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Immobilization of 4-amino-2-hydroxyacetophenone onto silica gel surface and sorption studies of Cu(II), Ni(II), and Co(II) ions

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ABSTRACT

The 4-amino-2-hydroxyacetophenone was immobilized onto silica gel modified with 3-aminopropyltrimethoxy silane. The carried reaction is classic condensation reaction. The obtained structure was characterized by infrared spectroscopy and thermo gravimetric analysis. The values of adsorption of Cu(II), Ni(II), and Co(II) ions were detected with an atomic absorption spectrometer. The experiment conditions for effective sorption of the studied metal ions were performed by using batch method. The maximum adsorption capacities and isotherm parameters were calculated with using 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 experimental results. The sorption results were used to explain the mechanism of the sorption. The modified structure was successfully used in the separation of Cu(II), Ni(II), and Co(II) from the aqueous solutions.

Keywords: Chemical analysis; Surface analysis; Thermal analysis; Surface treatments

1. Introduction

The high levels of heavy metals such as nickel, copper, and cobalt in wastewater are threat to human health and ecological systems. The high level of nickel in nature is hazardous to human health due to its allergic reaction, carcinogenic and toxic effects. Although copper is an essential element for life, its high levels caused mutagenic and carcinogenic effects just as nickel [1]. These heavy metal ions such as copper, nickel, and cobalt transmitted from industrial waste reason to pollution of water [2]. There are many techniques to purify the wastewater containing heavy metal ions [3], such as coagulation [4], co-precipitation [5], reverse osmosis [6], ion exchanges [7], and adsorption [8]. Among these methods, adsorption technique is one of the most hopeful techniques for this purpose. So, a lot of materials have been developed for the remediation of heavy metal pollutions. Among these materials, silica gel structures are attractive for removing of heavy metals from wastewaters. Thanks to the functionalization of silica gel structures with organic materials, it is increasingly utilized as an adsorbent [9]. Nowadays, silica gel structures functionalized with various organic compounds as metal chelating agent have been greatly paid attention. The modified silica gels generally provide to a higher adsorption capacity than other structures used as a support. The

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chemical modification with appropriate organic groups on silica gel formed a new surface. It could be used as an adsorbent for the removal of heavy metal ions [10,11].

Silica gel is a solid support, widely used in many chemical processes to provide new technical application [11–13]. It is an amorphous inorganic polymer composed of internal siloxane groups (Si–O–Si) with silanol groups (Si–OH) distributed on the surface [14–16]. The active hydrogen atom of the silanol groups of silica gel has the ability to react with agent containing organosilyl functions, to give some organic nature to the precursor inorganic support [17,18], which has been increasingly used because its surface offers many advantages due to its thermal and chemical stabilization during the reaction processes. It has a high surface area of 480–540 m^2/g, micro pore size of 60 Å, and it can be used at a relatively low cost [11].

From these advantages, modification of silica gels can be achieved via chemisorption of the active species onto the silica surface. Silica materials may also be modified via physisorption of active species leading to a variety of useful supported reagents [19]. Chemically modified silica gels are used extensively in many scientific and technological applications like, HPLC bonded phases for specific separations, supports for catalysts in specific organic reactions, supports for microorganism and pesticides [15], and in the extractions of metallic cations from aqueous and nonaqueous solvents by forming immobilized metallic complexes [20]. Adsorption capacities of silica gel surfaces are intimately related to the levels or values of several experimental factors [21]. Variables such as the type of immobilized ligand, the metal cation involved, the solvent used, the solid solution contact time, and the temperature which can change significantly the quantity of metal sorbed [21–23].

2. Materials and methods

2.1. Materials

All the chemicals used in the study were of analytical grade. The diluted NaOH and HNO_3 solutions were used for pH adjustments. A series of standard metal solutions from the stock metal solution was prepared appropriately according to the standard. Silica gel used in the study had high surface area of 480–540 m^2/g, micro pore size of 60 Å, diameter of 0.036–0.2 mm, pore volume of 0.74–0.84 cm^3/g, and particle size of 70–180 μm.

2.2. Instrument

Thermogravimetric (TG) data were measured on a Diamon system Extar SII TGA/DTA 6,300 analyzer at the temperature range of 298–1,273 K (gas 1: nitrogen, gas 2: dry air, platinum pans, 25–1,000 °C). The pH values of the samples were adjusted by an Orion ion meter with combined pH electrode. The infrared spectra were measured in the range of 650–4,000 cm^{-1} by a Perkin Elmer 100 FT-IR spectrometer (KBr pellets, 21 °C temperature, 39% moisture, 1 atm pressure). The metal concentrations in the filtrated solution were measured by a flame atomic absorption spectrometer (28 °C temperature, 43% moisture, 1 atm pressure, ContrAA 300, Analytikjena). Thermostatic shaker (A Heidolph Unimax 2010) was used for the sorption studies. All aqueous solutions were prepared with ultra pure water obtained from a water purification system (Millipore Milli-Q Plus).

