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Chemical modification of silica gel with 4,4´-((1Z,8Z)-2,5,8-triazanona-1,8-diene-1,9-diyl)diphenol and applications to chromium Cr(VI) ions in industrial wastewaters

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ABSTRACT

This study describes synthesis of a new resin through immobilization of the *4,4´-((1Z,8Z)-2,5,8-triazanona-1,8-diene-1,9-diyl)diphenol (TRI)* onto silica gel modified with *3-chloropropyltrimethoxy silane* 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 newly synthesized *Si-TRI* is characterized by scanning electron microscope and elemental analysis and Cr(VI) heavy metal ions were used as sorbate. The sorption of Cr(VI) ion was evaluated with using batch methods. The value of adsorption of Cr(VI) ion was detected by an atomic absorption spectrometer. The influences of concentration, temperature, amount of metal ions, contact time and pH to sorption on the *Si-TRI* were also investigated. The optimum pH range for the sorption of the metal ions is 5.0. The mean sorption energies for modified silica gel were found to be 21.32 and 17.68 kJ/mol for Cr(VI) in aqueous solution and industrial wastewater respectively, which may correspond to chemical ion-exchange. The maximum adsorption capacities and isotherm parameters were calculated from the *Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm* equations. The adsorption of Cr(VI) ion onto the immobilized material followed the Langmuir adsorption models. Thermodynamic parameters such as free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) were also calculated from the sorption results. It was reflected reactions were endothermic and spontaneous. The modified structure used as adsorbent was successfully employed in the removal of Cr(VI) ions on the samples of industrial wastewater.

Keywords: Adsorption; Immobilization; Silica gel; Wastewater; Chromium

1. Introduction

Silica modified with both inorganic and organic functionalities has been for metal ion preconcentration [1], ion exchange [2], biotechnology [3], catalysis [4], clean technology, and green chemistry [5]. The silica surface consists of two types of functional groups, siloxane (Si–O–Si) and silanol (Si–OH) [6–8], which provide functionalization with different functional groups. Thus, silica modification can occur via the

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reaction of particular molecules with either siloxane or silanol [9]. Among the different adsorbents, silica gel immobilized with various organic compounds with metal chelating ability has immense importance [10–12]. Modification of silica gels can be achieved via chemical sorptions 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 [13].

Silica gel provides good solid support for adsorption due to its thermal, chemical and mechanical stability [14]. It has a high surface area of 480–540 m^2/g and micropore size of 6 nm and can be used at a relatively low cost [15]. The use of silica gel as support material has many advantages like high thermal stability and high resistance to organic solvents, no swelling. The binding to the surface of silica gel is easier than the binding to the surface of the organic supports and the most popular substrate for the study of the surface. The modified silica gels generally provide higher adsorption capacities than other organic-inorganic structures used as a support. Therefore, immobilized molecules are used to removal of metal ions from industrial wastewater [16,17]. The 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.

Chromium compounds are used in a wide variety of industrial processes such as: metallurgy, chemical and refractory industries, textile dying, tanneries, metal electroplating, wood preserving, and preparation of chromate compounds. Therefore, chromium contamination has been often reported in many industrial sites, due to accidental leakages or improper disposals, measures [18–21]. In aquatic environments chromium is present mainly as hexavalent and trivalent species, characterized with markedly different chemical behavior and toxicity [22]. While Cr(VI) exists mainly as highly soluble oxyanions [23], Cr(III) is less soluble and readily precipitates as $Cr(OH)_3$ [24] with low toxicity and being considered an essential nutrient for many organisms [25]. In contrast, Cr(VI) is up to 1.000-fold more toxic than Cr(III) [26] and a well-established carcinogen by the inhalation route of exposure [22]. Cr (VI) ion, from industrial wastewater and polluted water from other sources has become serious problems [27] due to toxicity, non-biodegradable and tend to be accumulated in the human vital organs where they can act progressively over a long period through food chains [28]. Therefore, Cr(VI) must be removed from wastewaters before their disposal to natural aquatic environments.

The main effect of the immobilization of Schiff bases *TRI* 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 base *TRI* on the silica gel by using of batch method along with to check the capabilities of novel modified adsorbent for removal of Cr(VI) from aqueous solution.

2. Materials and methods

2.1. Materials

Silica gel (Merck Darmstadt Co.) with high surface area of 480–540 m^2/g, micropore size of 6 nm, 0.036–0.200 mm diameter, pore volume of 0.74–0.84 (cm^3/g) and particle size of 70–180 μm was used in the study. *3-chloropropyltrimethoxy silane (CPTS)* and $K_2Cr_2O_7$ 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 HNO_3 solutions were used for pH adjustments. All chemicals used in the study were analytical graded. Cr(VI) ion-containing industrial wastewater sample was obtained from the valve factory in Konya/Turkey.

2.2. Instruments

The functionalized silica gel was characterized by 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 298 ± 1 K. 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 ℃ temperature, 1 atm pressure, ContrAA 300, Analytik jena). All aqueous solutions were prepared with ultrapure distilled water obtained from a water purification system (Millipore Milli-Q Plus).

2.3. Preparation of Si-TRI

Silica gel was converted in to Si–OH [29]. The immobilization of the *CPTS* onto silica gel was carried out with suspended the silica gel (15.0 g) in dry toluene (100 mL) and *CPTS* (9 mL). The mixture was refluxed for 72 h and conditioned under vacuum conditions. In the next step, 10 g of *Si-CPTS* was treated with 25% *TRI* of solution (33 mL) dissolved in toluene and stirred for 15 h. After filtration of the suspension, the residue was washed with water and ether and dried under vacuum at 313 ± 1 K for 72 h to obtain *Si-TRI*. The scheme of target structure is given in Fig. 1.

2.4. Sorption studies

20 mg sorbent with various concentration of 10 mL sorbate and pH were shaken in a temperature controlled shaker incubator at 298 ± 1 K until equilibrium was reached (180 min). After extraction, the solid phase was separated by filtration. The residual metal concentration of the supernatant was measured by flame AAS and amount of cations sorbed was calculated with using following equation.

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

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).

2.4.1. pH studies

For pH studies, 20 mg of *Si-TRI* was stirred with the presence of 10 mL of Cr(VI) and Cr(VI) in wastewater solution and studied to different pH values (2.0, 3.0, 4.0, 5.0, 6.0, 7.0). The mixture was shaken for 180 min at 298 ± 1 K [30].

2.4.2. Effect of concentration

The sorption was investigated with batch method for aqueous solution of $K_2Cr_2O_7$ and wastewater at 298 ± 1 K. For these sorption measurements, 20 mg of modified silica gel was suspended in 10 mL of aqueous solution containing various amounts (0.01, 0.05, 0.015, 0.075, 0.025 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 min [31]. After equilibrium was established, the amount of metallic cations remaining in solution was determined by flame AAS.

2.4.3. Temperature studies

The experiments were carried out between 20 and 50 ± 1 °C at optimum pH values for Cr(VI) in aqueous solution and wastewater. The amount of the adsorbed metal ion was calculated from the change in the metal concentrations in the aqueous solution [32].

