Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23702

147 (2019) 116–124
April

Immobilization of 2-(2-hydroxybenzylidinoamino) pyridin-3-ol on silica gel and application to ındustrial wastewater

Aysel Çimen*, Ali Bilgiç

Faculty of Science, Department of Chemistry, Karamanoğlu Mehmetbey University, 70200 Karaman, Turkey, Tel. +90 338 226 2153; Fax: +90 338 226 21 50; email: ayselcimen42@hotmail.com

Received 22 May 2018; Accepted 27 December 2018

ABSTRACT

In this study, first silica gel surface was activated. The compound (3-Chloropropyl)triethoxysilane (CPTS) was immobilized on the modified SiO_2 surface. 2-(2-Hydroxybenzylidinoamino) pyridin-3-ol (HBAP) compound was covalently immobilized on the modified silica gel compound (Si-CPTS). The newly prepared Si-CPTS-HBAP was characterized with a variety of techniques, including Fourier transform ınfrared spectroscopy and scanning electron microscopy. Batch method was used for the adsorption study of Cr(III) ions. The amount of adsorption of Cr(III) ions was controlled and detected by ultraviolet-visible spectrophotometer. The influences of concentration, temperature, contact time, and pH on the adsorption of Si-CPTS-HBAP were investigated. The results were obtained by Langmuir, Freundlich, and Dubinin–Radushkevich isotherm equations. In addition, thermodynamic parameters such as free energy ($\Delta H°$), entropy ($\Delta S°$), and enthalpy ($\Delta G°$) were calculated from the sorption results and used to explain the adsorption mechanism. The optimum values obtained from this study are 6, 120 min, 0.05 g, and 303.15 K for pH, interaction time, adsorbent amount, and temperature, respectively. The results indicate that this adsorbent can successfully be employed in the separation of Cr(III) from aqueous solutions.

Keywords: Silica gel; Heavy metal; Immobilization; Adsorption

1. Introduction

Water is the most needed resource for living things. Population growth, urbanization, and industrialization cause water pollution. In parallel, clean water is also needed. Water pollutants are generally categorized in two groups, namely, organic pollutants and inorganic pollutants. Heavy metal pollution takes place in the second group.

Chromium is present mainly as hexavalent and trivalent species with different chemical behavior and toxicity in aquatic environments [1]. Cr(VI) is mainly present as highly soluble oxyanions [2] but Cr(III) is less soluble and readily precipitates as $Cr(OH)_3$ [3]. Also Cr(III) has a low toxicity for many organisms [4]. In contrast, Cr(VI) is up to 1,000-fold more toxic than Cr(III) [5], and if it is inhaled through the mouth, it has carcinogenic properties [1]. Cr(VI) ions cause serious problems in wastewater polluted by industrial foundations and the other sources. Toxic and nonbiodegradable substances tend to be accumulated in the human vital organs [1]. Therefore, Cr(VI) and Cr(III) must be removed from wastewaters before their disposal to natural aquatic environments.

Many heavy metals such as chromium have a toxic effect on the threshold limit values (TLV) in the human body. The TLV of Cr(III) and Cr(VI) are, respectively, 0.5 and 0.05 mg m^{-3}. Chromium has toxic effect for human body such as contact dermatitis, chromium ulcers, and nasal perforation, pharyngitis, bronchitis, and lung cancers. For this reason, a lot of techniques have been developed for removal of heavy metals from wastewater. These are chemical sedimentation, membrane separation, photocataly,

---

* Corresponding author.

reverse osmosis, electrodialysis, ultrafiltration, ion exchange, chemical precipitation, phytoremediation, adsorption, etc.

The adsorption method is applied in many wastewater treatment processes in developed countries [6,7]. Because of the adsorbing capacities of different ions in water, active coal and mud are mostly used as adsorbents in adsorption studies. From these considerations, new adsorbent development studies were carried out to recover valuable materials from solvents and water and to remove toxic substances. Adsorbent materials with high selectivity can be obtained by covalent bonding onto the solid support material. Among the supporting materials, silica gel has an important place because of its high thermal properties, chemical and mechanical strength, and chemical modification with functional compounds. Support molecules are modified by bonding molecules with various functional groups on the surfaces.

In this study, the surface of sporopollenin was activated and then the (3-Chloropropyl)triethoxysilane (CPTS) compound was bound to the activated surface (Si-CPTS). Afterward, the 2-(2-hydroxybenzylidinoamino) pyridin-3-ol (HBAP) compound was immobilized on an Si-CPTS compound using a batch method (Si-CPTS-HBAP). The newly synthesized compound was used as an adsorbent to remove the Cr(III) ions in the aqueous solution and the wastewater. The parameters affecting adsorption such as the amount of adsorbent, pH, duration of interaction, solution concentration, and temperature were investigated. The mechanism of adsorption is explained by examining the adsorption isotherms and thermodynamics.

2. Materials and methods

2.1. Materials

Silica gel (0.063–0.200 mm, 70–230 mesh american society for testing and materials (ASTM)), CPTS, HBAP, and $Cr(NO)_3{\cdot}9H_2O$ were purchased from Sigma (USA) and Merck (Darmstadt, Germany). Dilute NaOH and HNO_3 solutions were used for pH adjustments. Industrial wastewater sample (82.21 mg L^{-1} Cr(III), pH = 5.1, temperature: 318.15 K, current density: 12–20 A dm^{-2}, and H_2SO_4: 8.05 mg L^{-1}) containing Cr(III) ion was provided from an industrial corporation in Turkey.