2.3. Preparation of Si-AHAP

Silica gel that was selected as a support material was firstly converted to Si-OH [12]. The immobilization of the 3-aminopropyltrimethoxy silane (APTS) onto silica gel was carried out as follows: silica gel (15.0 g) was waited in dry toluene (100 mL) and APTS (9 mL) was added. The mixture was refluxed for 72 h under vacuum. In the next step, 10 g of Si-APTS (silica gel APTS) that was treated with 25% of 4-amino-2-hydroxyacetophenone (AHAP) solution (33 mL) was 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-APTS-AHAP. Fig. 1 shows the synthesized structure.

2.4. Sorption studies

Twenty milligram of sorbent and 10 mL of adsorbed substance at various pH and concentration were shaken in a temperature controlled shaker incubator at 298 ± 1 K until equilibrium was reached (120 min). After extraction, the solid phase was separated by filtration. The residual metal concentration was measured AAS and the amount of cations sorbed was calculated by:

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

where V is the volume of the aqueous phase (L), W is the dry weight of the adsorbent (g). C_0 and C_e are the

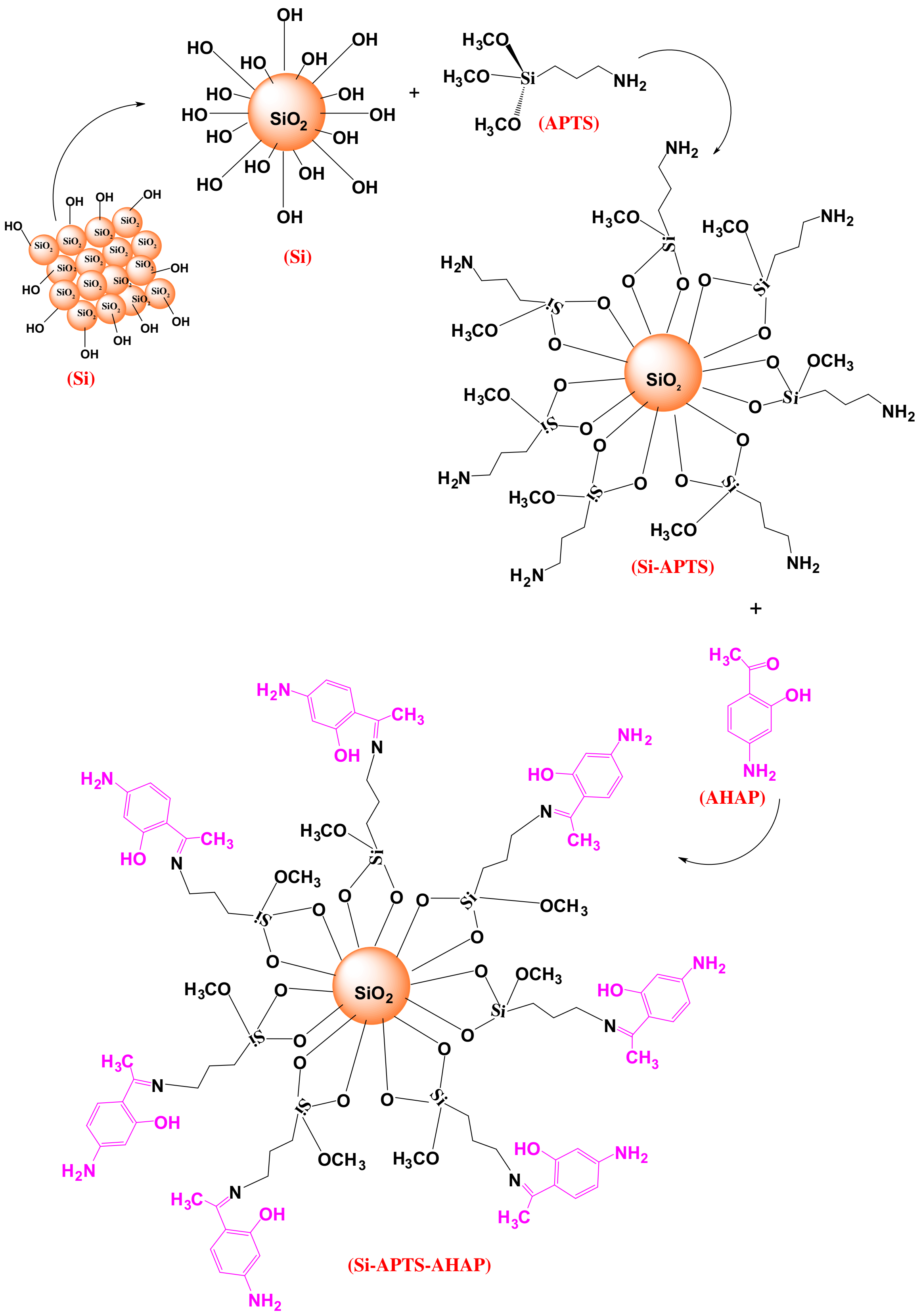

Fig. 1. Possible structure of silica gel bonded 4-amino-2-hydroxyacetophenone (AHAP) molecules.

initial and equilibrium concentrations of the metal ions in aqueous phase (mmol L^{-1}), q is the amount of metal ion sorbed onto unit amount of the adsorbent (mmol g^{-1}).

2.4.1. Effect of concentration

For sorption measurements, 20 mg of modified silica gel was waited in 10 mL of aqueous solution containing Cu(II), Ni(II), and Co(II) ions. These suspensions were shaken in the concentrations 8.0–40.0 ± 0.01 mmol L^{-1} in a shaker thermostat for 180 min [21,24]. After equilibrium was established, the amounts of cations remaining in solution were measured by AAS.

2.4.2. pH studies

