

# Silica gel functionalized with 4-phenylacetophynone 4-aminobenzoylhydrazone: Synthesis of a new chelating matrix and its application as metal ion collector

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## Abstract

The silica gel surface immobilized with 4-phenylacetophynone 4-aminobenzoylhydrazone (PAAH) after surface modification by 3-chloropropyltrimethoxysilane (CPTS). The modified silica gel was used for sorption of Cu(II), Ni(II) and Co(II) in aqueous solution. The effect of solution pH, sorption time, temperature and initial metal ion concentration onto metal ions sorption was investigated. The characteristics of the sorption process were evaluated by using the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) adsorption isotherms. The sorption of metal ions onto modified silica gel correlated well with the Langmuir type adsorption isotherm and adsorption capacities were found to be 0.012, 0.014 and 0.018 mmol g<sup>-1</sup> for Cu(II), Ni(II) and Co(II) metal ions, respectively. From the D–R adsorption isotherms, it was concluded that chemical interactions and chelating effects were playing an important role in the sorption of metal ions onto modified silica gel.

Thermodynamic parameters such as the standard free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were calculated to determine the nature of sorption process. From these parameters,  $\Delta H^\circ$  were found to be endothermic values: 38.39, 18.0, and 14.7 kJ mol<sup>-1</sup> for the same sequence of divalent cations and  $\Delta S^\circ$  values were calculated to be positive for the sorption of each metal ion onto the modified silica gel. Negative  $\Delta G^\circ$  values indicated that sorption process for all metal ions were spontaneous in nature although they presented an endothermic enthalpy for the interaction, resulting in an entropically favoured process.

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## 1. Introduction

Heavy metal pollution is spreading throughout the world with the expansion of industrial activities. Many industries, especially plating and battery, heavy metals are released in wastewaters. Many methods to removal of heavy metals from wastewaters such as chemical precipitation, membrane filtration, coagulation, complexing, solvent extraction, ion exchange and adsorption are used. Among them, inorganic supports immobilized with ion-chelating agents have received considerable attention for separation processes of heavy metals from aqueous solutions. The technique is the result of advances in the development of commercial extractants

for metal ion separation in the hydrometallurgical industries [1].

Silica gel is an amorphous inorganic support composed of internal siloxane groups (Si–O–Si) with silanol groups (Si–OH) distributed on the surface [2,3]. The active hydrogen atom of the silanol groups of silica gel has the ability to react with agents containing organosilyl functions, to give some organic nature to the precursor inorganic support [3,4]. The direct attachment of organic molecules to inorganic surfaces is difficult due to the relative inertness of the surfaces. Therefore, organic extractants can be attached to an inorganic surface by using surface modification procedures which are commonly used for enzyme immobilization and chromatographic separation [5,6]. A number of previous studies have shown that silica substrates can be modified with ion-chelating organic compounds to remove or concentrate metal ions in aqueous solutions. The advantage of using inorganic supports compared with polymeric supports can

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be summarized as follows: (1) excellent selectivity for a specific heavy metal ion; no swelling and good mechanical stability; (2) no interference from accompanying cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ), anions ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ) and complexing agents; (3) easy regeneration of the adsorbent and recovery of the adsorbed heavy metal ions; (4) no irreversible adsorption of organic compounds [7].

The aim of this work is to immobilize of Schiff base derivative 4-phenylacetophynone 4-aminobenzoylhydrazone (PAAH) onto silica gel for obtaining of new sorbent capable of remove heavy metals from wastewaters. The immobilization on the silica surface was performed after surface modification by 3-chloropropyltrimethoxysilane. The prepared sorbent was used to investigate the capabilities of removal of Cu(II), Ni(II) and Co(II) ions which are known to be commonly heavy metals from aqueous solution. In addition, the adsorption characteristics and thermodynamic properties of sorbent were examined.

## 2. Experimental

### 2.1. Materials and apparatus

Powdered silica (Merck) was used as the support, the characteristics of the support is listed in Table 1. 4-Phenylacetophynone 4-aminobenzoylhydrazone was synthesized according to method described in Section 2.2. 3-Chloropropyltrimethoxysilane (CPTS) (Merck) was used for treatment of the silica supports.  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck) were used to prepare metal ion solutions. The solutions (1000 mg/L) were prepared by dissolving appropriate amounts of metal salts in deionised water. The working solutions were prepared by diluting the stock solutions to appropriate volumes. The metal ion concentrations were measured using a UNICAM 930 model flame atomic absorption spectrometer equipped with deuterium lamp background correction, Hollow Cathode Lamp and air acetylene burner. ACHN Corder (Leco, Model CHNS-932) was used for elemental analysis to determine the amount of organic molecules in the substrates. IR (Perkin-Elmer) was used to investigate the degree of immobilization of 4-phenylacetophynone 4-aminobenzoylhydrazone on the surface of the silica support. In addition to this, scanning electron microscope was used for the characterization.