2.2. Instruments

The infrared spectra were characterized by Fourier transform infrared (FT-IR). The pH of solutions was adjusted by pH meter. In addition, thermostatic shaker, ultraviolet-visible (UV-VIS) spectrophotometer, and ultrapure water devices were used for all experiments.

3. Experimental section

3.1. Activation of silica gel surface

SiO_2 surface was activated as shown in Fig. 1 [8–10]. One hundred milliliters of HCl was added onto 100 g of commercial silica gel placed in a round bottom flask. The reaction mixture was heated up to 100°C under a nitrogen atmosphere for 6 h under back cooler. Afterward, the mixture was filtered under vacuum, and the resulting precipitate was washed with excess water to get rid of HCl. Then the silica gel, which is completely free of HCl, was activated in a vacuum oven at 170°C for 24 h [11].

3.2. Synthesis of Si-CPTS-HBAP

Batch method (solid-liquid sorption) was used for the preparation of the compound Si-CPTS-HBAP. Si-OH was obtained by adding HCl onto silica gel [12]. Dry toluene (100 mL) was used for the immobilization of CPTS onto silica gel. The mixture was refluxed for 72 h under vacuum (Fig. 2(a)). In the next step, 10 g of Si-CPTS was treated with 25% of HBAP solution (33 mL) in toluene and shaked for 15 h. After filtration of the suspension, the residue was washed with water and diethylether and dehyrated beneath vacuum at 40°C for 72 h to obtain Si-CPTS-HBAP. The scheme of target structure is given in Fig. 2(b).

3.3. Adsorption studies

Adsorbent of 0.1, 0.015, 0.025, 0.05, and 0.075 g with 10 mL adsorbate was shaken in a temperature-controlled shaker incubator at 25°C ± 1°C (30, 60, 90, 120, 150, and 180 min) until it reached the equilibrium (180 min). The solid phase was separated by filtration. The residual metal ions were measured by UV-VIS spectrophotometer.

3.4. pH studies

Si-CPTS-HBAP of 20 mg was stirred in the presence of 10 mL $Cr(NO)_3{\cdot}9H_2O$ in wastewater solution. Studies were performed at various pH values (2.0, 3.0, 4.0, 5.0, 6.0, and 7.0). The mixture was shaken for 180 min at 25°C ± 1°C [13].

3.5. Effect of concentration

The adsorption was measured by using batch method for aqueous solution of $Cr(NO)_3{\cdot}9H_2O$ and wastewater at 25°C ± 1°C. For these sorption measurements, the modified silica gel was suspended in the $Cr(NO)_3{\cdot}9H_2O$ solution at various concentrations and the wastewater sample. These

Fig. 1. Activation of silica gel surface.

