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Chemical modification of silica gel with hydrazine carbothioamide derivative for sorption studies of Cu(II), Ni(II) and Co(II) ions

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ABSTRACT

2-((1H-pyrrol-2-yl)methylene)hydrazinecarbothioamide was chemically immobilized onto silica gel modified with *3-chloropropyltrimethoxy silane*. The modified surfaces were characterized by infrared spectroscopy and thermogravimetric analysis. The sorption of Cu(II), Co(II), and Ni(II) ions were evaluated by using batch methods. The values of adsorption of metal ions were detected by an atomic absorption spectrometer. The influences of concentration, temperature, amount of metal ions, and pH to sorption on the modified silica gel with Schiff base were also investigated. The maximum adsorption capacities and isotherm parameters were calculated from the *Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm equations*. Thermodynamic parameters such as free energy (ΔG°), entropy (ΔS°), and enthalpy (ΔH°) were also calculated from the sorption results. The modified structure used as adsorbent was successfully employed in the removal of Cu(II), Ni(II), and Co(II) traces from the aqueous solutions.

Keywords: Adsorption; Immobilization; Silica gel; Thermal analysis

1. Introduction

Silica modified with both inorganic and organic functionalities have been used for metal ion preconcentration [1], ion exchange [2], biotechnology [3], catalysis [4], adsorption [5], clean technology, and green chemistry [6]. Among these methods; adsorption technique is one of the most hopeful important techniques for the purification of waste water containing heavy metal ions [7]. Silica gel provides good solid support for adsorption due to its thermal, chemical, and mechanical stability [8]. It has a high surface area of 480–540 m^2/g, micro pore size of 6 nm and can be used at a relatively low cost [9]. Silica surface consist of two types of functional groups, siloxane (Si–O–Si), and silanol (Si–OH) functionalized with different functional groups [9–11].

The modified silica gels generally provide higher adsorption capacities than other solid structures lot of organic used as a support. So immobilized molecules have got a good adsorption capacity for metal ions [12,13]. The chemical immobilization with appropriate organic groups on silica gel forms a new surface. It could be used as an adsorbent for the removal of heavy metal ions.

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Environmental contamination with heavy metals represents a potential threat to humans, plants, and animals. Many heavy metal compounds are highly soluble in water, thus becoming more available for living systems [14]. After being absorbed by organisms, heavy metals can bind to different biomolecules altering their normal structure and function.

Cu(II), Ni(II), and Co(II) ions from industrial wastewater and polluted water from other sources have become a serious problem [14] as these ions are toxic, nonbiodegradable and tend to be accumulated in the human vital organs where they can act progressively over a long period through food chains [15]. The main effect of the immobilization of *Schiff bases* [2-((1H-pyrrol-2-yl)methylene)hydrazinecarbothioamide (*PHTA*)] 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 *PHTA* on the silica gel by using batch method and to check the capabilities of novel modified adsorbent for removal of Cu(II), Co(II), and Ni(II) ions from aqueous solution.

The novelty of the study is synthesis of the *PHTA* in our lab followed by immobilization of Schiff base on to silica gel surface. The substance synthesized (*PHTA*) is not soluble in water and can contribute to separation and purification methods.

2. Materials and methods

2.1. Materials

Silica gel (Merck Darmstadt Co.) with high surface area of 480–540 m^2/g, micro pore size of 6 nm, diameter of 0.036–0.200 mm, pore volume of 0.74–0.84 ($cm^3\ g^{-1}$) and particle size of 70–180 μm was used in the study. *3-chloropropyltrimethoxy silane* (*CPTS*) and Cu(II), Ni(II), and Co(II) nitrate salts were also purchased from Merck. A series of standard metal solution with appropriate dilution of the stock metal solution were prepared. The diluted NaOH and HNO_3 solutions were used for pH adjustments. All the chemicals used in the study were analytical graded.

2.2. Instruments

The infrared spectra were obtained in the range of 650–4,000 cm^{-1} by using Perkin Elmer 100 FTIR spectrometer (KBr pellets, 21°C temperature, 1 atm pressure). Thermogravimetric (TG) curves were obtained on a Setaram TG Analyzer/Setsys analyzer at temperature range of 298–1273 K (in N_2, 10°C/min) with heating rate of 20°C/min. 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°C temperature, 1 atm pressure, ContrAA 300, Analytikjena). All aqueous solutions were prepared with ultra pure distilled water obtained from a water purification system (Millipore Milli-Q Plus).