The interaction between Cu(II), Ni(II), Co(II), and adsorbent (Si-APTS-AHAP) can be influenced by changing pH value. The effect of the pH on Cu(II), Co (II), and Ni(II) sorption was investigated over the range of pH 2.0–7.0 [24]. At pH 4.0–5.5, 0.1 mmol L^{-1} of acetic acid–sodium acetate buffer solution was used and at pH 2.0–7.0, phosphate buffer solution was used to maintain an approximate equal ionic strength for the working solutions. An amount of 20 mg of Si-APTS-AHAP was stirred in solutions (10 mmol L^{-1}) of Cu(II), Ni(II), and Co(II) ions and at the different pH levels (1.0, 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0). The mixture was shaken for 180 min at 298 ± 1 K.

2.4.3. Temperature studies

The experiments were carried out between 20 and 50 ± 1˚C at optimum pH values for each metal ion, respectively. The amount of the adsorbed metal ion was calculated from the change in the metal concentrations in the aqueous solution [19].

3. Result and discussion

3.1. Characterization

The immobilization onto silica surface can be confirmed through infrared spectra for the silica. Infrared spectrum of SiO_2 shows the appearance of bands at 799, 1,055, and 3,374 cm^{-1}, due to (Si–O–Si), SiO_2, and Si–OH, respectively. OH stretching vibration in Si-APTS was shifted to 3,456 cm^{-1} from 3469 cm^{-1} (Si). A large decrease of OH stretching vibration in silanol was observed at 799 cm^{-1}. Hence, frequency of CH_2 stretching vibrations in Si-APTS was observed at 2,920–2,885 cm^{-1}. The formation of broad –OH peak at 3,271 cm^{-1} was obtained in Si-APTS-AHAP because of the presence of –OH groups which are in the structure of silica-based organic compounds. The stretching of C=N group observed at 1,617 cm^{-1} showed primer amine group of Si-APTS and AHAP and organic substance. Stretching of C=C in the benzene ring, bending of –C–OH peak and $–CH_2$ and $–NH_2$ peaks were observed between 1552 and 1420, 1111, 3028, and 3100 cm^{-1}, respectively [11].

Consequently, the above analysis of infrared spectrum suggested that the existence of strong interaction at the interface of SiO_2–Si-APTS and Si-APTS–AHAP and Si-APTS was successfully modified by AHAP [16] (Fig. 2).

According to the results of elemental analysis [12], the percentage amounts of carbon, nitrogen, and hydrogen are shown in SiO_2, Si-APTS, and Si-APTS-AHAP (Table 1).