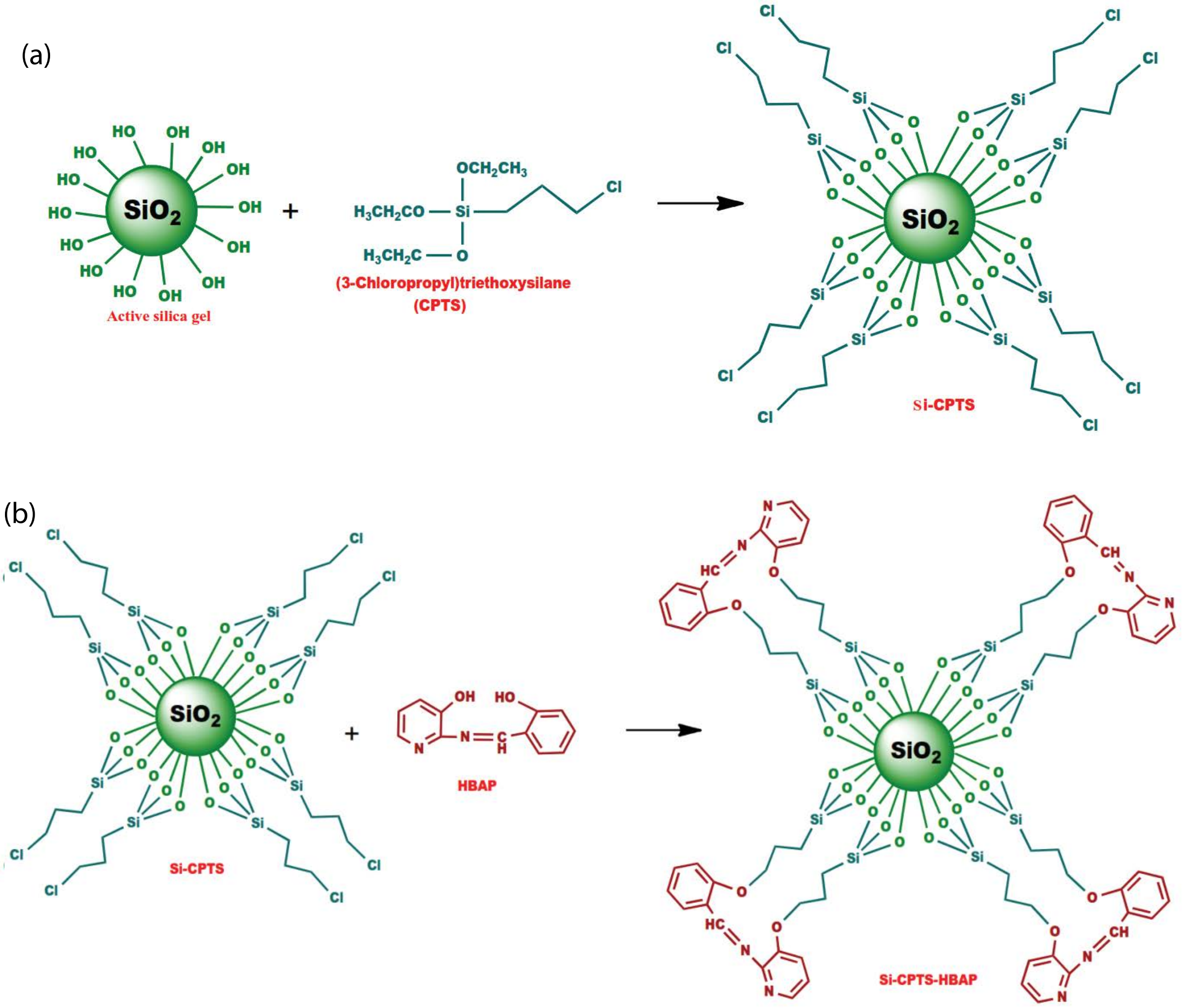

Fig. 2. (a) Modification of (3-chloropropyl)triethoxysilane to silica gel surface and (b) immobilization of the compound 2-(2-hydroxybenzylidinoamino) pyridin-3-ol (HBAP) with Si-CPTS.

resulting suspensions with different concentrations (8, 12, 20, and 40 mg L^{-1}) were stirred for 180 min [14]. After equilibrium was established, the amounts of metal ions remaining in solution were determined by UV-VIS spectrophotometer.

3.6. Temperature studies

Experimental studies were performed for Cr(III) aqueous solution and wastewater between 20°C–50°C ± 1°C at optimum pH values. The amount of the adsorbed metal ion was calculated from the change in the concentration of metal ions in the solution [15].

4. Results and discussion

4.1. Characterization

The functionalized silica gel was characterized by FT-IR spectroscopy. The infrared spectra of the prepared surface were compared with raw silica gel shown in Fig. 3(a). OH stretching vibration in Si-CPTS was shifted from 2,946 to 2,865 cm^{-1} (Fig. 3(b)). Spectrum of Si-CPTS-HBAP has broad –OH peak at 3,387 cm^{-1} owing to the –OH groups which are in the structure of silica-based organic compounds (Fig. 3(c)). [16]. Stretching of C=N group observed at 1,643 cm^{-1} showed primer amine group of Si-CPTS-HBAP and organic substances. The peaks at 1,410–1,643 and 2,774 cm^{-1} were interpreted as stretching of C=C and C–H in the benzene ring, respectively [17].

According to the results of elemental analysis [12], the percentage amounts of carbon, nitrogen, and hydrogen are shown in Table 1.

Since the adsorption is a surface phenomenon, the rate and degree of adsorption is mainly dependent on the surface functional groups, pore size, and surface area of the adsorbent. Scanning electron microscopy (SEM) is one of the most widely used surface diagnostic tools [18]. For this reason, SEM was utilized (by applying 0.5 kV electron acceleration voltage) to characterize the surface morphology of pure silica gel, Si-CPTS, and Si-CPTS-HBAP. The SEM images of pure silica gel (Fig. 4(a)) show a very smooth morphology after the immobilization of HBAP onto the surface of pure silica gel (Fig. 4(b) and (c)); it shows an irregular morphology covered