2.4.4. Sorption of evaporating Cr(VI) ion in industrial wastewater

100 mL chromium industrial wastewater (chromium and chromic acid) was added to 250-mL beaker. 1 g *Si-TRI* compound was stuck on watch glass. Watch glass was closed over the beaker and the beaker was heated at 50°C as in Fig. 2. 5 mL sample was taken from the solution on days 3, 6, 9, 12, and 15. Initially dark yellow color of chromium wastewater solution was changing with time. Color of waste solution was lighter yellow color the end of 15 d (Fig. 2). Meanwhile, it was observed that the white color *Si-TRI* which was stuck to watch glass surface yellow. The samples were taken apart three days were also measured with AAS.

3. Result and discussion

3.1. Characterization

On the basis of the results of elemental analysis [33], the percentage amounts of carbon, nitrogen and hydrogen are shown in Table 1.

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

OH stretching vibration in *Si-CPTS* was shifted from 2,951 to 2,926 cm^{-1} (Si). A small decrease of OH stretching vibration in silanol was observed at 794 cm. Hence frequency of CH_2 stretching vibrations in *Si-TRI* were observed at 2,979–2,926 cm^{-1}, Fig. 3; spectrum of *Si-TRI* has broad –OH peak at 3,100 cm^{-1} due to the –OH groups which are in the structure of silica-based organic compounds [34]. Stretching of C=N group observed at 1,657 cm^{-1} showed primer amine group of *Si-CPTS, TRI* and organic substances. The peak at 1,208–1,149 cm^{-1} was bending of –C–OH. The peaks at 1,483–1,500 and 2,853 cm^{-1} were interpreted as stretching of C=C and C–H in the benzene ring respectively [6,17].

The infrared spectra of the prepared surface (*Sİ-TRI*) were compared with wastewater vapor treated Si-TRI-Cr(VI) and this was shown in Fig. 3(b). Although small shifts observed in other peak, C=N stretching vibration in *Si-TRI* was shifted from 1,657 to 1,616 cm^{-1} (*Si-TRI*-Cr(VI)) by complex formation. The peak at 1,208–1,149 cm^{-1} belongs to bending of –C–OH or C-O. C–OH makes a connection with

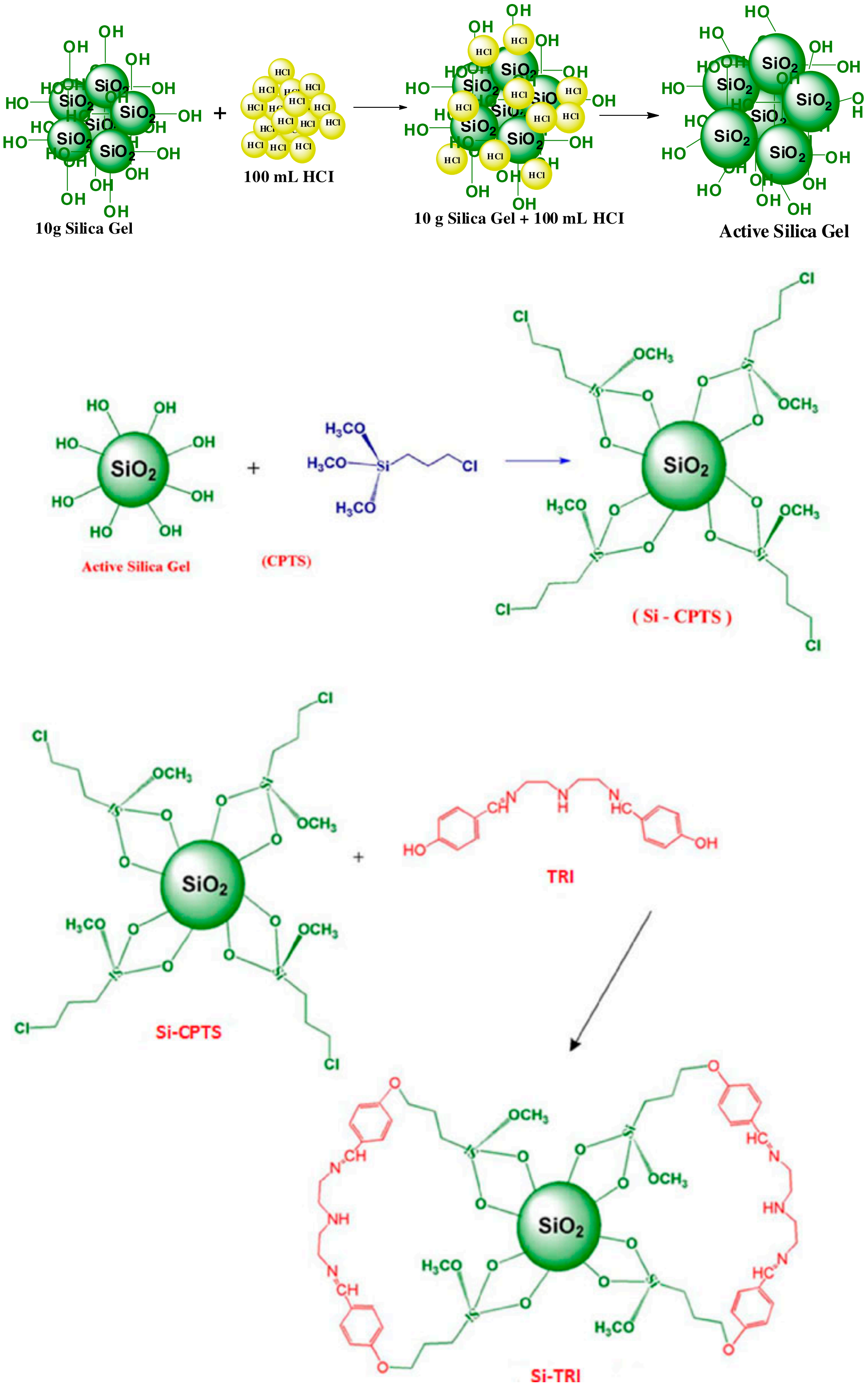

Fig. 1. Possible structure of silica gel bonded *4,4´-((1Z,8Z)-2,5,8-triazanona-1,8-diene-1,9-diyl)diphenol (TRI)* molecules.

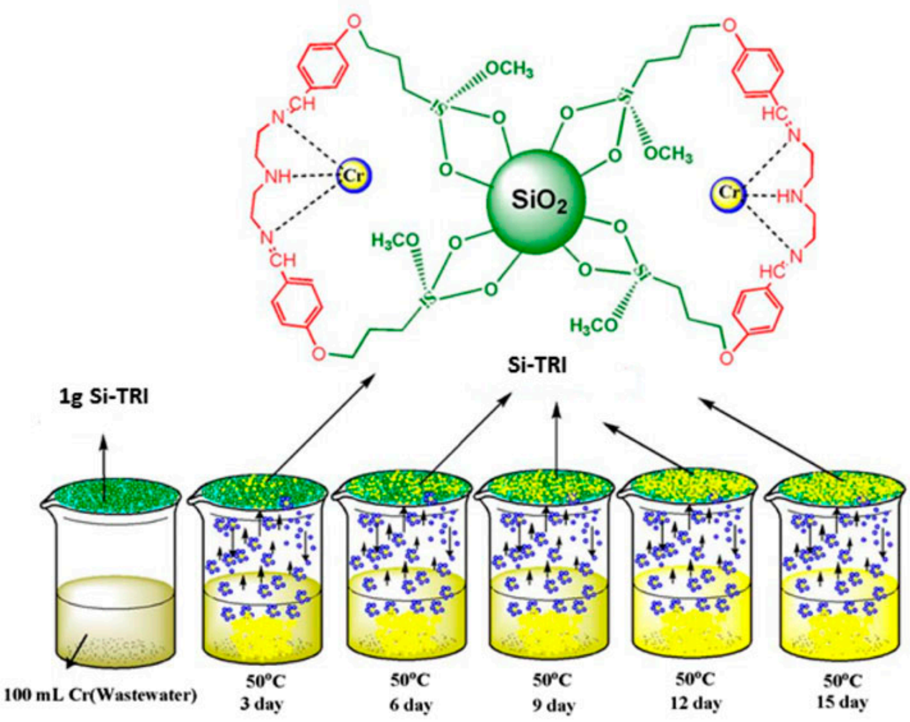

Fig. 2. Sorption diagram of evaporating Cr(VI) in industrial wastewater ions.