The TG curve of Si-APTS-AHAP is given in Fig. 3. According to the TGA curves of the modified materials, Si-APTS decomposes in third step while Si-APTS-AHAP decomposes in three steps. Si-APTS-AHAP has more thermal stability than Si-APTS and distinct mass losses, reflecting the molar mass of the pendant groups covalently bonded to inorganic phase. Physically adsorbed waters initially bonded on Si-APTS and Si-APTS-AHAP were lost at low temperature (1.80–2.10%, respectively). Increase in temperature caused to the condensation of surface groups resulted in first mass loss step for Si-APTS and Si-APTS-AHAP, 15 and 27.6%, between 341 and 513˚C and 372–1,000˚C, respectively. The second mass losses can be attributed to the immobilized organic molecules. An abrupt loss in mass was detected in the third mass loss region, (% 30.20), from 513 to 1,000˚C, suggesting the progressive release of the silica gel attached to silane molecules [25].

3.2. Adsorption studies

3.2.1. Effect of adsorption

Fig. 4(a) shows the effect of the amount of sorbent on sorption of Cu(II), Ni(II), and Co(II) ions. The adsorption ratios change depending upon increase of adsorbent. When the amount of adsorbent increased, the total amount of adsorbing metal ions increased and reached steady state values [19]. The maximum amount of adsorbent for Cu(II) = Ni(II) = Co(II) ions was found as 0.05 g. The excess metal ion might be adsorbed by the adsorbent owing to the increase of the active surface. The effect of amount of adsorbent

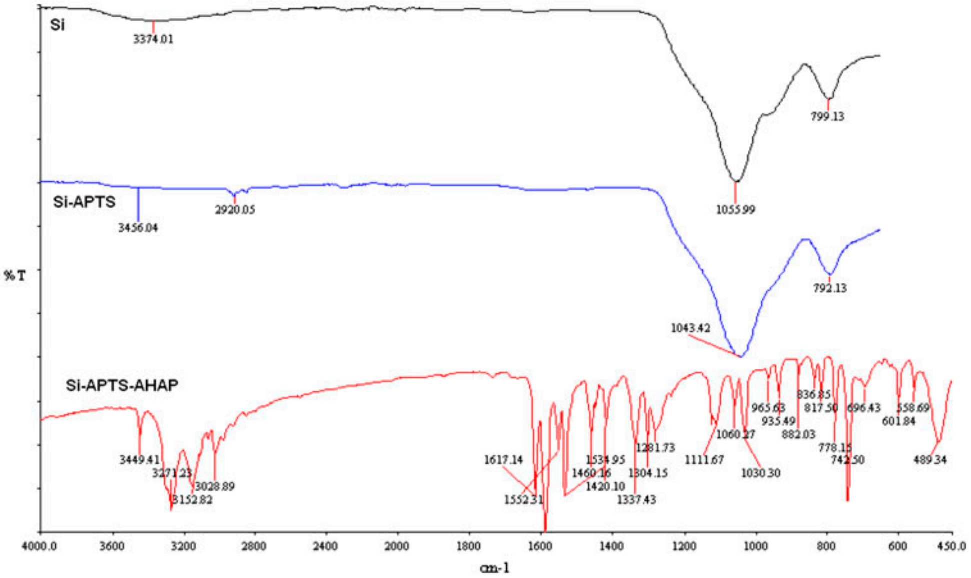

Fig. 2. FTIR spectra of Si (a), Si-APTS (b), and Si-APTS-AHAP (c).

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

Surface	Nitrogen (%)	Carbon (%)	Hydrogen (%)	Carbon ($mmolg^{-1}$)
SiO_2	0	0	0	–
Si-APTS	2.29	9.23	2.25	2.55
Si-APTS-AHAP	5.50	28.32	3.10	1.03

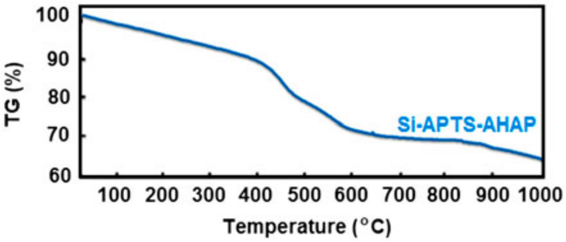

Fig. 3. TG curves of Si-APTS-AHAP.

on sorption of Cu(II), Co(II), and Ni(II) ions by Si-APTS-AHAP can be attributed to more chelating effect.

3.2.2. *Effect of contact time*

Fig. 4(b) shows the effect of contact time on the adsorption for Cu(II), Co(II), and Ni(II) ions. As expected, the contact time increased the amount of sorption for the studied metal ions and reached at steady state values.