### 2.2. Synthesis of 4-phenylacetophynone 4-aminobenzoylhydrazone

4-Aminobenzoylhydrazone was prepared by refluxing ethyl 4-aminobenzoate (10 mmol, 1.65 g) with hydrazine hydrate (2.5 mL) for 4 h. The compound separated on standing over

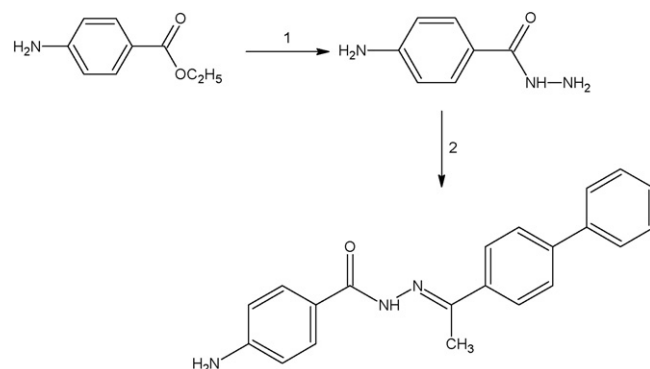


Fig. 1. (1)  $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ , reflux 4 h. (2) 4-Acetylbiphenyl, EtOH,  $\text{CH}_3\text{COOH}$ , reflux 2 h.

night, filtered and washed with distilled water. Pure hydrazine was obtained by recrystallization from hot ethanol.

4-Aminobenzoylhydrazone (10 mmol, 1.51 g) in hot ethanol (20 mL) was added to the solution of 4-acetylbiphenyl (10 mmol, 1.96 g) with two drops of glacial acetic acid in ethanol (30 mL). The reaction mixture was stirred while refluxing for 2 h and left over night. The separated compound was filtered off and washed several times with cold ethanol and dried in at room temperature to obtain the product, PAAH, as shown in Fig. 1. Mp 233–235 °C, yield 2.37 g (72%). IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3472 and 3373  $\nu(\text{NH}_2)$ , 3183  $\nu(\text{N-H})$ , 3052  $\nu(\text{Ar-H})$ , 2887–2978  $\nu(\text{CH}_3)$ , 1656  $\nu(\text{C=O})$ , 1629  $\nu(\text{C=N})$ , 1581  $\delta(\text{N-H})_{\text{amide II}}$ , 1320  $\nu(\text{C-N})$ , 1025  $\nu(\text{N-N})$ .  $^1\text{H NMR}$  ( $\delta$ , ppm) ( $\text{DMSO-}d_6$ ): 11.12 (s, 1H, NH,  $\text{D}_2\text{O}$  exchange), 6.93–7.95 (m, 13H, Ar-H), 6.51 (s, 2H,  $\text{NH}_2$ ,  $\text{D}_2\text{O}$  exchange), 2.60 (s, 3H,  $\text{CH}_3$ ). Anal Calcd. for  $\text{C}_{21}\text{H}_{13}\text{N}_3\text{O}$ : C 76.59, H 5.77, N 12.76; found C 76.94, H 5.55, N 12.92. UV–vis (ethanol, nm): 240, 267 sh, 323.

### 2.3. Functionalization

Silica was activated in a stream of dry nitrogen by heating at 423 K for 10 h and used immediately [8]. A sample of 2.0 g of activated silica gel was suspended in 50  $\text{cm}^3$  of dry toluene and 2.0  $\text{cm}^3$  (10.6 mmol) of CPTS was added to this suspension. The mixture was mechanically stirred under reflux of the solvent in an inert atmosphere for 72 h. The mixture was filtered and the solid was washed with toluene and dried under vacuum at room temperature for several hours, to give the modified silica, named SiCl [9,10] (Fig. 2a).

### 2.4. Preparation of silica immobilized with 4-phenylacetophynone 4-aminobenzoylhydrazone

A sample of 9.32 mmol of SiCl reacted with 1.97 mmol of the compound PAAH in 50  $\text{cm}^3$  of toluene, containing 2.0  $\text{cm}^3$  of triethylamine in order to favour the reaction equilibrium [11]. Triethylamine was used as disprotonant agent to increase the efficiency of the reaction. The mixture was kept under reflux and mechanically stirred for 72 h at 373 K. The final product, 4-phenylacetophynone 4-aminobenzoylhydrazone immobilized silica, was filtered, washed with toluene and ethanol, and dried under vacuum at room temperature for 24 h (Fig. 2b).