Table 1
Percentages (%) of hydrogen (H), carbon (C), and nitrogen (N) for the matrices SiO_2, *Si-CPTS*, and *Si-TRI*

Surface	Nitrogen (%)	Carbon (%)	Hydrogen (%)	Carbon (mmol/g)
SiO_2	0	0	0	–
Si–Cl	0	7.20	0.81	1.23
Si-TRI	5.05	34.27	2.33	1.04

metals and this shift occurs because of the C–O– bond metal. Interaction between the metal and donor atom concerns most of these two bonds. Therefore, these two bonds are the most affected. The peak at around 1,000 and 1,400–1,600 cm^{-1} was stressed Si–O and aromatic C=C, respectively [6].

Since the sorption is a surface phenomenon, the rate and degree of sorption are mainly dependent on the surface functional groups, pore size, and surface area of the sorbent. Therefore, that SEM is known as one of the most widely used surface diagnostic tools [35] 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-TRI*. The SEM micrograph of pure silica gel (Fig. 4(a)) shows a very smooth morphology while after the immobilization of *TRI* onto the surface of pure silica gel (Fig. 4(b)); it shows an irregular morphology covered with foreign material, i.e. *TRI*. The presence of attached particles, i.e. *TRI* onto the surface of silica gel confirms the immobilization.

3.2. Adsorption studies

3.2.1. Effect of adsorption

Fig. 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 increase of amount of adsorbent. When the amount of adsorbent 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 as 0.075 g. The excess of the metal ion might be adsorbed with the adsorbent owing to the increase of the active surface.

3.2.2. Effect of contact time

Fig. 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.

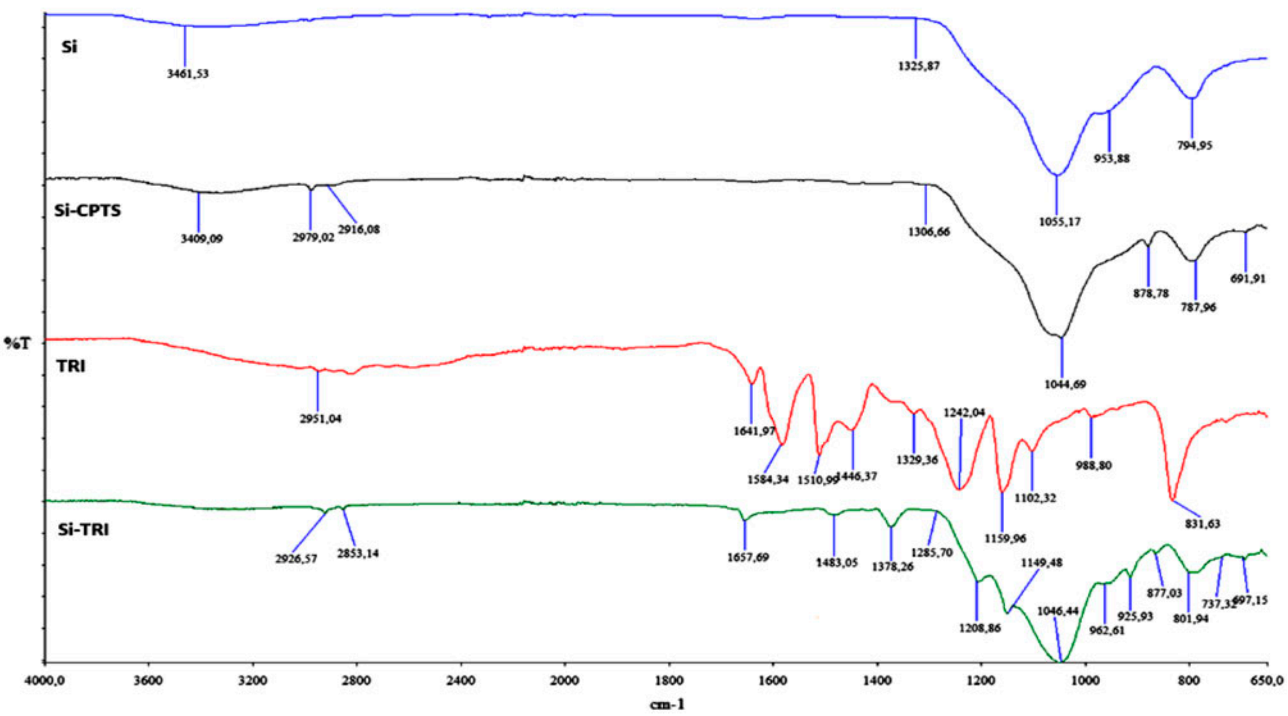

Fig. 3(a). FTIR spectra of *Si*, *Si-CPTS*, *TRI*, and *Si-TRI*.

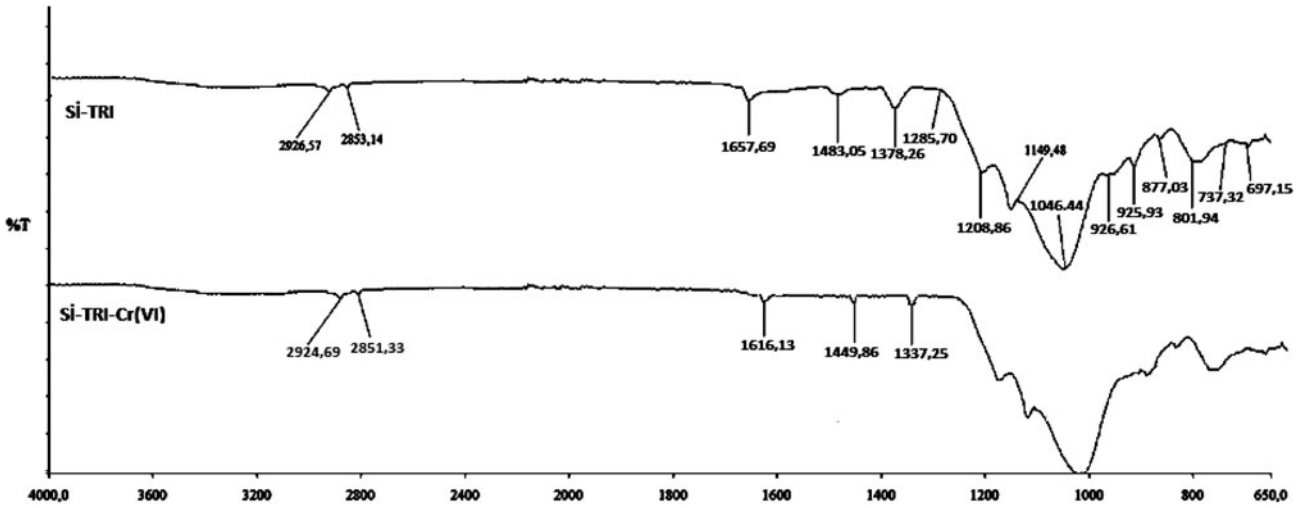

Fig. 3(b). FTIR spectra of *Si-TRI* and *Si-TRI(CrVI)*.