3.2.3. *Optimum pH studies*

The effect of pH on the sorption studied for Cu (II), Co(II), and Ni(II) ions is as shown in Fig. 4(c). The results showed that the adsorption of Cu(II), Co(II), and Ni(II) 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 [26]. The pH value for maximum sorption of Cu(II) = Ni(II) = Co(II) ions was found to be 6.

3.2.4. *Effect of concentration*

Fig. 4(d) shows that the adsorption effect depends on the concentration of metal ions. The curves of the graph showed that the adsorption increases with the increasing concentration of metal ions and reaches steady state values. This behavior can be ascribed with the high driving force for the charge transfer and the concentration is important for design purposes.

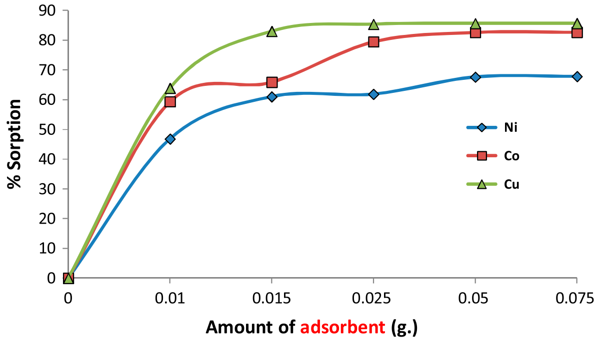

Fig. 4(a). The effect of the amount of Cu(II), Co(II), and Ni(II) ions on sorption.

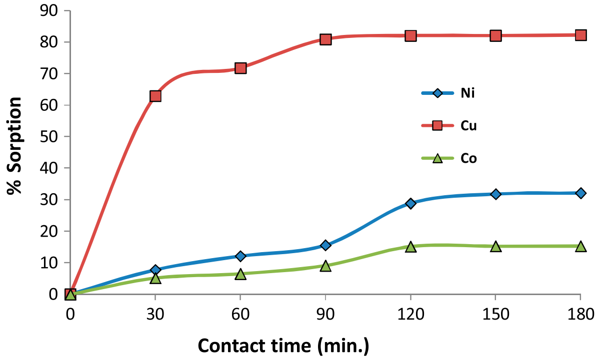

Fig. 4(b). The effect of the contact time on the adsorption of Cu(II), Co(II), and Ni(II) ions.

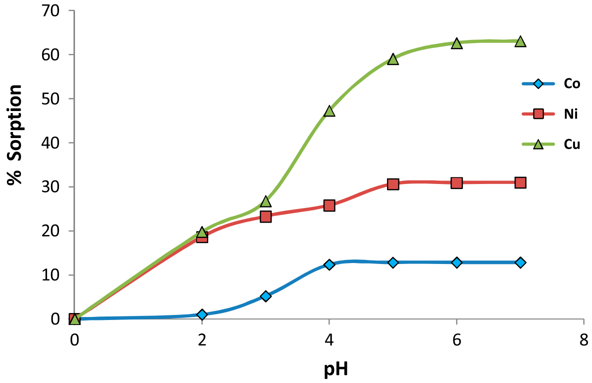

Fig. 4(c). The effect of pH on the sorption of Cu(II), Co(II), and Ni(II) ions.

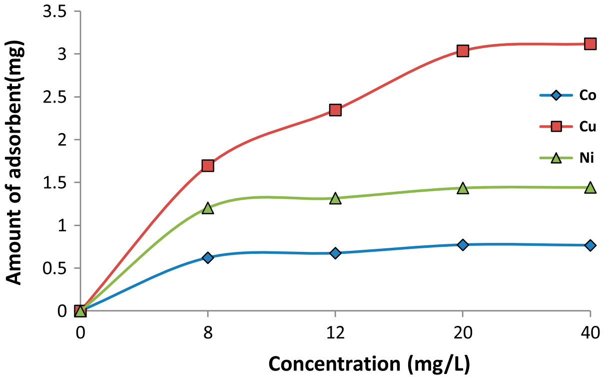

Fig. 4(d). The adsorption effect dependence on concentration of Cu(II), Co(II), and Ni(II) ions.

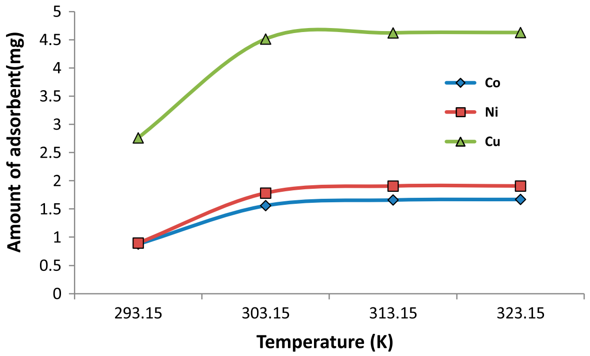

Fig. 4(e). The effect of temperature on the adsorption of Cu(II), Co(II), and Ni(II) ions.