2.3. Synthesis of PHTA

Thiosemicarbazide (0.91 g, 10 mM) was dissolved in 30 mL absolute ethanol and then 20 mL solution of *pyrrole-2-carboxaldehyde* (0.951 g, 10 mM was added). The mixture was refluxed for 2 h at 60–70°C, and then left to stand overnight at room temperature. The solid product was filtered, washed several times with ethanol, and dried in vacuum (yield 1.45 g, 86%; m.p. 198°C). Infrared spectroscopy (IR) spectroscopy (KBr pellet, ν, cm^{-1}) was recorded as 3568 (Si–OH) 2978–2927 (aromatic and aliphatic CH), 1651 (C=S or HC=N), 1442 (aromatic C=C stretching), 1352 (vinyl C–NH_2 bending), 1050 (classic Si–O), 845–699 (NH, out of plane bending), Characteristic ^1H NMR peaks (DMSO-d_6, TMS, δ ppm): 6.08 (dd, 1H, pyrrole), 6.38 (m, 1H, pyrrole), 6.95 (d, 1H, pyrrole), 7.81 (s, 1H, –N=CH–), characteristic ^{13}C NMR peaks (DMSO-d_6, TMS, δ ppm): 110.09 (C1), 119.2 (C2),124.8 (C3), 132.7 (C4), 152.2 (C5), 178.5 (C6). The scheme of target structure is given in Fig. 1.

2.4. Activation of silica gel

A 100 mL concentrated HCl solution was added on to 100 g silica gel and the mixture was heated at 150°C under reflux for 72 h. It was filtered in vacuum and washed with distilled water until the medium was

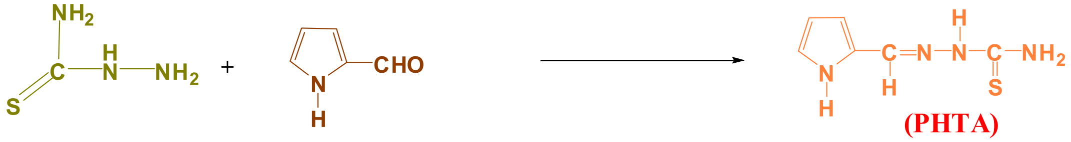

Fig. 1. Scheme of the preparation of the *PHTA*.