3.2.3. 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 Fig. 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 [36]. The pH for maximum sorption of Cr(VI) in aqueous solution and Cr(VI) in industrial wastewater ions was found as 5.

3.2.4. Effect of concentration

Fig. 5(d) shows that the adsorption effect depends on the concentration of metal ions. The curves of the

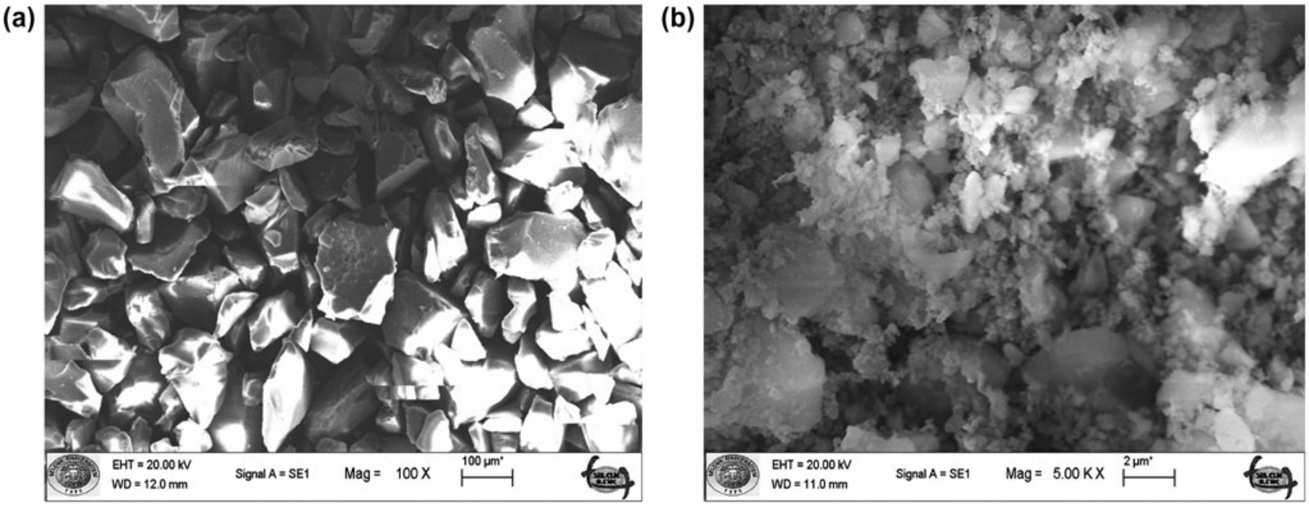

Fig. 4. SEM images of *Si* (a) and *Si-TRI* (b).

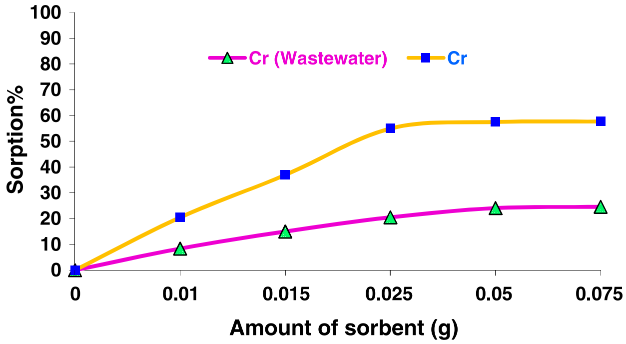

Fig. 5(a). The effect of the amount of Cr(VI) in aqueous solution and Cr(VI) in industrial wastewater ions on the amount of sorbent.

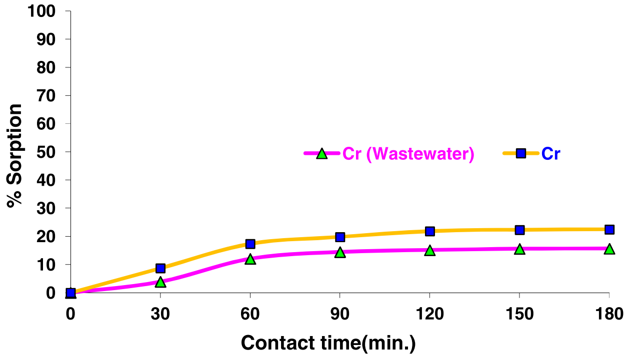

Fig. 5(b). The effect of the contact time on the adsorption of Cr(VI) in aqueous solution and Cr(VI) in industrial wastewater ions.

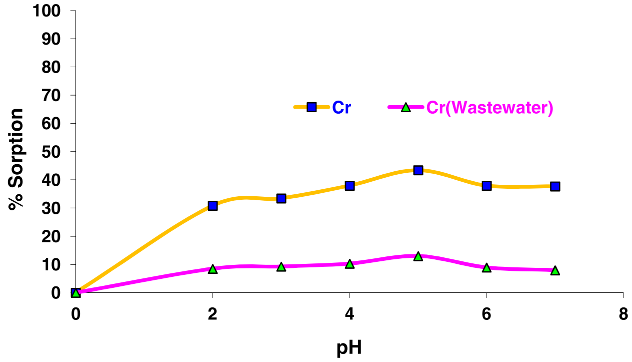

Fig. 5(c). The effect of pH on the sorption of pH of Cr(VI) in aqueous solution and Cr(VI) in industrial wastewater ions.

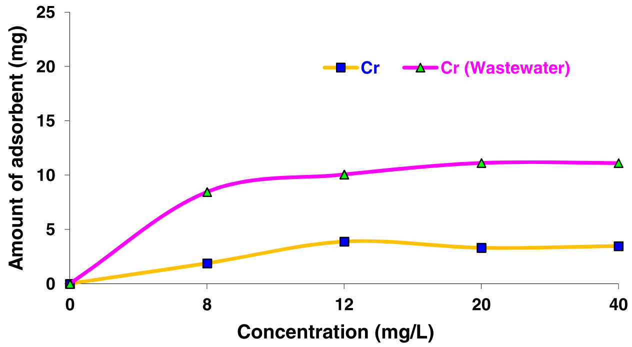

Fig. 5(d). The adsorption effect depends on concentration of Cr(VI) in aqueous solution and Cr(VI) in industrial wastewater ions.

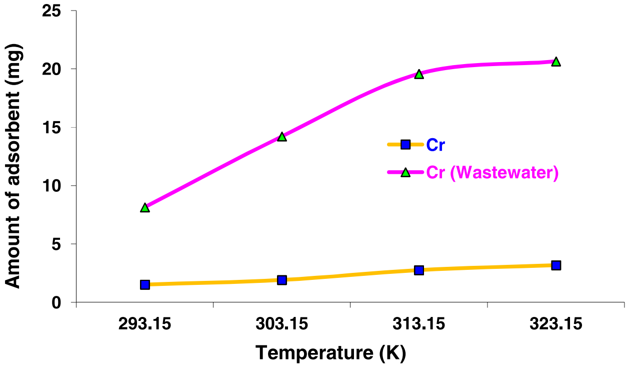

Fig. 5(e). The effect of temperature on the adsorption of Cr (VI) and Cr(VI) in industrial wastewater ions.