3.2.5. *Effect of temperature*

Fig. 4(e) exhibits the effect of temperature on the adsorption. The amount of adsorption increased with temperature and reached steady state values. Depending on endothermic nature of the sorption, the thermodynamic parameters' values also changed with increasing temperature.

3.3. *Adsorption Isotherms*

The experimental measurements were evaluated with Langmuir isotherm, Freundlich isotherm, and Dubinin-Radushkevich (DR) isotherm. The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases and is as follow.

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

where q_e, C_e, q_o, and b are the amount of solute sorbed on the surface of the sorbent (mmol g^{-1}), the equilibrium ion concentration in the solution (mmol L^{-1}), the maximum surface density at monolayer coverage, and

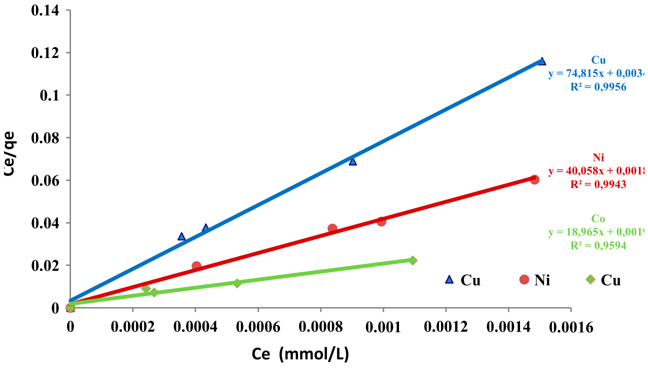

Fig. 5(a). Langmuir isotherms of removal of Cu(II), Co(II), and Ni(II) by Si-APTS-AHAP.

the Langmuir adsorption constant ($\mathrm{L\,mmol^{-1}}$), respectively. The plot of C_e/q_e vs. C_e for the sorption gives a straight line of slope $1/q_o b$ and intercepts $1/q_o$ (Fig. 5(a)).

According to the DR isotherm, metal ions are chemically adsorbed at a fixed number of sites where each site can hold only one ion and all sites are energetically equivalent without any interaction between the ions [27].

The Freundlich isotherm is an empirical isotherm model which is used for adsorption on heterogeneous surfaces or surfaces supporting sites of varied affinities [28]. The Freundlich isotherm can be written as:

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

where q_e, C_e, and K_F are the equilibrium solute concentration on adsorbent ($\mathrm{mmol\,g^{-1}}$), the equilibrium concentration of the solute ($\mathrm{mmol\,L^{-1}}$), and the Freundlich constant, respectively.

According to Eq. (3), the plot of $\ln q_e$ vs. $\ln C_e$ gives a straight line, K_F and n values can be calculated from the intercept and slope of this straight line [29].

The K_F values calculated for Cu(II), Co(II), and Ni(II) were 0.50, 0.03, and 0.10, respectively [30]. Values of $n > 1$ represent favorable adsorption conditions [31]. Values of K_F and n are calculated from the intercept and slope of the plot (Fig. 5(b)) and are shown in Table 2. The Dubinin-Radushkevish (DR) isotherm was used to estimate the adsorption energy in this study and can be expressed as:

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

where ε (polanyi potential) is $[RT\ \ln(1+(1/C))]$, q_e is the amount of solute adsorbed per unit weight of adsorbent ($\mathrm{mol\,g^{-1}}$), k is a constant related to the adsorption energy ($\mathrm{mol^2(kJ^2)^{-1}}$), and q_m is the adsorption capacity ($\mathrm{mol\,g^{-1}}$). Hence, by plotting ln q_e vs. ε^2, it is possible to generate the value of q_m from the intercept, and the value of k from the slope (Fig. 5(c)). The mean free energy (E), calculated by the Dubinin–Radushkevich isotherm, is shown in Table 2. The energy values were calculated using the following equation:

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

The mean free energy values (E) are between 16.22 and 25.00 kJ $\mathrm{mol^{-1}}$ for the three metal ions (Table 2). The sorption of Co(II), Cu(II), and Ni(II) occurs via chemisorptions. The energy adequate for the realization of the chemical sorption is between 8 and 16 kJ $\mathrm{mol^{-1}}$ [32,33].