Table 1  
Properties of silica used as a support in this study

Surface area ( $\text{m}^2/\text{g}$ )	480–540
Diameter (mm)	0.063–0.2
Pore volume ( $\text{cm}^3/\text{g}$ )	0.74–0.84

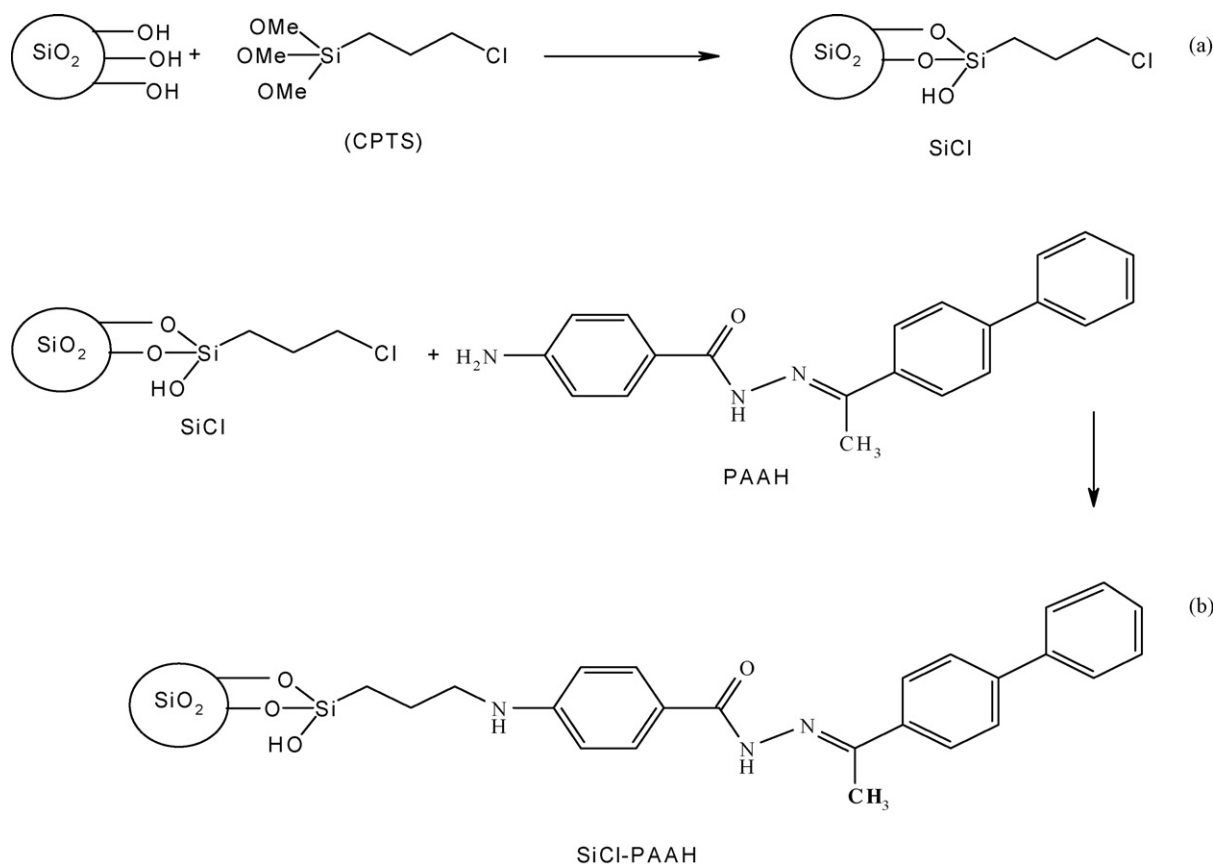


Fig. 2. (a) Attachment of the 3-chloropropyltrimethoxysilane onto silica support; (b) immobilization of 4-phenylacetophynone 4-aminobenzoylhydrazone onto SiCl.

### 2.5. Sorption experiments

The effects of solution pH, sorption time, temperature and metal ion concentration on the sorption were obtained by using the batchwise method, in which a series of samples of 50.0 mg of SiCl-PAAH were suspended in 10.0 cm<sup>3</sup> of Cu(II), Ni(II) and Co(II) aqueous solutions. The samples were mechanically stirred for predetermined time period at room temperature and the solid was separated by filtration. Temperature experiments were carried out between 20 and 50 °C.

Experiments were repeated three times in each case. Initial and equilibrium metal ion concentrations in the aqueous solutions were determined by using flame atomic absorption spectrometer. The amount of metal ions sorbed by sorbent was calculated as

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

where  $q$  is the amount of metal ions adsorbed onto unit amount of the adsorbent (mmol g<sup>-1</sup>),  $C_0$  and  $C$  the concentrations of metal ions in the initial and equilibrium concentrations of the metal ions in aqueous phase (mmol L<sup>-1</sup>),  $V$  the volume of the aqueous phase (L), and  $W$  is the dry weight of the adsorbent (g).