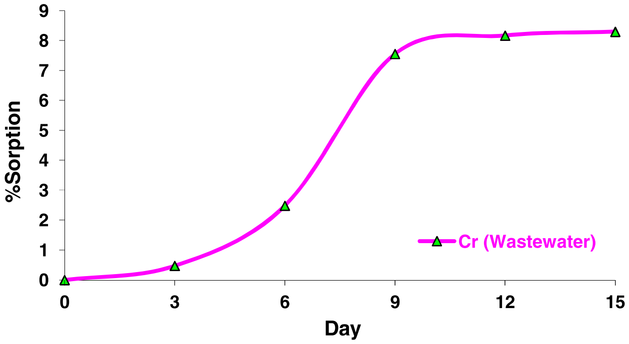

Fig. 5(f). According to contact time, percentage sorption of Cr(VI) ions in industrial wastewater vapor by *Si-TRI* compound.

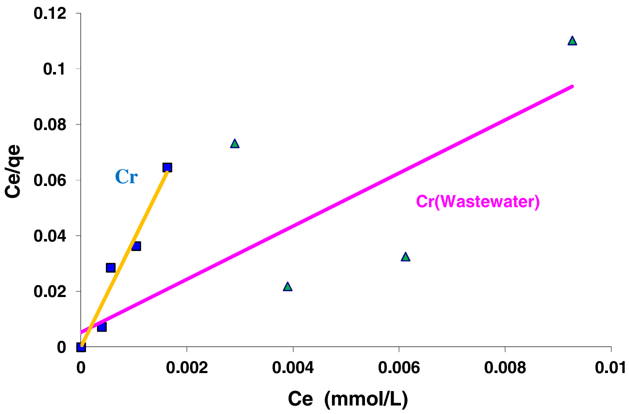

Fig. 6(a). Langmuir isotherms of Cr(VI) in aqueous solution and Cr(VI) in industrial wastewater removal by *Si-TRI*.

graph show that the adsorption increases with the increasing concentration of metal ions and reaches steady state values.

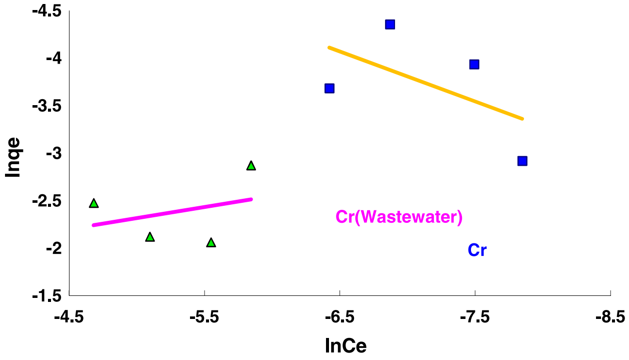

Fig. 6(b). Freundlich isotherms of Cr(VI) in aqueous solution and Cr(VI) in industrial wastewater ions removal by *Si-TRI*.

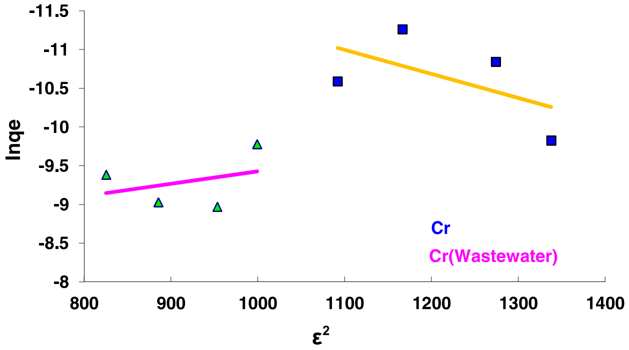

Fig. 6(c). D-R isotherms of Cr(VI) in aqueous solution and Cr(VI) in industrial wastewater ions removal by *Si-TRI*.

3.2.5. Effect of temperature

Fig. 5(e) exhibits the effect of temperature on the adsorption. The amount of adsorption increases with temperature. Depending on endothermic nature of the sorption, the thermodynamic parameters values also change with increasing temperature.

3.2.6. Sorption of evaporating Cr(VI) ion

Fig. 5(f) shows the percentage sorption of Cr(VI) ions in industrial wastewater vapor by *Si-TRI* compound. According to experimental results, Cr(VI) ions carried with water vapor is hold onto *Si-TRI* compound. Sorption (%) is in line with the results found by the batch method, but sorption time is longer (15 d).

3.3. Isotherm studies

The experimental measurements were evaluated with *Langmuir isotherm*, *Freundlich isotherm*, and

Table 2
Isotherms parameters for Cr(VI) in aqueous solution and Cr(VI) in industrial wastewater by *Si-TRI* (T = 298 K)

Freundlich isotherm				Langmuir isotherm			D-R isotherm			
Metal	$1/n$	K_F	R^2	q_o (mmol)	b (L/mmol)	R^2	k (mol^2/K/J)	q_m (mmol/g)	E (kJ/mol)	R^2
Cr	0.233	0.149	0.31	0.00002	1795.18	0.95	0.0011	0.169	21.32	0.15
Cr (wastewater)	0.112	0.982	0.12	0.092	541.06	0.87	0.0016	0.150	17.68	0.16

Dubinin–Radushkevich (D–R) isotherm. The *Langmuir isotherm* represents the equilibrium distribution of metal ions between the solid and liquid phases and as follows (Eq. (2)).

$$\frac{C_e}{q_e} = \frac{C_e}{q_o} + \frac{1}{q_o b} \tag{2}$$

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 constant (mol/L). The plot of C_e/q_e vs. C_e for the sorption gives a straight line of slope $1/bq_0$ and intercepts $1/q_o$ (Fig. 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 [37]. The *Freundlich isotherm* can be written as Eq. (3);

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{3}$$

where q_e, C_e, and K_F are the equilibrium solute concentration on adsorbent (mmol/g), the equilibrium concentration of the solute (mol/L), the Freundlich constant, respectively. According to Eq. (3), the plot of ln q_e vs. 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 [38].