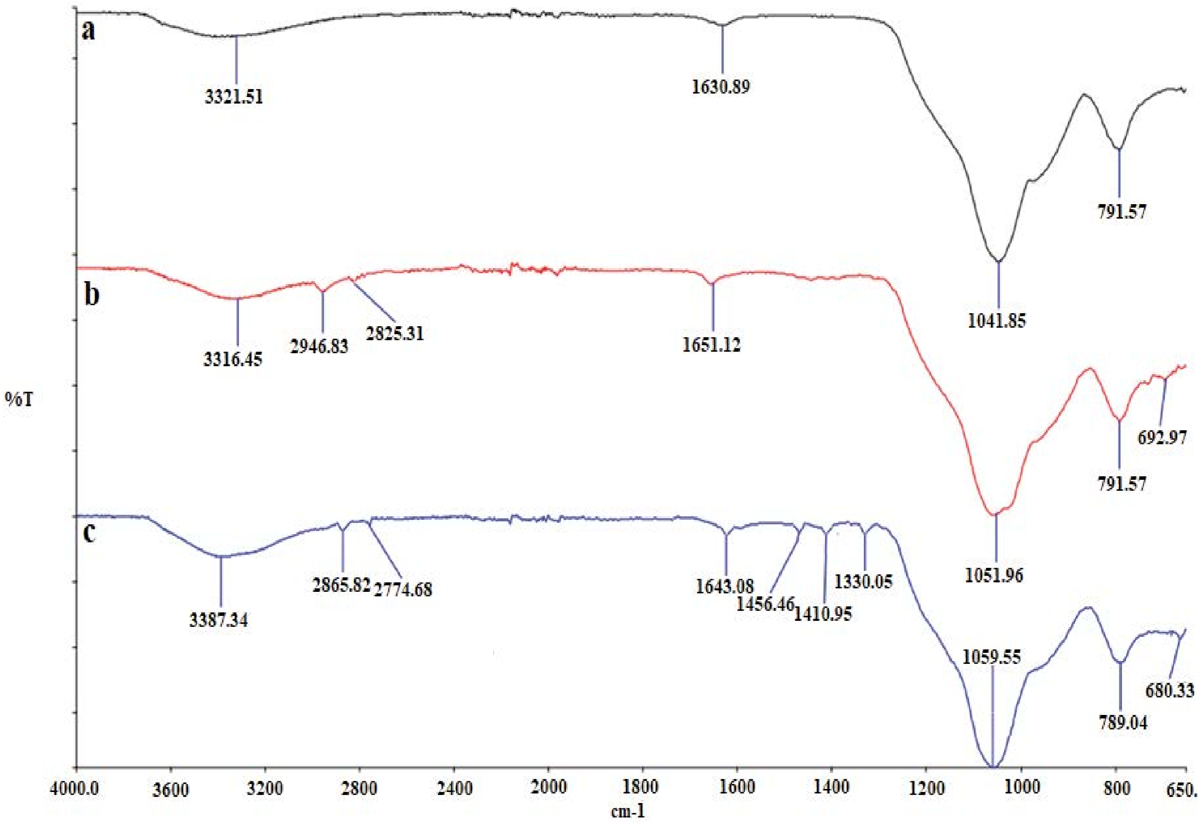

Fig. 3. FT-IR spectra of (a) Si, (b) Si-CPTS, and (c) Si-CPTS-HBAP compounds.

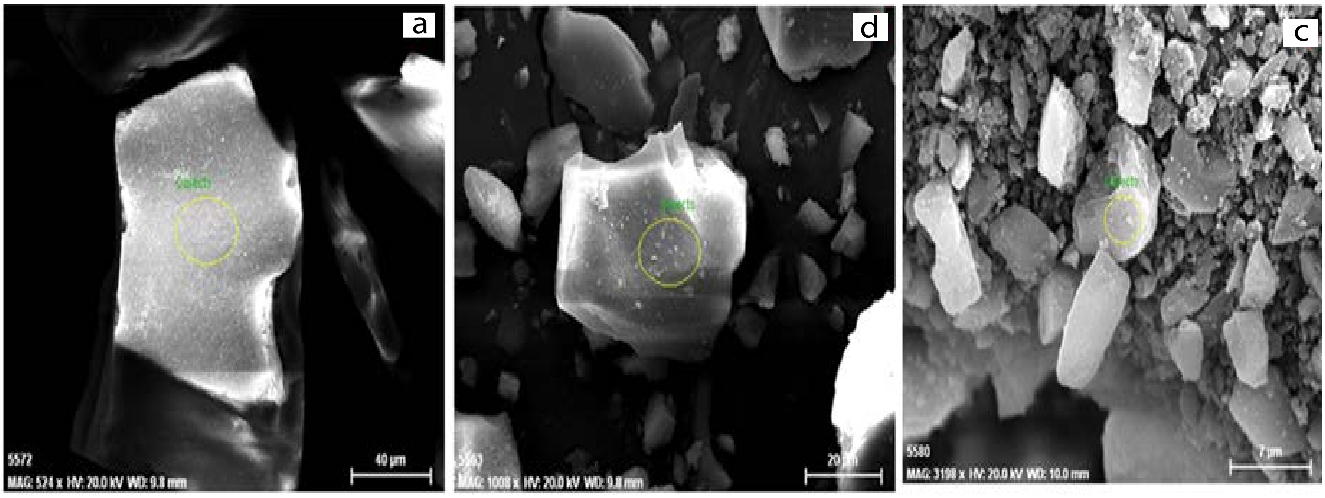

Fig. 4. SEM images of Si (a), Si-CPTS (b), and Si-CPTS-HBAP (c).

with foreign material, i.e., HBAP. The presence of attached particles, i.e., HBAP, onto the surface of silica gel confirms the immobilization.

4.2. Adsorption studies

4.2.1. Effect of adsorption

The amount of ions adsorbed was calculated using Eq. (1).

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

where q is the amount of metal ion adsorbed (mol L^{-1}), C_0 and C_e are the initial and equilibrium concentrations of the metal ions in aqueous phase (mol L^{-1}), V is the volume of the aqueous phase (L), and W is the dry weight of the adsorbent (g) [19].

The effect of the amount of adsorbent on the adsorption of Cr(III) ions in aqueous solution and in wastewater is shown in Fig. 5(a). As shown in Fig. 5(a), as the amount of adsorbent increases, the total amount of adsorbed metal increases. The maximum adsorbent amount for the adsorption of Cr(III) ions in aqueous solution (Cr(NO)3·9H2O) and wastewater was found to be 0.075 g. The excess of the metal ion might be adsorbed by the adsorbent owing to the increase of the active surface area.