## 3. Results and discussion

### 3.1. Synthesis and characterization 4-phenylacetophynone 4-aminobenzoylhydrazone anchored silica gel

In spite of the variety of coupling strategies, only few satisfy the most important demands such as the formation of stable bonds between ligand and matrix as well as the high yield. One of the methods most widely used for the activation of silica involves the formation of an intermediate silane-coupling agent, which is chosen according to the anchoring group of the organic ligand [10]. In this case, the ligand has an aminoalkyl group attached to the chelating moiety. Aminoalkyl group does not direct attach to silica surface. Firstly, attachment to silica surface of 3-chloropropyltrimethoxysilane is the most adequate for bonding the ligand by nucleophilic attack.

For immobilization of PAAH onto the surface of a commercially available silica gel in the first step, the silica was grafted 3-chloropropyltrimethoxysilane onto silica gel to yield the new surface, SiCl, as represented in Fig. 2a. In the next stage, this precursor was reacted with 4-phenylacetophynone 4-aminobenzoylhydrazone, presented in Fig. 2b.

The degree of immobilization on the surface was determined by considering the elemental analysis data. From the percentage amount of carbon, 7.27 and 43.22 for SiCl and SiCl-PAAH. The number of moles of compounds attached onto surface were

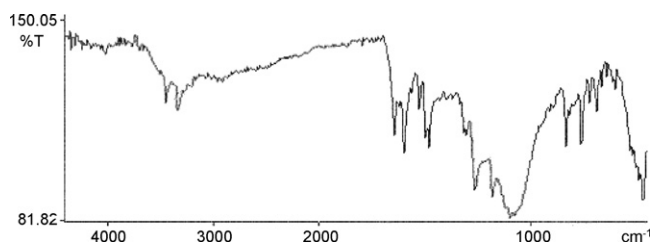


Fig. 3. Infrared spectra of SiCl-PAAH.

calculated as 2.01 and 1.50 mmol/g for the SiCl and SiCl-PAAH surfaces, respectively.

The immobilization onto silica surface can also be confirmed through infrared spectra for the silica, the modified SiCl surface and the anchored SiCl-PAAH final surface. The main features of the silica spectra are connected to the similarity of bands associated with the inorganic backbone such as (i) a large broad band between 3400 and 3200  $\text{cm}^{-1}$ , which is attributed to the presence of the O–H stretching frequency of silanol groups and also to the remaining adsorbed water, (ii) the intense band related to the siloxane stretching (Si–O–Si) of these groups at 1100  $\text{cm}^{-1}$ , (iii) a band assigned to Si–OH stretching frequency for silanol groups at 900  $\text{cm}^{-1}$  and (iv) the band around 1650  $\text{cm}^{-1}$ , assigned to angular vibration of water molecules [10,12]. Adsorption bands 3344, 1090, and 850  $\text{cm}^{-1}$  was observed for PAAH, which is presented N–H stretching. The phenyl vibrations appear at 1595, 1535, 500, 1460, 1415, and 1345  $\text{cm}^{-1}$  and further support the immobilization of PAAH, as shown in Fig. 3 [13].

In addition to this, the images of the sorbent surface were examined by scanning electron microscopy. Firstly, it could be found that the surface of silica gel support was smooth. After immobilization of the 4-phenylacetophynone 4-aminobenzoylhydrazone material, the surface could have large surface area. Fig. 4 presented SEM of the surface of PAAH immobilized onto silica [14,15].

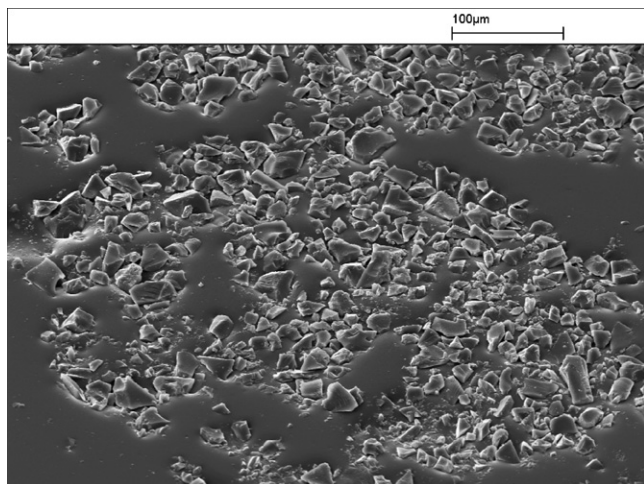


Fig. 4. SEM of the surface of 4-phenylacetophynone 4-aminobenzoylhydrazone immobilized silica.