The values of $1/n$ for *Si-AHAP* are <1 is an indication of high sorption intensity [34]. The K_F values showed that immobilized silica gel has higher adsorption capacity for Cr(VI) in aqueous solution and Cr in industrial wastewater (0.15 and 0.98 mol/L) [39]. Values of $n > 1$ represent favorable adsorption conditions [40,41]. Values of K_F and n were calculated from the intercept and slope of the plot (Fig. 6(b)) and were listed in Table 3. The *Dubinin–Radushkevish (D–R) isotherm* was chosen to estimate the adsorption energy. The model is expressed as Eq. (4):

$$\ln q_e = \ln q_m - k\varepsilon^2 \tag{4}$$

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)), and q_m is the adsorption capacity (mol/L). Hence by plotting ln q_e vs. ε^2, it

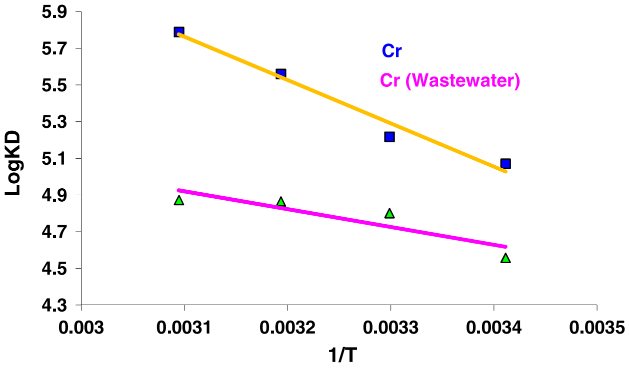

Fig. 7. Plots of log K_D vs. $1/T$ for Cr(VI) in aqueous solution and Cr(VI) in industrial wastewater removal by *Si-TRI*.

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

Metal	ΔH° (kJ/mol)	ΔS° (J/K/mol)	$-\Delta G^\circ$ (kJ/mol)			
			297	303	313	323
Cr	45.13	202.59	13.12	13.91	14.47	14.97
Cr (wastewater)	58.75	311.376	14.55	15.09	16.05	16.74

is possible to generate the value of q_m from the intercept and the value of k from the slope (Fig. 6(c)). The mean free energy (E), calculated by the *Dubinin–Radushkevich isotherm*, is presented in Table 2. The energy values were calculated with using Eq. (5):

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

The mean free energy was 21.32 and 17.68 kJ/mol for the Cr(VI) in aqueous solution and Cr(VI) in industrial wastewater respectively (Table 2). The adsorption of Cr(VI) in aqueous solution and Cr(VI) in industrial wastewater occurs via chemisorptions. The energy adequate for the realization of the chemical sorption is between 8 and 16 kJ/mol [42].

3.4. 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 (293–323 K) under optimized conditions of pH values for each ion.

$$K_D = \frac{C_o - C_e}{C_e} \times \frac{V}{W} \tag{6}$$

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

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8}$$

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). Also, in Eq. (6), ΔG° is the change in Gibbs free energy (kJ/mol), ΔH° is the change in enthalpy (kJ/mol), ΔS° is the change in entropy (J/(mol/K)), T is the absolute temperature (K), and R is the gas constant (8.314×10^{-3}, kJ/mol/K).

The enthalpies and entropies values for the sorption of metal ions onto *Si-TRI* were evaluated from the van't Hoff plots: log K_D vs. $1/T$. ΔG° was

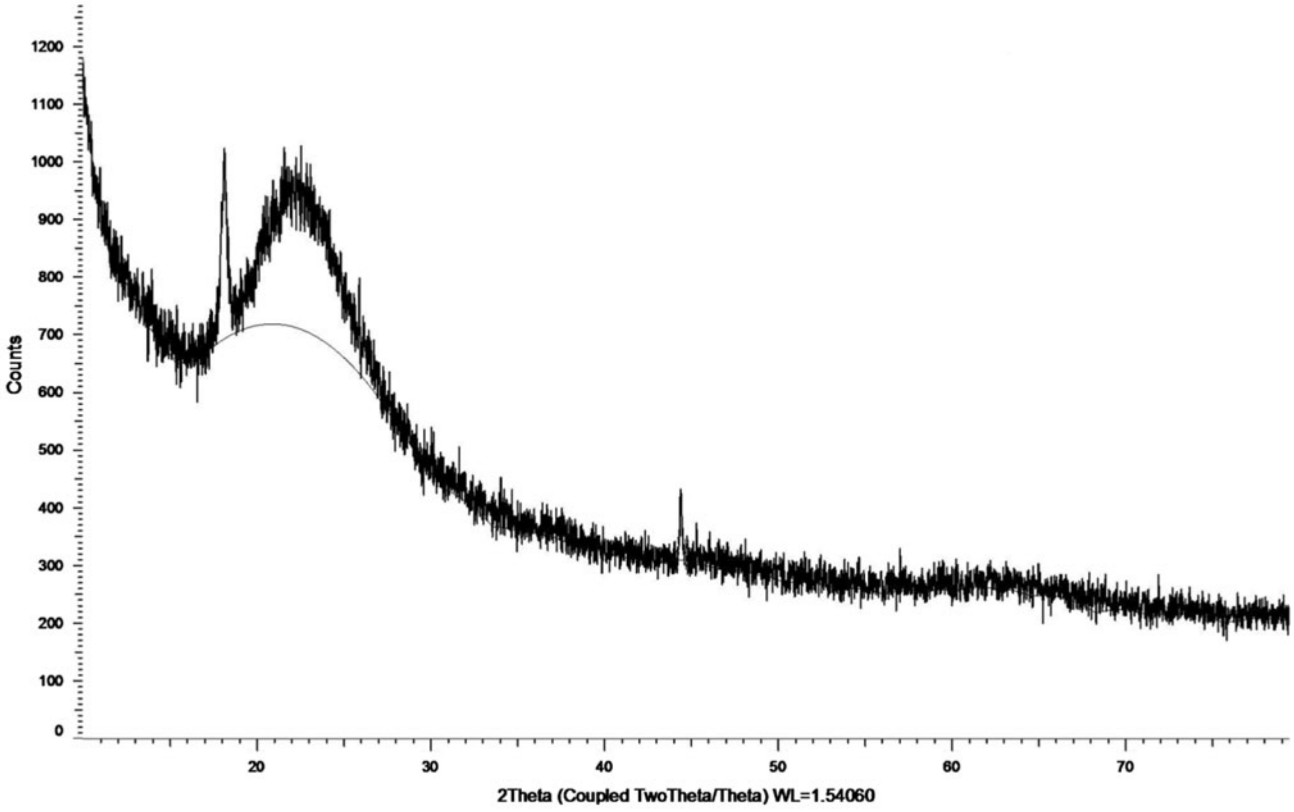

Fig. 8. X-ray diffraction pattern of *Si-TRI(CrVI)*.

also calculated by using Eq. (7) and results were listed in Table 2 [32]. Fig. 7 shows value of logarithmic plot of distribution coefficient K_D against $1/T$.

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 feasible and spontaneous process and required 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 have also supported 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 that ion replacement reactions occurs. When metal ion, which is coordinated with water molecules in solution, binds to sorbent through coordinate covalent bond formation. Due 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 4–8 kJ/mol are required by London, van der Waals interactions compared from 8 to 40 kJ/mol for hydrogen bond. In contrast, the enthalpy associated with chemical sorption is about 40 kJ/mol which has been recognized as the transition boundary between both types of sorption processes [43]. ΔH° values for Cr(VI) in aqueous solution (45.13 kJ/mol) and in industrial wastewater (58.75 kJ/mol) were recorded in the temperature range of 297–323°K. The calculated ΔH° values for Cr(VI) in aqueous solution and in industrial wastewater and sorption were higher than 40 kJ/mol which indicates the strong interactions of the compound with the *Si-TRI* surface at this temperature range.