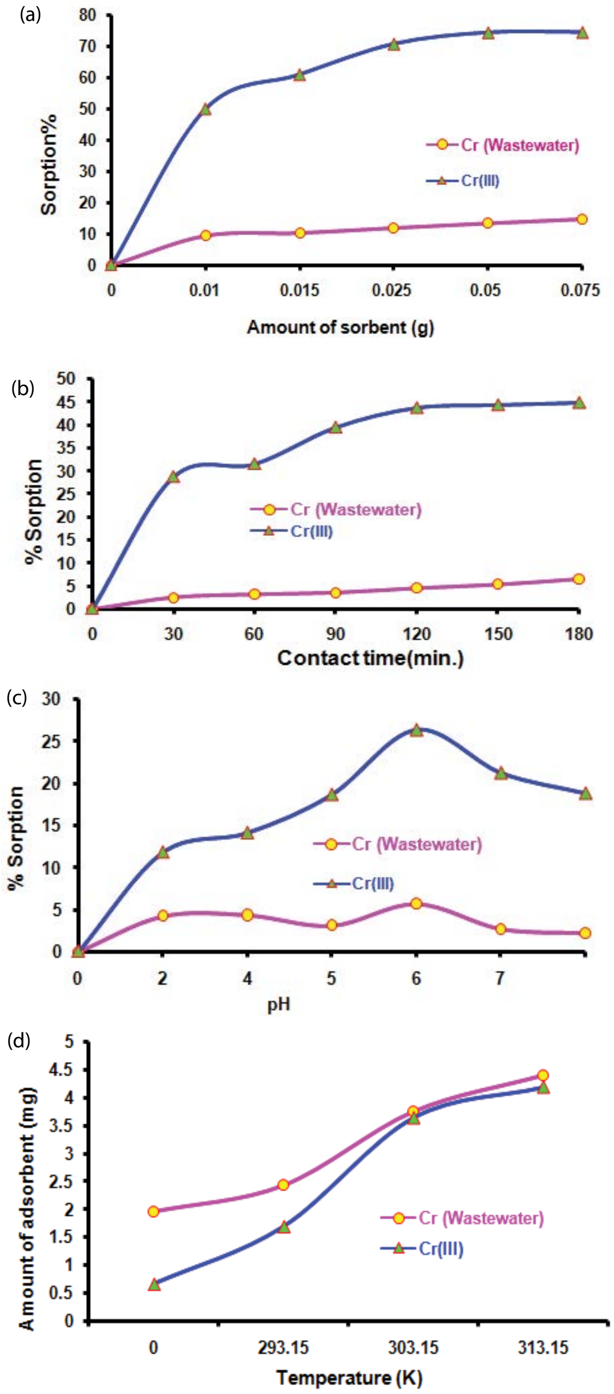

Fig. 5. (a) The effect of the amount of Cr(III) and Cr(III) in wastewater ions on the amount of sorbent, (b) the effect of the contact time on the adsorption of Cr(III) and Cr(III) in wastewater ions, (c) the effect of pH on the sorption of pH of Cr(III) and Cr(III) in wastewater ions, and (d) the effect of temperature on the adsorption of Cr(III) and Cr(III) in wastewater ions.

4.2.2. Effect of contact time

Fig. 5(b) shows the effect of the contact time on the adsorption of Cr(III) ions in aqueous solution and wastewater. As expected, the contact time increased the amount of sorption for the studied metal ions and reached the steady-state values. The adsorbent having hydrophilic groups is defined as the best effect adsorbent. In our paper, the detected rapid uptake kinetics can be attributed to the hydroxy group and nitrogen unit of imine bond (C=N) of the silica gel [19,20].

4.2.3. Effect of pH

The acidity of a solution has two effects on metal adsorption. First, protons in an acidic solution can protonate the binding sites of the chelating molecules. Second, the hydroxide in a basic solution may complex and precipitate many metals. Therefore, the pH of a solution is the first parameter to be optimized. The reaction between Cr(III) and the adsorbent (Si-CPTS-AHAP) can be influenced by changes of the pH value. In order to determine this parameter, the effect of the pH on Cr(III) sorption onto Si-CPTS-AHAP was investigated over the range of 2–7 using the batch procedure. It can be seen from Fig. 5(c) that the adsorption quantity of Cr(III) increases with the increases in pH values in the studied pH ranges. The optimum pH values for maximum Cr(III) aqueous solution and Cr(III) wastewater are at pH ≥ 3. This can be explained by the different binding affinity of the binding sites for Cr(III) of the adsorbent [21]. In this study, the pH value at which maximum sorption of chromium ions occurred was found to be 6 [19,22].

4.2.4. Effect of temperature

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

4.3. Isotherm studies

The experimental measurements were evaluated by using Langmuir isotherm, Freundlich isotherm, and Dubinin–Radushkevich (D-R) isotherm. The Langmuir isotherm expresses the equilibrium distribution of metal ions between solid and liquid phases, and the required calculations are made according to Eq. (2).

$$\frac{C_e}{q_e}=\frac{C_e}{q_0}+\frac{1}{q_0 b} \tag{2}$$

where q_e is the amount of solute sorbed on the surface of the adsorbent (mol L^{-1}), C_e is the equilibrium ion concentration in the solution (mol L^{-1}), q_o is the maximum surface density at monolayer, and b is the Langmuir adsorption constant (mol L^{-1}). The plot of C_e/q_e vs. C_e for the adsorption gives a straight line of slope $1/bq_0$ and intercepts $1/q_o$ (Fig. 6(a)).

The Freundlich isotherm is an experimental isotherm model which is used for adsorption on heterogeneous surfaces [19,23]. It can be written as Eq. (3).