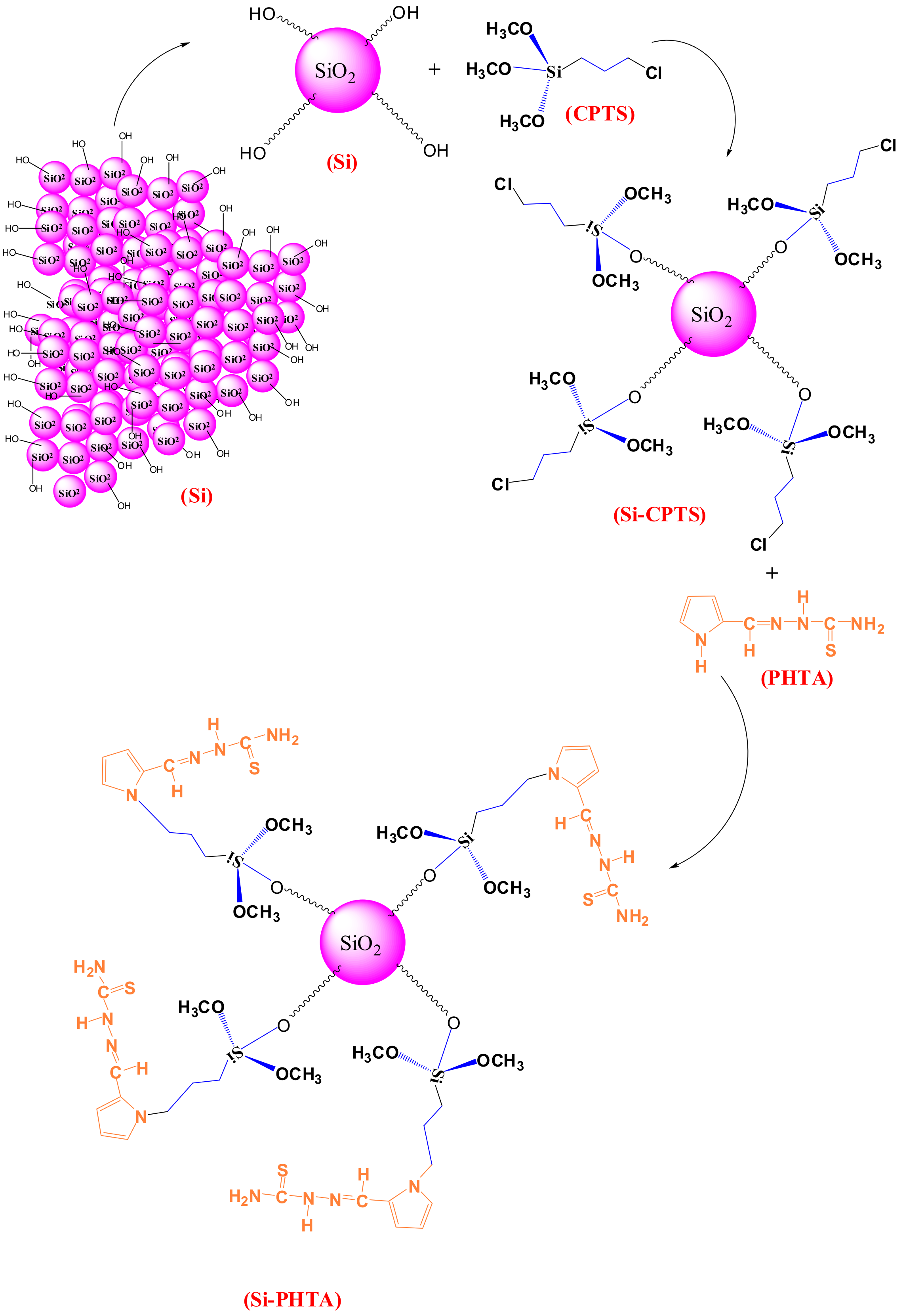

Fig. 2. Possible structure of silica gel bonded *PHTA* molecules.

completely removed from HCl. The sample dried in vacuum oven for 24 h at 180 °C.

2.5. Preparation of Si-PHTA

Silica gel was converted into Si–OH [16]. The immobilization of the *CPTS* onto silica gel was carried out by the suspended 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% of *PHTA* 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-PHTA*. The scheme of target structure is given in Fig. 2.

2.6. Sorption studies

A 20 mg of sorbent with 10 mL of sorbate of various concentration, and pH was 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 a flame AAS, and the amount of cations sorbed was calculated with using Eq. (1):

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

where q is the amount of metal ion sorbed onto unit amount of the adsorbent (mM g^{-1}), C_0 and C_e are the initial and equilibrium concentrations of the metal ions in aqueous phase (mML^{-1}), V is the volume of the aqueous phase (L), and W is the dry weight of the adsorbent (g).

2.6.1. pH studies

A 20 mg of *Si-PHTA* was stirred in the presence of 10 mL of Cu(II), Ni(II), and Co(II) solutions in 10 mML^{-1} concentration, and studied to different pH values (2.0, 3.0, 4.0, 5.0, 6.0, 7.0). The mixture was shaken for 180 min at 298 ± 1 K [17].

2.6.2. Effect of concentration

The sorption was investigated by batch method for aqueous solution of Co(II), Cu(II), and Ni(II) nitrates at 298 ± 1 K. For these sorption measurements, 20 mg of *Si-PHTA* was suspended in 10 mL of aqueous solution containing various amounts (0.01, 0.015. 0.025, 0.05, and 0.075 g) of each cation. These suspensions were shaken in concentrations between 8.0 and 40.0 ± 0.01mMdm^{-3} in a shaker thermostat for 180 min [18]. After equilibrium was established, the amounts of metallic cations remaining in solution were determined by AAS.

2.6.3. Temperature studies

The experiments were carried out between 20 and 50 ± 1 °C at different 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 two main stages for the organofunctionalization of the silica gel surface is given in Fig. 3. The functionalized silica gel was characterized by FTIR, TGA. The infrared spectra of the prepared surface (*Si-CPTS* and *PHTA*) were compared with raw silica gel shown in Fig. 3. The location of the different silanol groups at the mid IR range (650–4,000 cm^{-1}) was shown in Table 1. Three bands placed at 3,747, 3,680, and 3,535 cm^{-1} are available germinal, vicinal and silanol groups respectively.