3.5. Mechanism

The sorption mechanism of Cr(VI) in aqueous solution and in industrial wastewater metal ions on *Si-TRI* can be explained with a classical chelating effect. However, the chelating effect of the Schiff base

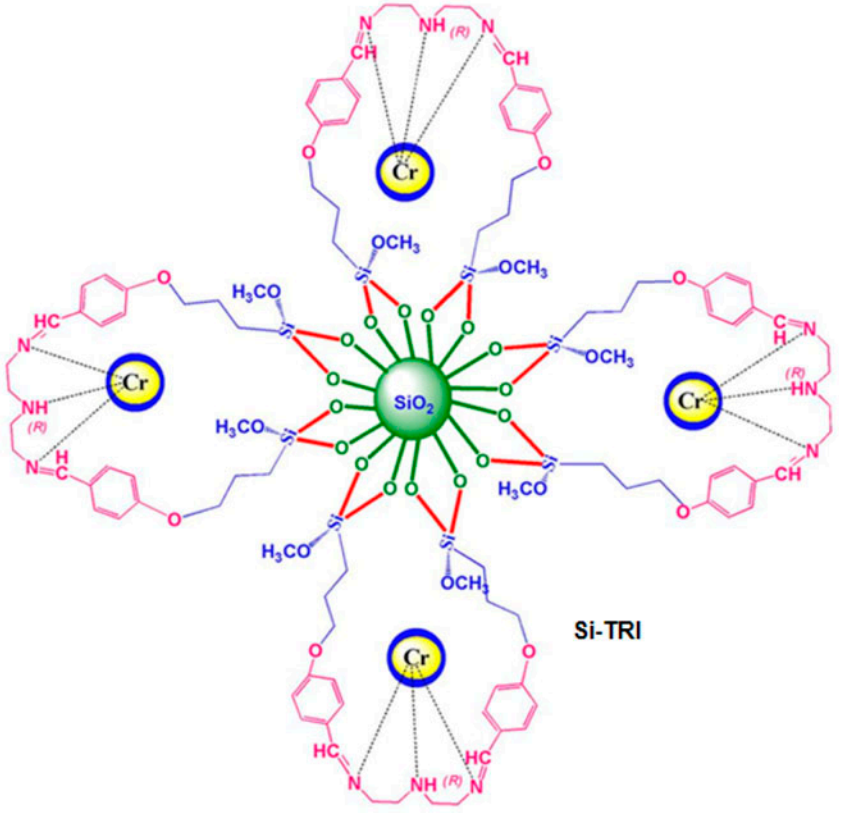

Fig. 9. The estimated perspective of *Si-TRI* metal ions combination.

functional group on *Si-TRI* is also thought to take part in the sorption process. It is possible to say that donor nitrogens and hydroxyl groups on surface coordinate to the chemical sorption of heavy metal ions. The presence of Cr(VI) on the surface of adsorbent was confirmed by X-ray diffraction pattern of *Si-TRI(CrVI)* and showed in Fig. 8. The complex perspective of *Si-TRI* metal ions combination can be estimated as given in Fig. 9.

4. Conclusions

The optimum pH range for the sorption of the metal ions is 5.0. The mean sorption energies for modified silica gel were found to be 21.32 and 17.68 kJ/mol for Cr(VI) in aqueous solution and in industrial wastewater, respectively, which may correspond to chemical ion exchange.

The calculated thermodynamic parameters prove that reactions were endothermic and spontaneous. For spontaneous processes, the values of ΔG° are negative in the range of 297–323 K. ΔG° values decrease with increase in temperature, which indicates that sorption of selected heavy metal ions on *Si-TRI* becomes better at higher temperatures. The results of this study indicate that *Si-TRI* has high capacity to adsorb Cr(VI) from the wastewater.

The novelty of the study is synthesis of the *Si-TRI* in our laboratory followed by immobilization of Schiff base on to silica gel surface. The new material obtained is not soluble in water and can contribute to separation and purification methods.

With this study, the effect of chromium steam can be reduced. This study is important in providing complete steps of characterization as well as providing effective usage of *Si-TRI* to remove Cr(VI) ions in industrial wastewater and industrial wastewater vapor.

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References

[1] P.M. Padilha, L.A.M. Gomes, C.C.F. Padilha, J.C. Moreira, N.L. Dias Filho, Determination of metal ions in natural waters by flame-AAS after preconcentration on a 5-amino-1, 3, 4-thiadiazole-2-thiol modified silica gel, Anal. Lett. 32 (1999) 1807–1820.

[2] A. Çimen, M. Torun, A. Bilgiç, Immobilization of 4-amino-2-hydroxyacetophenone onto silica gel surface and sorption studies of Cu(II), Ni(II), and Co(II) ions, Desalin. Water Treat. 53 (2015) 2106–2116.

[3] K.M.R. Kallury, W.E. Lee, M. Thompson, Enhanced stability of urease immobilized onto phospholipid covalently bound to silica, tungsten, and fluoropolymer surfaces, Anal. Chem. 65 (1993) 2459–2467.

[4] H.E. Fisher, S.A. King, J.B. Miller, J.Y. Ying, J.B. Benzinger, J. Schwartz, Surface cristobalite formation by mild hydrothermal treatment of silica gel and its effect on the deposition of tris(allyl)rhodium and subsequent reactivity of (silica)rhodium(allyl)2, Inorg. Chem. 30 (1991) 4403–4408.

[5] J.H. Clark, D.J. Macquiarrie, Catalysis of liquid phase organic reactions using chemically modified mesoporous inorganic solids, Chem. Commun. 8 (1998) 853–860.

[6] A.N. Kursunlu, E. Guler, H. Dumrul, O. Kocyigit, I.H. Gubbuk, Chemical modification of silica gel with synthesized new Schiff base derivatives and sorption studies of cobalt (II) and nickel (II), Appl. Surf. Sci. 255 (2009) 8798–8803.

[7] A. Çimen, A. Bilgiç, A.N. Kursunlu, İ.H. Gübbük, H.İ. Uçan, Adsorptive removal of Co(II), Ni(II), and Cu(II) ions from aqueous media using chemically modified sporopollenin of *Lycopodium clavatum* as novel biosorbent, Desalin. Water Treat. 52 (2014) 4837–4847.

[8] P. Antonio, K. Iha, M.E.V. Suarez-Iha, Adsorption of di-2-pyridyl ketone salicyloyl hydrazone on silica gel: Characteristics and isotherms, Talanta 64 (2004) 484–491.

[9] A.R. Cestari, E.F.S. Vieira, A.J.P. Nascimento, F.J.R. de Oliveira, R.E. Bruns, C. Airoldi, New factorial designs to evaluate chemisorption of divalent metals on aminated silicas, J. Colloid Interface Sci. 241 (2001) 45–51.

[10] O. Zaporozhets, N. Petruniock, O. Bessarabova, V. Sukhan, Determination of Cu(II) and Zn(II) using silica gel loaded with 1-(2-thiasolylazo)-2-naphthol, Talanta 49 (1999) 899–906.

[11] A.G.S. Prado, C. Airoldi, Adsorption, preconcentration and separation of cations on silica gel chemically modified with the herbicide 2,4-dichlorophenoxyacetic acid, Anal. Chim. Acta 432 (2001) 201–211.

[12] J.S. Kim, J. Yi, The removal of copper ions from aqueous solutions using silica supports immobilized with 2-hydroxy-5-nonylacetophenoneoxime, Sep. Sci. Technol. 34 (1999) 2957–2971.