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

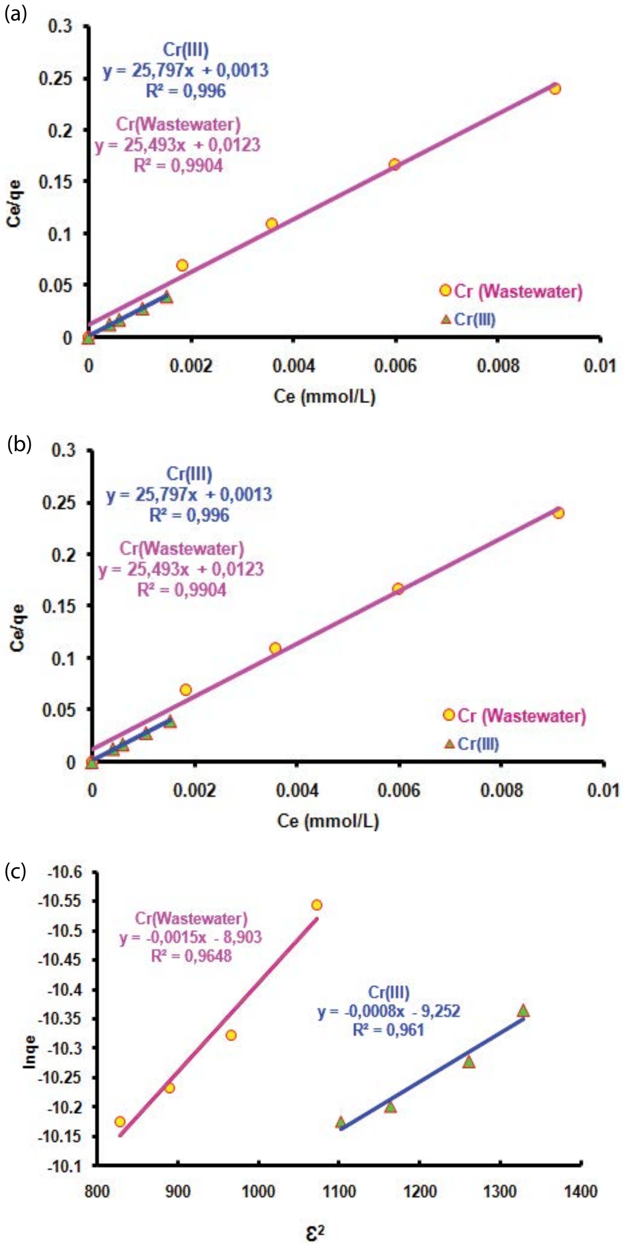

Fig. 6. (a) Langmuir isotherms of Cr(III) and Cr(III) in wastewater removal by Si-CPTS-HBAP, (b) Freundlich isotherms of Cr(III) and Cr(III) in wastewater ion removal by Si-CPTS-HBAP, and (c) D-R isotherms of Cr(III) and Cr(III) in wastewater ion removal by Si-CPTS-HBAP.

where q_e is the equilibrium solute concentration (mol g^{-1}), C_e is the equilibrium concentration of the solute (mol L^{-1}), and K_F is the Freundlich constant. According to Eq. (3), the graph of lnq_e versus lnC_e gives a straight line, and the K_F value can be calculated from the intersection point of this straight line, and the n value is the slope [19,24].

The values of $1/n$ for Si-CPTS-HBAP are <1, so they are an indication of high adsorption intensity [25]. The K_F values showed that immobilized silica gel has higher adsorption capacity for Cr(VI) in aqueous solution and wastewater (0.50 and 0.10 mol L^{-1}) [26]. Values of $n > 1$ represent favorable adsorption conditions [27]. K_F and n values were calculated with the intercept and slope of the plot (Fig. 6(b)) and are listed in Table 1. The 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 (mol g^{-1}), k is a constant related to the adsorption energy (mol^2 $(kJ^2)^{-1}$), and q_m is the adsorption capability (mol g^{-1}). Hence, by plotting lnq_e versus $\varepsilon^{2,}$ it 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 value (E) calculated using Eq. (5) and Dubinin–Radushkevich isotherm is presented in Table 2.

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

The mean energies were 25.00 and 18.25 $kJmol^{-1}$ for the chromium ions in aqueous solution and wastewater, respectively (Table 2). The adsorption of Cr(III) in aqueous solution and wastewater occurs via chemical adsorptions. The energy required for the substantiation of the chemical sorption is between 8 and 16 kJ mol^{-1} [28,29].

4.4. Thermodynamic studies

The thermodynamic parameters such as enthalpy change ($\Delta H°$), entropy change ($\Delta S°$), and free energy change ($\Delta G°$) are crucial and must be taken into consideration in order to determine the spontaneity of a process. The effect of temperature on the adsorption for the modified silica gel was investigated at optimized pH values and at a temperature range of 20°C–50°C.

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

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

Surface	Nitrogen (%)	Carbon (%)	Hydrogen (%)
SiO_2	0	0	0
Si-Cl	0	7.22	0.82
Si-HBAP	5.04	34.25	2.31

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

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

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 adsorbent (g). Also, in Eqs. (6) and (7), ΔG° is the change in Gibbs free energy (kJ mol^{-1}), ΔH° is the change in enthalpy (kJ mol^{-1}), ΔS° is the change in entropy (J $(\text{molK})^{-1}$), T is the absolute temperature (K), and R is the gas constant (8.314×10^{-3}, kJ mol^{-1} K^{-1}).

The enthalpy and entropy values for the adsorption of metal ions onto Si-CPTS-HBAP were evaluated from the Van't Hoff plots: log K_D vs. $1/T$. ΔG° was also calculated by using Eq. (8). Results are listed in Table 3 [19,30]. Fig. 7 shows the value of logarithmic plot of distribution coefficient K_D against $1/T$.