OH stretching vibration in *Si-CPTS* was shifted to 3,321 cm^{-1} from 3,374 cm^{-1} (Si). Hence, the frequency of CH$_2$ stretching vibrations in *Si-CPTS* was observed at 2,975–2,885 cm^{-1}, Fig. 3; spectrum of *Si-PHTA* has broad –OH peak at 3,268 cm^{-1} due to the –OH groups which are in the structure of silica-based organic compounds [20]. Stretching of C=N observed at 1,651 cm^{-1} indicates the presence primer amine groups in *Si-CPTS* and *PHTA* and organic substances. The peak at 1,111 cm^{-1} was bending of –C–OH and 1,442 cm^{-1} peak was interpreted as stretching of C=C in the pyrrole ring [13].

The TG curves of the synthesized compounds are given in Fig. 4 and the results of TGA are also summarized in Table 2. The curves showed that the synthesis compounds decompose in the third step. *Si-PHTA* has more thermal stability than *Si-CPTS* and distinct mass losses, reflecting the molar mass of the pendant groups covalently bonded to inorganic phase. Losses of moisture, adsorbed solvent was initially lost at low temperature (2.60–2.65%, respectively). An increase in temperature caused to the condensation of surface groups resulted in first mass loss step. The second mass losses can be organic groups

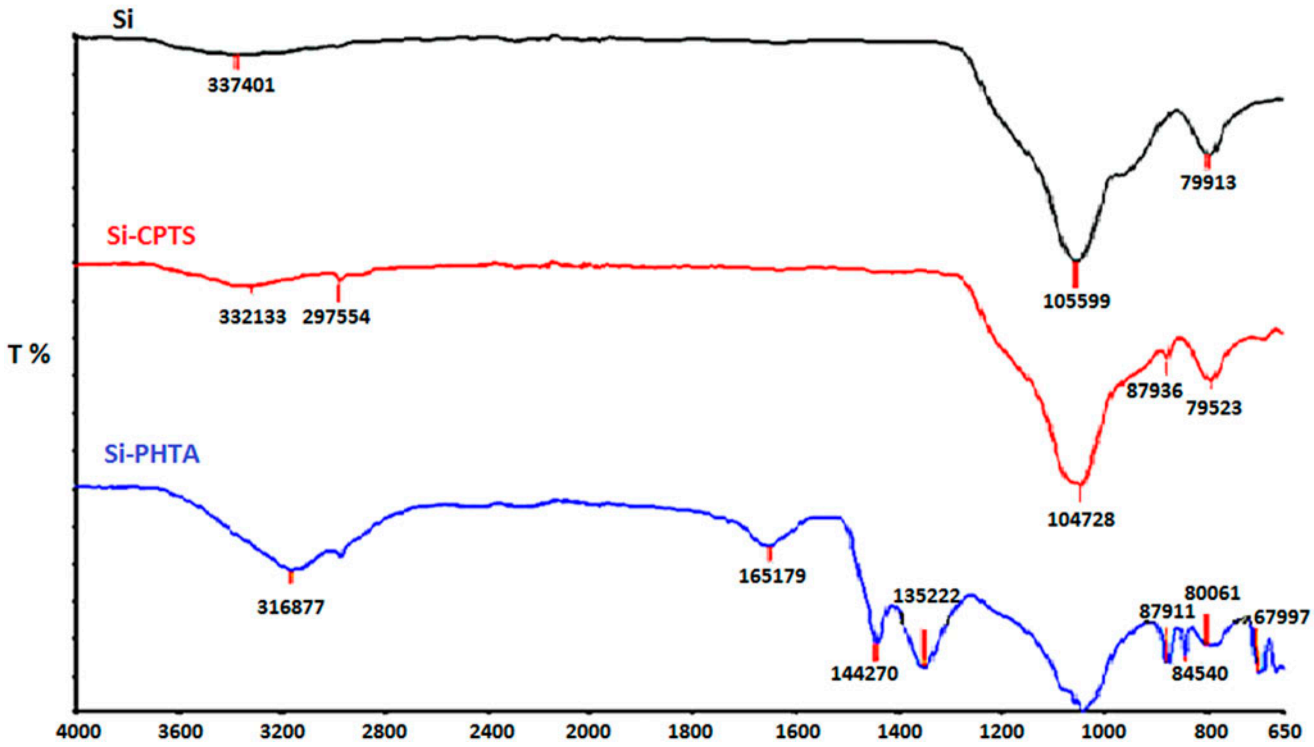

Fig. 3. FTIR spectra of Si (a), *Si-CPTS* (b), and *Si-PHTA* (c).