[13] U. Pyell, G. Stork, Preparation and properties of an 8-hydroxyquinoline silica gel, synthesized via mannich reaction, J. Anal. Chem. 342 (1992) 281–286.

[14] J.A.A. Sales, F.P. Faria, A.G.S. Prado, C. Airoldi, Attachment of 2-aminomethylpyridine molecule onto grafted silica gel surface and its ability in chelating cations, Polyhedron 23 (2004) 719–725.

[15] O.G. da Silva, M.G. da Fonseca, L.N.H. Arakaki, Silylated calcium phosphates and their new behavior for copper retention from aqueous solution, Colloids Surf. A 301 (2007) 376–381.

[16] E.M. Soliman, M.E. Mahmoud, S.A. Ahmed, Synthesis, characterization and structure effects on selectivity properties of silica gel covalently bonded diethylenetriamine mono- and bis-salicyaldehyde and naphthaldehyde Schiff, s bases towards some heavy metal ions, Talanta 54 (2001) 243–253.

[17] Y. Cui, X. Chang, X. Zhu, H. Luo, Z. Hu, X. Zou, Q. He, Chemically modified silica gel with p-dimethylaminobenzaldehyde for selective solid-phase extraction and

preconcentration of Cr(III), Cu(II), Ni(II), Pb(II) and Zn (II) by ICP-OES, Microchem. J. 87 (2007) 20–26.

[18] R. Shrivastava, R.K. Upreti, U.C. Chaturvedi, Various cells of the immune system and intestine differ in their capacity to reduce hexavalent chromium, FEMS Immunol. Med. Microbiol. 38 (2003) 65–70.

[19] B. Flury, U. Eggenberger, U. Mader, First results of operating and monitoring an innovative design of a permeable reactive barrier for the remediation of chromate contaminated groundwater, J. Appl. Geochem. 24 (2009) 687–696.

[20] M. Ragosta, R. Caggiano, M. D'Emilio, M. Macchiato, Source origin and parameters influencing levels of heavy metals in TSP, in an industrial background area of Southern Italy, Atmos. Environ. 36 (2002) 3071–3087.

[21] J.A. Zazo, J.S. Paull, P.R. Jaffe, Influence of plants on the reduction of hexavalent chromium in wetland sediments, Environ. Pollut. 156 (2008) 29–35.

[22] D.E. Kimbrough, Y. Cohen, A.M. Winer, A critical assessment of chromium in the environment, Crit. Rev. Environ. Sci. Technol. 29 (1999) 1–46.

[23] S.E. Fendorf, Surface reactions of chromium in soil and waters, Geoderma 67 (1995) 55–71.

[24] D. Rai, B.M. Sass, D.A. Moore, Chromium(III) hydrolysis constants and solubility of chromium(III) hydroxide, Inorg. Chem. 26 (1987) 345–349.

[25] A. Pechova, L. Pavlata, Chromium as an essential nutrient: A review, Vet. Med. 52 (2007) 1–18.

[26] M. Costa, Potential hazards of hexavalent chromate in our drinking water, Toxicol. Appl. Pharmacol. 188 (2003) 1–5.

[27] H. Dumrul, A.N. Kursunlu, O. Kocyigit, E. Guler, S. Ertul, Adsorptive removal of Cu(II) and Ni(II) ions from aqueous media by chemical immobilization of three different aldehydes, Desalination 271 (2011) 92–99.

[28] F. Xie, X. Lin, X. Wu, Z. Xie, Solid phase extraction of lead (II), copper (II), cadmium (II) and nickel (II) using gallic acid-modified silica gel prior to determination by flame atomic absorption spectrometry, Talanta 74 (2008) 836–843.

[29] I.H. Gübbük, R. Güp, M. Ersöz, Synthesis, characterization, and sorption properties of silica gel-immobilized Schiff base derivative, J. Colloid Interface Sci. 320 (2008) 376–382.

[30] A.R. Cestari, E.F.S. Vieira, A.J.P. Nascimento, F.J.R. de Oliveira, R.E. Bruns, C. Airoldi, New factorial designs to evaluate chemisorption of divalent metals on aminated silicas, J. Colloid Interface Sci. 241 (2001) 45–51.

[31] X. Zhu, X. Chang, Y. Cui, X. Zou, D. Yang, Z. Hu, Solid-phase extraction of trace Cu(II) Fe(III) and Zn(II) with silica gel modified with curcumin from biological and natural water samples by ICP-OES, Microchem. J. 86 (2007) 189–194.

[32] J.A.A. Sales, C. Airoldi, Calorimetric investigation of metal ion adsorption on 3-glycidoxypropyltrimethyl siloxane + propane-1,3-diamine immobilized on silica gel, Thermochim. Acta 427 (2005) 77–83.

[33] I. Hilal Gübbük, R. Güp, M. Ersöz, Synthesis, characterization and sorption properties of silica gel-immobilized Schiff base derivative, J. Colloid Interface Sci. 320 (2008) 376–382.

[34] I. Hilal Gubbuk, Isotherms and thermodynamics for the sorption of heavy metal ions onto functionalized sporopollenin, J. Hazard. Mater. 186 (2011) 416–422.

[35] G.Z. Memon, M.I. Bhanger, M. Akhtar, F.N. Talpur, J.R. Memon, Adsorption of methyl parathion pesticide from water using watermelon peels as a low cost adsorbent, Chem. Eng. J. 138 (2008) 616–621.

[36] W. Ngeontae, W. Aeungmaitrepirom, T. Tuntulani, Chemically modified silica gel with aminothioamidoanthraquinone for solid phase extraction and preconcentration of Pb, Talanta 71 (2007) 1075–1082.

[37] C.W. Oo, M.J. Kassim, A. Pizzi, Characterization and performance of *Rhizophora apiculata* mangrove polyflavonoid tannins in the adsorption of copper (II) and lead (II), Ind. Crops Prod. 30 (2009) 152–161.

[38] G. Asgari, B. Ramavandi, L. Rasuli, M. Ahmadi, Kinetics and isotherm studies of hexavalent chromium adsorption from water using bone charcoal, Fresenius Environ. Bull. 21(5a) (2012) 1296–1302.

[39] G. Vazquez, J.G. AAlvarez, S. Freire, M.L. Lorenzo, G. Antorrena, Removal of cadmium and mercury ions from aqueous solution by sorption on treated *Pinus pinaster* bark: Kinetics and isotherms, Bioresour. Technol. 82 (2002) 247–251.

[40] B.H. Hameed, J.M. Salman, A.L. Ahmad, Adsorption isotherm and kinetic modeling of 2, 4-D pesticide on activated carbon derived from date stones, J. Hazard. Mater. 163 (2009) 121–126.

[41] G. Asgari, B. Ramavandi, L. Rasuli, M. Ahmadi, Cr (VI) adsorption from aqueous solution using a surfactant-modified Iranian zeolite: Characterization, optimization, and kinetic approach, Desalin. Water Treat. 51 (2013) 6009–6020.

[42] X. Tang, Z. Li and Y. Chen, Adsorption behavior of Zn(II) calcinated Chinese loess, J. Hazard. Mater. 161 (2009) 824–834.

[43] M. Cea, J.C. Seaman, A. Jara, M.L. Mora, M.C. Diez, Kinetic and thermodynamic study of chlorophenol sorption in an allophanic soil, Chemosphere 78 (2010) 86–89.