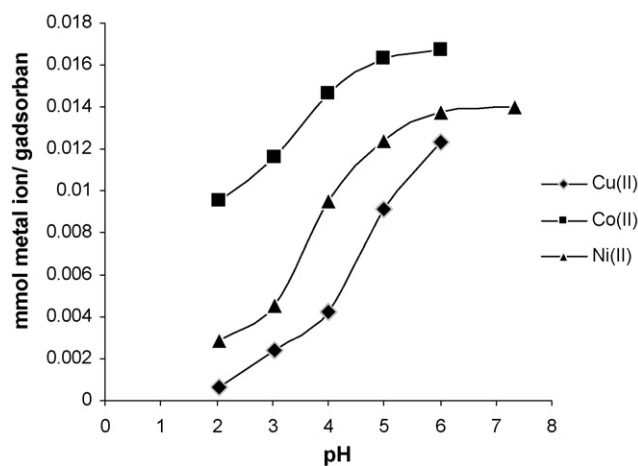


Fig. 5. The effect of pH on the sorption of Cu(II), Co(II) and Ni(II) metal ions. ( $C_0 = 1.10^{-4} \text{ mol L}^{-1}$ ;  $t = 120 \text{ min}$ ;  $m (\text{adsorbent}) = 0.05 \text{ g}$ ; temperature: 25 °C).

### 3.2. Optimum conditions for sorption

#### 3.2.1. Effect of pH

The pH value of medium is one of the most important factors controlling the sorption of metal ions by modified silica gel due to the competitive reactions between chelate forming groups and hydrogen ions in solution. Since the SiCl-PAAH has nitrogen atoms, pH dependencies of the metal ions uptake have to be determined. The sorption of metal ions on sorbent was examined at different pH values and were presented in Fig. 5.  $\text{pH} > 7.0$  was not studied, due to all divalent cations are sensible to suffer hydrolysis and degeneration of silica gel in strong alkali [11]. Cu(II) and Co(II) can be hydrolyzed at  $\text{pH} > 6.0$ .

A general increase in adsorption with increasing pH of solution was observed. At very low pH, the competition between  $\text{M}^{2+}$  and the higher concentration of  $\text{H}^+$  ions for sorption sites is favour of  $\text{H}^+$ , and as a result, less removal efficiency was observed at low pH. As the pH increased, the adsorption surface becomes less positive and therefore electrostatic attraction between the metal ions and sorbent surface is likely to be increased. The optimum pH value at which the maximum metal uptake could be achieved, were obtained as 6.0, 7.0 and 5.0 for Cu(II), Ni(II) and Co(II), respectively.

#### 3.2.2. Equilibrium time

Metal ions sorption capacities were determined as a function of time to determine an optimum contact time for the sorption of heavy metal ion on sorbent. The sorption equilibrium time are attained within 120 min for each metal ions.

### 3.3. Effect of initial concentration and sorption isotherms

The effect of initial concentrations on metal ion sorption was investigated by varying the initial concentrations of the metal ions at optimum pH values and 2 h of equilibration time and obtained results was presented in Fig. 6. The higher is the initial concentration of the metal ion, the larger is the amount of the metal ion taken up. This increase in loading capacity of the sorbent with relation to the metal ions concentration can

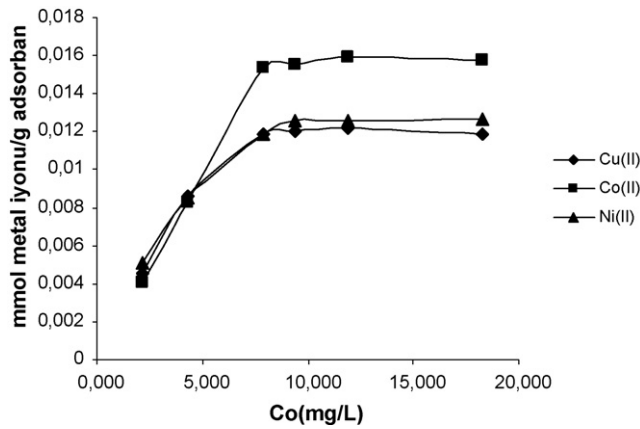


Fig. 6. Effect of initial concentration for metal ions adsorption on adsorbent. (Cu(II) pH 6.0; Co(II) pH 5.0; Ni(II) pH 7.0;  $t$ : 120 min;  $m$  (adsorbent): 0.05 g; temperature: 25 °C).