The positive value of ΔH° is shown in Table 3. These values indicate the endothermic nature of adsorption, and the negative values of ΔG° indicate that adsorption onto the adsorbents is feasible and spontaneous process. The adsorbent has a complexing capability, and complex formation must be the predominant mechanism. Positive enthalpy values also support this argument. The values of ΔG° decreased with increasing temperature. The formation of adsorption is inversely proportional to the temperature. The positive value of entropy change (ΔS°) reflects the increase in random adsorption in solid-solution interface. It also indicates that ion replacement reactions occur. When metal ion is coordinated with water molecules in solution, it binds to adsorbent through coordinate covalent bond formation. Due to the released water molecules, the degree of randomness increases the magnitude of ΔH°, related to the adsorption energy indicating the type of binding mechanism involved, i.e., physical and/or chemical adsorption. The process is fast and usually reversible due to the small energy requirement in physical adsorption. The energy required for the hydrogen bond formation is 4–8 kJ mol^{-1} while the energy needed for the London and Van der Waals interactions is 8–40 kJ mol^{-1}. Unlike, the enthalpy associated with chemical adsorption accepted as the transition limit between the physical and chemical sorption processes was about 40 kJ mol^{-1} [31]. The ΔH° values in aqueous solution and wastewater were found to be 28.75 and 25.59 kJ mol^{-1}, respectively, for the Cr(III) ions in the 25°C–50°C temperature range.

3.5. Mechanism

The sorption mechanism of Cr(III) metal ions on Si-CPTS-HBAP can be explained with an ion exchange process. However, the chelating effect of the functional group of the organic compound on Si-CPTS-HBAP 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 chemisorption of heavy metal ions [29]. The complex perspective of Si-CPTS-HBAP metal ion combination can be estimated as given in Fig. 8.

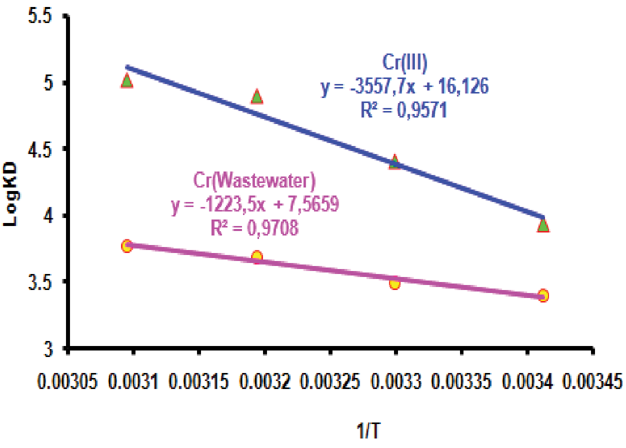

Fig. 7. Plots of log K_D versus $1/T$ for Cr(III) and Cr(III) in wastewater removal by Si-CPTS-HBAP.

Table 2
Isotherm parameters for Cr(III) and Cr(III) in wastewater by Si-CPTS-HBAP (T = 298 K)

Freundlich isotherm			Langmuir isotherm		D-R isotherm		
Metal	$1/n$	K_F	Q_o (L mol^{-1})	b (mol^2 $(\text{KJ}^2)^{-1}$)	k (mol^2 K^{-1} J^{-1})	q_m (mol g^{-1})	E (kJ mol^{-1})
Cr	0.1422	0.07	0.174	10,609.12	0.0008	0.062	25.00
Cr (wastewater)	0.2294	0.17	0.060	1,113.92	0.0015	0.231	18.25

Table 3
Thermodynamic parameters for sorption of Cr(III) and Cr(III) in wastewater ions of Si-CPTS-HBAP

Metal	ΔH° (kJmol^{-1})	ΔS° ($\text{JK}^{-1}\text{mol}^{-1}$)	$-\Delta G^\circ$ (kJmol^{-1})			
			298	303	313	323
Cr	68.12	265.09	9.59	11.12	12.76	13.48
Cr (wastewater)	23.42	108.20	8.29	8.82	9.62	10.12

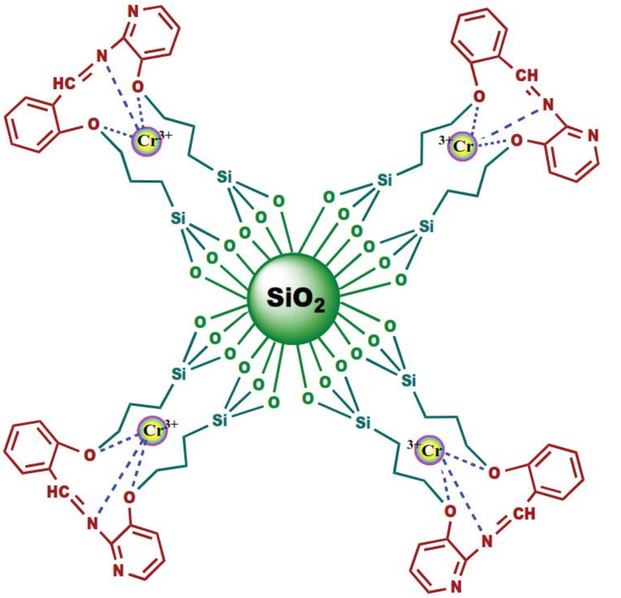

Fig. 8. The estimated perspective of Si-CPTS-HBAP metal ion combination.

5. Conclusion

HBAP has successfully been immobilized by the batch technique on a silica gel. It has been seen that the compound newly synthesized (Si-CPTS-HBAP) was acquired selectivity, sensitive to metal ions, and has highly active surface area. Thus, the adsorbent which is cheap, suitable for heavy metal removal, has more active surface, and water insoluble was obtained. FT-IR spectroscopy and SEM confirmed the synthesis of Si-CPTS-HBAP.

According to parameters discussed above, the best chromium removal was carried out at pH = 6.0, with 0.075 g adsorbent, at 323.15°C, in a final concentration of 40 mg L^{-1} in 180 min. It is found that the adsorption is mainly pH dependent. It was observed that the adsorption tendency was in accordance with Langmuir isotherm model. The mean adsorption energies for modified silica gel were found to be 50.00 and 20.41 kJ mol^{-1} for Cr(III) in aqueous solution and wastewater, respectively. This result indicates that the reaction on the adsorbent has occurred chemically.