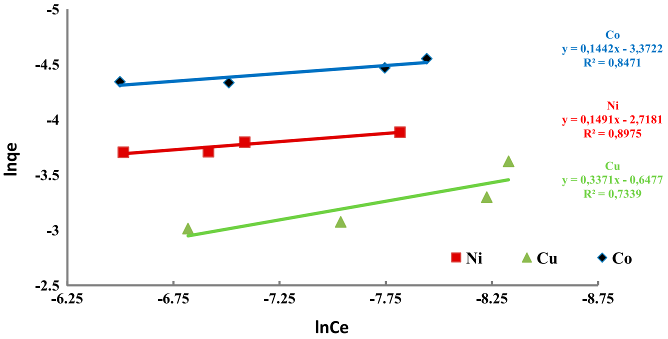

Fig. 5(b). Freundlich isotherms of removal of Cu(II), Co(II), and Ni(II) by Si-APTS-AHAP.

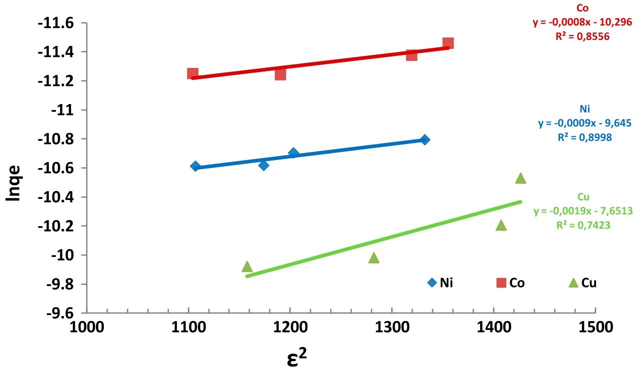

Fig. 5(c). DR isotherms of removal of Cu(II), Co(II) and Ni (II) by Si-APTS-AHAP.

3.4. Thermodynamic studies

The thermodynamic parameters such as enthalpy change (ΔH°), entropy change (ΔS°), and free energy change (ΔG°) must be used to determine the spontaneity of a process. The effect of temperature on the sorption of immobilized silica gel was investigated at temperatures (293–323 K) under suitable 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 (L), and W is the dry weight of the sorbent (g) (Eq. (6)). Also, 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 (mol K)$^{-1}$), 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 sorption of metal ions onto Si-APTS-AHAP were evaluated from the van't Hoff plots: log K_D vs. $1/T$. ΔG° was also calculated by using Eq. (7) and results are shown in Table 3 [34]. Values of logarithmic plot of distribution coefficient K_D against $1/T$ are shown in Fig. 6.

The positive value of ΔH° indicates the endothermic nature of adsorption. The negative values of ΔG° for metal ions indicate that the adsorption onto the adsorbents is a feasible and spontaneous process and energy input from outside of the system is required. This study supports positive enthalpy values. The values of ΔG° decrease with increase in the temperature which indicates that the spontaneous nature of adsorption was inversely proportional to the temperature. The positive value of entropy change (ΔS°) indicates that the increasing randomness at the solid–solution interface during sorption and ion replacement reactions occurs. The enthalpy associated with chemical sorption which was about 40 kJ mol^{-1}, [35]. The ΔH° values observed were 38.82 kJ mol^{-1}, 25.00 kJ mol^{-1}, and 20.00 kJ mol^{-1} for Cu(II), Ni(II), and Co(II) in the temperature range of 293–323 K, respectively. ΔH° values calculated for metal ions sorption were lower than 40 kJ mol^{-1}, indicative of the weak interactions of the compound with the Si-APTS-AHAP surface at this temperature range.

Table 3
Thermodynamic parameters for sorption of metal ions of Si-APTS-AHAP (metal ion concentration 10 mmol L^{-1})

Metal	ΔH° (kJmol^{-1})	ΔS° (JK^{-1} mol^{-1})	$-\Delta G^\circ$ (kJmol^{-1})			
			297	303	313	323
Cu(II)	38.82	169.89	10.98	12.87	13.48	13.93
Ni(II)	25.00	114.97	8.62	9.90	10.34	10.67
Co(II)	20.00	90.05	8.74	9.80	10.21	10.55

Table 2
Isotherms parameters for Cu(II), Co(II), and Ni(II) by Si-APTS-AHAP (T = 298 K)