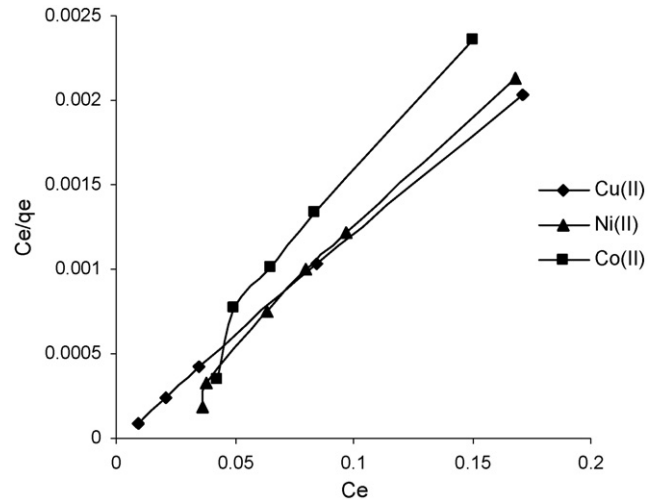


Fig. 7. The Langmuir sorption isotherms for each metal ions.

be explained with the high driving force for mass transfer [16]. Experimental data obtained from the effect of initial concentration on sorption capacity were fitted to Langmuir, Freundlich and D–R adsorption isotherms. The linearized forms of the equations representing the models were used.

### 3.3.1. Langmuir isotherm

The sorption data were firstly adjusted to the Langmuir adsorption model, shown in Eq. (2). In this model, it is assumed that monolayer is formed on a structurally homogeneous adsorbent surface. It is valid for monolayer adsorption onto a surface containing a finite number of identical sites [17].

$$\frac{C_e}{q_e} = \frac{C_e}{Q^0} + \frac{1}{bQ^0} \quad (2)$$

where  $q_e$  is the amount of solute adsorbed on the surface of the adsorbent ( $\text{mmol g}^{-1}$ ),  $C_e$  the equilibrium ion concentration in the solution ( $\text{mmol L}^{-1}$ ),  $Q^0$  the maximum surface density at monolayer coverage and  $b$  is the Langmuir adsorption constant ( $\text{L mmol}^{-1}$ ). When  $C_e/q_e$  is plotted against  $C_e$ , a straight line with slope  $1/Q^0$  and intercept  $1/bQ^0$  is obtained. The Langmuir parameters for each metal ion,  $Q$  and  $b$ , are calculated from the slope and intercept of the graphs (Fig. 7) and are given in Table 2.

### 3.3.2. Freundlich isotherm

The Freundlich adsorption model [18], which assumes that the adsorption occurs on heterogeneous surfaces, can be expressed using Eq. (3)

$$q_e = K_F C_e^{1/n} \quad (3)$$

The Freundlich equation is basically empirical but is often useful as a means for data description. Data are usually fitted to the logarithmic form of the equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

where  $q_e$  is the equilibrium solute concentration on adsorbent ( $\text{mmol g}^{-1}$ ),  $C_e$  the equilibrium concentration of the solute ( $\text{mmol L}^{-1}$ ),  $K_F$  the Freundlich constant ( $\text{mmol g}^{-1}$ ) which indicates the adsorption capacity and represents the strength of the adsorptive bond and  $n$  is the heterogeneity factor which represents the bond distribution. When  $\ln q$  is plotted against  $\ln C$ , a straight line with slope  $1/n$  and intercept  $\ln K$  is obtained. The Freundlich parameters for the adsorption of Cu(II), Ni(II) and Co(II) ions are given in Table 2. On the comparison of the  $R^2$  values given Freundlich and Langmuir, we can conclude that in all cases for the sorption of metal ions to the adsorbent. Langmuir equation represents a better fit to the experimental data than the Freundlich equation. This reflects the satisfaction of the langmuir isotherm model for the adsorption of each metal ion.

The Freundlich type adsorption isotherm is an indication of surface heterogeneity of the adsorbent while the Langmuir type isotherm corresponds to surface homogeneity of the adsorbent. This led to the conclusion that the surface of the immobilized silica with PAAH is made up of small homogeneous adsorption patches. This also confirms of the images of SEM is homogeneous structure of immobilized PAAH on the silica gel.