The thermodynamic parameters in the measurements show that the reactions are endothermic and spontaneous. If the values of $\Delta G°$ are negative at 25°C–50°C, the process is spontaneous and decreased with warming. The sorption of selected heavy metal ions on Si-CPTS-HBAP increases at high temperatures. The Si-CPTS-HBAP compound has quite high capacity to adsorb chromium from the wastewater [32].

The novelty of the study is the synthesis of the Si-CPTS-HBAP and immobilization of organic substances on to silica gel surface. The new material obtained is not soluble in water and can contribute to separation and purification methods.

This study is important in providing complete steps of characterization as well as providing effective usage of Si-CPTS-HBAP to remove Cr(III) ions in wastewater. If the organizations with heavy metal waste use Si-CPTS-AHAP in wastewater treatment systems, they will provide both low-cost and high-efficiency heavy metal removal. Also desorption of the adsorbent is easy. Thus, this study will contribute to the world economy and water and environmental cleanliness.

Acknowledgements

The authors acknowledge financial support for this research by Scientific Research Project Commission of Karamanoğlu Mehmetbey University (BAP-Grant number 11-M-15 and 28-M-15).

References

[1] D.E. Kimbrough, Y. Cohen, A.M. Winer, A critical assessment of chromium in the environment, Crit. Rev. Env. Sci. Technol., 29 (1999) 1–46.
[2] S.E. Fendorf, Surface reactions of chromium in soil and waters, Geoderma, 67 (1995) 55–71.
[3] D. Rai, B.M. Sass, D.A. Moore, Chromium(III) hydrolysis constants and solubility of chromium(III) hydroxide, Inorg. Chem., 26 (1987) 345–349.
[4] A. Pechova, L. Pavlata, Chromium as an essential nutrient: a review, Vet. Med., 52 (2007) 1–18.
[5] M. Costa, Potential hazards of hexavalent chromate in our drinking water, Toxicol. Appl. Pharmacol., 188 (2003) 1–5.
[6] E.S. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res., 33 (1999) 2469–2479.
[7] A. Kumar, N.N. Rao, S.N. Kaul, Alkali-treated straw xanthate as low cost adsorbents for heavy metal removal-preparation, characterization and application, Bioresour. Technol., 71 (2000) 133–142.
[8] A. Cimen, M. Torun, A. Bilgic, Immobilization of 4-amino-2-hydroxyacetophenone onto silica gel surface and sorption studies of Cu(II), Ni(II), and Co(II) ions, Desal. Wat. Treat., 53 (2015) 2106–2116.
[9] 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.
[10] 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.
[11] 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.
[12] I.H. Gübbük, R. Güp, M. Ersöz, Synthesis, characterization and sorption properties of slica gel-immobilized Schiff base derivative, J. Colloid Interface Sci., 320 (2008) 376–382.
[13] A.R. Cestari, E.F.S. Viera, A.J.P. Nascimento, F.J.R.O. Bruns, R.E. Airoldi, New factorial designs to evaluate chemisorption of divalent metals on aminated silicas, J. Colloid Interface Sci., 241 (2001) 45–51.
[14] 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.
[15] J.A.A. Sales, C. Airoldi, Calorimetric investigation of metal ion adsorption on 3-glycidox ypropyl trimethyl siloxane+ propane-1, 3-diamine immobilized on silica gel, Thermochim. Acta, 427 (2005) 77–83.
[16] 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.

[17] 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.

[18] 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.

[19] M. Naushad, T. Ahamad, B.M. Al-Maswari, A.A. Alqadami, S.M. Alshehri, Nickel ferrite bearing nitrogen-doped mesoporous carbon as efficient adsorbent for the removal of highly toxic metal ion from aqueous medium, Chem. Eng. J., 330 (2017) 1351–1360.

[20] S.K.R. Yadanaparthi, D. Grabill, R.V. Wandruszka, Adsorbents for the removal of arsenic, cadmium, and lead from contaminated, J. Hazard. Mater., 171 (2009) 1–15.

[21] W. Ngeonta, W. Aeungmaitrepirom, T. Tuntulani, Chemically modified silica gel with aminothioamidoanthraquinone for solid phase extraction and preconcentration of Pb (II), Cu (II), Ni (II), Co (II) and Cd (II), Talanta, 71 (2009) 1075–1082.

[22] 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.

[23] 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.

[24] G. Asgari, R. Bahman, R. Leila, A. Mehdi, Kinetics and isotherm studies of hexavalent chromium adsorption from water using bone charcoal, Fresenius Environ. Bull., 21 (2012) 1296–1302.

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

[26] G. Vázquez, J.G. Alvarez, 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.

[27] 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.

[28] 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.

[29] Y. Wang, X. Tang, Y. Chen, L. Zhan, Z. Li, Q. Tang, Adsorption behavior and mechanism of Cd (II) on loess soil from China, J. Hazard. Mater., 172 (2009) 30–37.

[30] A. Çimen, 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, J. Water Reuse Desal., 5 (2015) 312–325.

[31] 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) 86–91.

[32] A. Çimen, A. Bilgiç, I. Yılmaz, Chemical modification of silica gel with hydrazine carbothioamide derivative for sorption studies of Cu (II), Ni (II) and Co (II) ions, Desal. Wat. Treat., 55 (2015) 420–430.