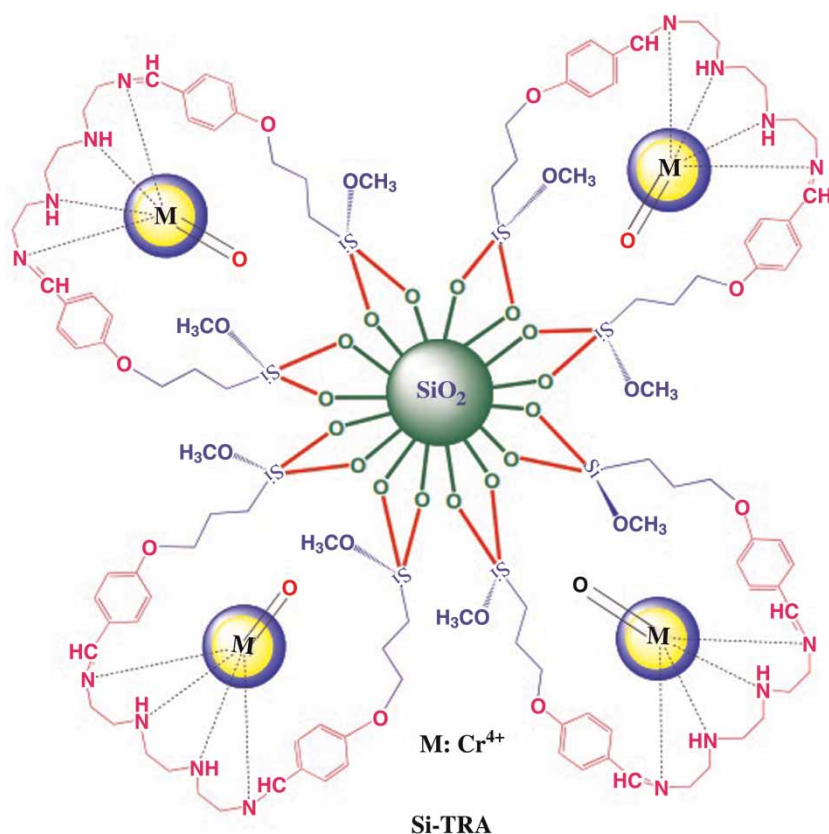


Figure 8 | The estimated perspective of Si-TRA metal ions combination.

of 20–50 °C. The calculated ΔH° values for Cr(VI) in aqueous solution and in industrial wastewater sorption were higher than 40 kJmol⁻¹, which indicated the strong interactions of the compound with the Si-TRA surface at this temperature range.

Mechanism

The sorption mechanism of Cr(VI) in aqueous solution and in industrial wastewater metal ions on Si-TRA can be explained with a classical chelating effect. However, the chelating effect of the Schiff base functional group on Si-TRA is also thought to take part in the sorption process. It is possible to say that donor nitrogen and hydroxyl groups on surface coordinate with the chemical sorption of heavy metal ions. The complex perspective of Si-TRA metal ions' combination can be estimated as given in Figure 8 (Gandolfi *et al.* 2010).

CONCLUSIONS

The optimum pH value for the sorption of the metal ions is 5.0. The mean sorption energies for modified silica gel was found to be 50.00 kJmol⁻¹ and 21.32 kJmol⁻¹ for Cr(VI) in aqueous solution and in industrial wastewater, respectively, which may correspond to chemical ion-exchange. The calculated thermodynamic parameters reflected reactions were endothermic and spontaneous. For spontaneous processes, the values of ΔG° were negative in the range of 20–50 °C. The value of ΔG° decreased with an increase in temperature, which indicates that sorption of selected heavy metal ions on Si-TRA becomes better at higher temperatures. Si-TRA has a high capacity to adsorb Cr(VI) from contaminated wastewater. The new material synthesized is not soluble in water and can contribute to separation and purification methods. The effect of chromium steam can be reduced, and the study was tested for the first time in

steam which enhanced the novelty and originality of the work.

This study is important in providing complete steps of characterization as well as providing effective usage of Si-TRA to remove Cr(VI) ions in industrial wastewater and industrial wastewater vapor.

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