Freundlich isotherm			Langmuir isotherm		DR isotherm		
Metal	$1/n$	K_F	Q_o (mmol)	b (L m mol^{-1})	k (mol^2 K^{-1} J^{-1})	q_m (m mol g^{-1})	E (k J mol^{-1})
Cu(II)	0.34	0.50	0.053	12,342	0.0019	0.401	16.22
Ni(II)	0.21	0.10	0.025	45,897	0.0009	0.068	23.57
Co(II)	0.12	0.03	0.013	23,399	0.0008	0.031	25.00

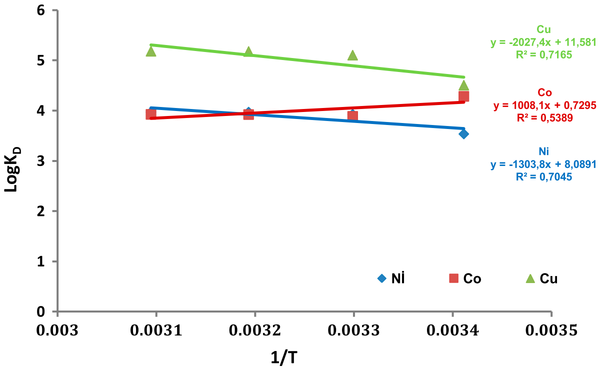

Fig. 6. Plots of log K_D vs. $1/T$ for removal of Cu(II), Co(II) and Ni(II) by Si-APTS- AHAP.

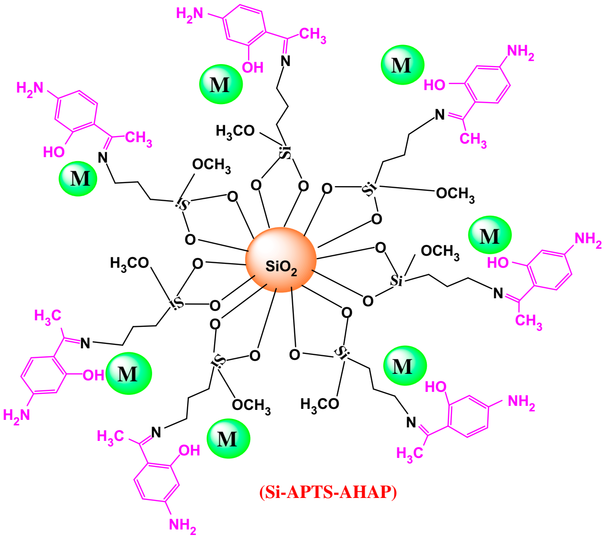

Fig. 7. The estimated perspective of Si-APTS-AHAP metal ions combination.

3.5. Mechanism

The sorption mechanism of Cu(II), Co(II), and Ni(II) metal ions on Si-APTS-AHAP can be explained with a classical chelating effect. However, the chelating effect 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. The complex perspective of Si-APTS-AHAP metal ions combination can be estimated as given in Fig. 7.

4. Conclusions

In this study, the chemical modification of silica gel was performed with AHAP by using the immobilization method and chelating solid surface Si-APTS-AHAP was obtained. The suitable pH was 6.0 for the sorption of the metal ions. The behavior of the chelating structures and the effect of metal ion concentration were studied in the range of 8–40 ± 0.01 mmol L^{-1}. The metal sorption is ordered as Cu(II) > Co(II) > Ni(II) for the removal of metal ion. The adsorption of Cu(II), Co (II), and Ni(II) onto the modified material put to use Langmuir and Freundlich adsorption models. The mean sorption energies for modified silica gel were found to be 16.22, 23.57, and 25.00 kJ mol^{-1} for Cu(II), Co(II), and Ni(II) ions. An amount of 18.25 kJ mol^{-1} may correspond to chemical sorption [33].

The efficient modification of Si-APTS-AHAP on silica gel surfaces was verified with FT-IR. According to the TG analysis results, Si-APTS-AHAP had a higher stability than the other material (Si-APTS) [36].

According to the calculated experimental data, reactions were endothermic and spontaneous. For spontaneous processes, the values of ΔG° were negative in the range of 293–323 K, as expected. While temperature increases, ΔG° value decreases. Sorption of Cu(II), Co(II), and Ni(II) ions on Si-APTS-AHAP becomes better at higher temperatures.

Consequently, the modified compound with AHAP (Si-APTS-AHAP) which was used for the first time in the metal sorption studies, is original. Modified structures can act as chelate and it is used for the removal of metal ion from aqueous solution [37]. When Si-APTS-AHAP was compared with raw silica gel, chelating effect increases with the sorption of the metal ions. The present study reveals that this system is economic and environmental friendly for the use of wastewater. This study is also important for the removal of metal with Si-APTS-AHAP.

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