Table 2  
Langmuir and Freundlich constants

Langmuir isotherm parameters				Freundlich isotherm parameters		
Metal	$Q^0$ ( $\text{mmol g}^{-1}$ )	$b$ ( $\text{L mmol}^{-1}$ )	$R^2$	$K_F$ ( $\text{mmol g}^{-1}$ )	$n$	$R^2$
Cu	0.012	13,888	0.9995	0.039	5.977	0.8898
Ni	0.014	4,411	0.9872	0.32	2.133	0.9209
Co	0.018	4,347	0.9745	1.47	1.513	0.9525

Table 3  
D–R isotherm parameters

	$q_m$ (mmol g <sup>-1</sup> )	$k$ (mol <sup>2</sup> kJ <sup>-2</sup> )	$E$ (kJ mol <sup>-1</sup> )	$R^2$
Cu	0.0252	0.0013	19.61161	0.9887
Ni	0.094	0.004	11.18034	0.9322
Co	0.257	0.005	9.449112	0.9626

### 3.3.3. D–R isotherm

Another equation that has been used to determine the possible adsorption mechanisms is the Dubinin–Radushkevich equation. The D–R isotherm is more general than the Langmuir isotherm, because it does not assume a homogeneous surface or constant sorption potential [19].

The D–R isotherm which is given with the following Eq. (5)

$$q_e = q_m \exp(-k\varepsilon^2) \quad (5)$$

and linearized form of the equation is given as Eq. (6)

$$\ln q_e = \ln q_m - k\varepsilon^2 \quad (6)$$

where  $\varepsilon$  (Polanyi potential) is  $[RT \ln(1 + (1/C_e))]$ ,  $q_e$  the amount of solute adsorbed per unit weight of adsorbent (mol g<sup>-1</sup>),  $k$  a constant related to the adsorption energy (mol<sup>2</sup> kJ<sup>-2</sup>) and  $q_m$  is the adsorption capacity (mol g<sup>-1</sup>). The values of  $q_m$  and  $k$  were calculated from the intercept and slope of the  $\ln q_e$  versus  $\varepsilon^2$  plots and presented in Table 3. The mean free energy of adsorption ( $E$ ) was calculated from the  $k$  values using Eq. (7)

$$E = (-2k)^{-1/2} \quad (7)$$

The magnitude of  $E$  is useful for estimating the type of sorption reaction, i.e., an energy range from about 8 to 16 kJ mol<sup>-1</sup> indicates electrostatic processes (ion exchange). In the case of  $E < 8$  kJ mol<sup>-1</sup>, physical forces such as van der Waals and hydrogen bonding may affect the sorption mechanism [19]. In this study,  $E$  values are calculated to be 11.18034, 9.449112 for Ni(II) and Co(II), respectively. Therefore, it is possible to say that adsorption mechanism of Ni(II) and Co(II) metal ions can be explained with an ion-exchange process, but the  $E$  value (19.61161) obtained for Cu(II) is showed that chemisorption takes part in the adsorption process with chelating effects of the functional groups available on the surface adsorbent.

### 3.4. Thermodynamic parameters

Thermodynamic parameters such as free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were determined using the following Eqs. (8)–(10)

$$\Delta G^\circ = -RT \ln K_d \quad (8)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

$$\log K_d = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (10)$$

where  $\Delta G^\circ$  = change in free energy, kJ mol<sup>-1</sup>;  $\Delta H^\circ$  = change in enthalpy, kJ mol<sup>-1</sup>;  $\Delta S^\circ$  = change in entropy, J (mol K<sup>-1</sup>)<sup>-1</sup>;  $T$  = absolute temperature, K;  $R$  = gas constant =  $8.314 \times 10^{-3}$ ;  $K_d$  = equilibrium constant.

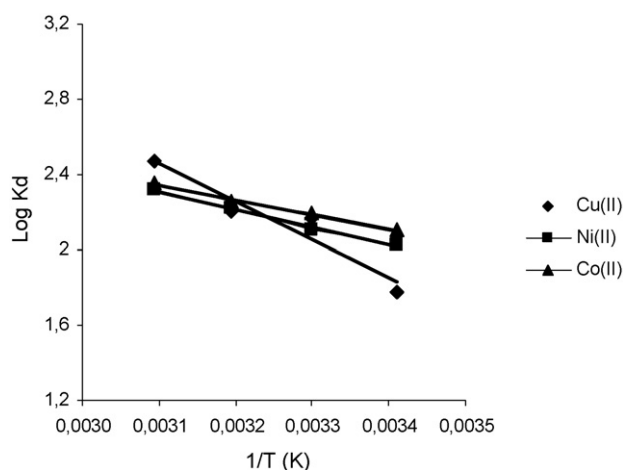


Fig. 8. Log  $K_d$ – $1/T$  graphs for the sorption of Cu(II), Ni(II) and Co(II) onto modified silica gel. (Cu(II) pH 6.0; Co(II) pH 5.0; Ni(II) pH 7.0;  $t$ : 120 min;  $m$  (adsorbent): 0.05 g)

When  $\log K_d$  is plotted against  $1/T$ , a straight line with slope  $\Delta H^\circ/2.303RT$  and intercept  $\Delta S^\circ/2.303R$  is obtained (Fig. 8) and the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were obtained from the slope and intercept of the van't Hoff plots. The obtained thermodynamic parameters for the sorption process are given in Table 4. Positive values of  $\Delta H^\circ$  suggest the endothermic nature of the adsorption. Although there are no certain criteria related to the  $\Delta H^\circ$  values that define the adsorption type, the heat of adsorption values between 5.0 and 100 kcal mol<sup>-1</sup> (20.9–418.4 kJ mol<sup>-1</sup>), which are heats of chemical reactions, are frequently assumed as the comparable values for the chemical adsorption processes [20].  $\Delta H^\circ$  values were found as 38.39, 14.7 and 18 kJ mol<sup>-1</sup> for Cu(II), Co(II) and Ni(II), respectively. Observed value of the heat sorption of Cu(II) ions on sorbent are of the same magnitude as the heat of chemisorption, moreover this result has showed reasonable agreement with  $E$  value obtained from the D–R isotherms.

The negative values of  $\Delta G^\circ$  indicate spontaneous nature of the adsorption process. However, the negative value of  $\Delta G^\circ$  decreased with an increase in temperature, indicating

Table 4  
Thermodynamic parameters for the sorption of Cu(II), Co(II), Ni(II) metal ions onto adsorbent

Metal	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (kJ K <sup>-1</sup> mol <sup>-1</sup> )	$T$ (K)	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$R^2$
Cu	38.39	0.166	293	-10.28	0.9189
			303	-11.94	
			313	-13.60	
			323	-15.26	
Co	14.7	0.09	293	-11.80	0.9905
			303	-12.70	
			313	-13.60	
			323	-14.51	
Ni	18.0	0.100	293	-11.32	0.993
			303	-12.32	
			313	-13.32	
			323	-14.32	

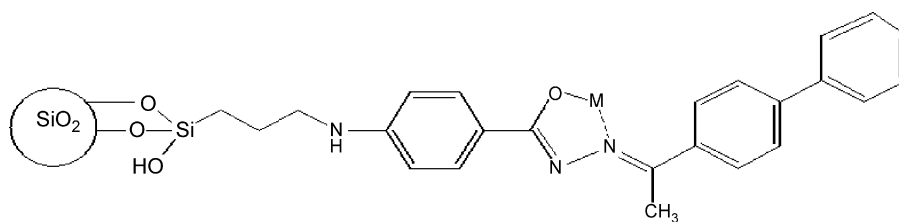


Fig. 9. Proposed scheme for adsorption of divalent cations from aqueous solution onto a SiCl-PAAH surface.

that the spontaneous nature of adsorption is inversely proportional to the temperature. The positive values of  $\Delta S^\circ$  show the increased randomness at the solid/solution interface during the adsorption process. The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational energy than is lost by the adsorbate ions, thus allowing the prevalence of randomness in the system. Enhancement of adsorption capacity at higher temperatures may be attributed to the enlargement of pore size and/or activation of the adsorbent surface [19].

The thermodynamic data obtained for the adsorption processes indicated that the reactions between divalent metal ions and modified silica gel were spontaneous. However, all of the interactions presented endothermic enthalpy values produced by chelating effect of metal ion complexation (Fig. 9). Hence, the spontaneity of adsorption was a consequence of the increase in entropy [21–23].

#### 4. Conclusion

In the presented study, the preparation and use of modified silica gel was discussed. The immobilization of organic reagents on to the surface of a silica gel offers a number of advantages. Silica gel can easily be modified with a wide variety of functional groups, thus leading to their use in numerous applications.

In the present work, 4-phenylacetophenone 4-aminobenzoyl-hydrazone was immobilized on the surface of silica after surface modification by 3-chloropropyltrimethoxysilan. The new material contains many nitrogen basic centers, has ability to adsorb divalent cations from aqueous solutions. The resulting organically modified silica gel has the potential to sorption Cu(II), Co(II) and Ni(II) ions from aqueous solutions. The removal of metal ions strongly depends on the solution pH. The maximum removal of Cu(II), Co(II) and Ni(II) was observed at an optimum pH of 6.0, 5.0 and 7.0, respectively.

Sorption of all the metal ions on the prepared sorbent can be expressed better with Langmuir type adsorption isotherms which shows the homogenous characteristics of the sorption sites on sorbent. Sorption capacities order was found as Co(II) > Ni(II) > Cu(II). Although the sorption process of Co(II) and Ni(II) ions onto modified silica gel can be explained with an ion-exchange process. It was found that chelating effect of the functional groups for the sorption of Cu(II) ion on sorbent was showed. Chelating interactions are accompanied by an increase in entropy and exhibit endothermic enthalpy values.

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