Table 1
Assignments of IR bands of silica gel samples

Cinnoline types	Adsorption band (cm^{-1})
Isolated silanol on the surface	3,745
Vicinal silanol on the surface	3,660 (wide)
Molecular water adsorbed on the surface	3,400

immobilized to surface. An abrupt loss in mass detected in the third mass loss region, suggesting the progressive release of the silica gel attached to silane molecules [21].

According to the results of elemental analysis, the percentage amounts of carbon, nitrogen and hydrogen are shown in Table 3.

3.2. Adsorption studies

3.2.1. Effect of adsorption

Fig. 5(a) shows effect of the amount of sorbent on the sorption of Cu(II), Ni(II), and Co(II). The adsorption change depending on the increase of the amount of adsorbent. When the amount of adsorbent increased, the total amount of adsorbing metal ions increased and reached steady state values. The maximum sorption amount of adsorbent most effective for Cu(II) = Ni(II) = Co(II) ions was found as 0.05 g. The excess of the metal ion might be adsorbed by 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 Cu(II), Co(II), and Ni(II) ions. As expected, the contact time increased to the amount of adsorption for the studied metal ions and reached at steady state values.

3.2.3. Effect of pH

The effect of pH on the sorption studied for Cu(II), Co(II), and Ni(II) ions is as shown in Fig. 5(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 [22]. The pH for maximum sorption of Cu(II) = Ni(II) = Co(II) ions was found as 5.

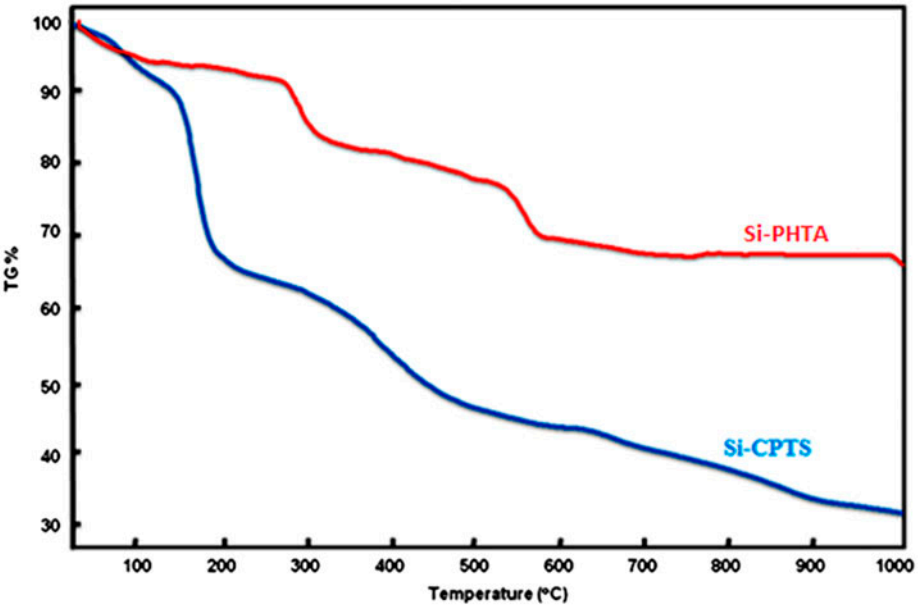

Fig. 4. TG curves of Si, *Si-CPTS*, and *Si-PHTA*.

Table 2
Thermal degradation values of the synthesized compounds

	First degradation temperature (℃)				Second degradation temperature (℃)				Third degradation temperature (℃)					
Compounds	T_{on}	T_{max}	T_{end}	Weight loss (%)	T_{start}	T_{max}	T_{end}	Weight loss (%)	T_{start}	T_{max}	T_{end}	Weight loss (%)	Loss of absorbed water (%)	Char at 1,000℃
1	104	192	436	40.40	436	555	766	6.60	766	806	1,000	14.40	2.60	26
2	97	165	278	6.30	278	394	604	21.50	604	751	1,000	6.20	2.65	66

Table 3
Percentages (%) of hydrogen (H), carbon (C), and nitrogen (N) for the matrices SiO_2, *Si-CPTS*, and *Si-PHTA*

Surface	Nitrogen (%)	Carbon (%)	Hydrogen (%)	Carbon (mM g^{-1})
SiO_2	0	0	0	–
Si-Cl	0	7.21	0.83	1.24
Si-PHTA	5.02	34.24	2.32	1.02

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

3.2.5. Effect of temperature

Fig. 5(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 parameter values also changed with increasing temperature.

3.3. Adsorption isotherms

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

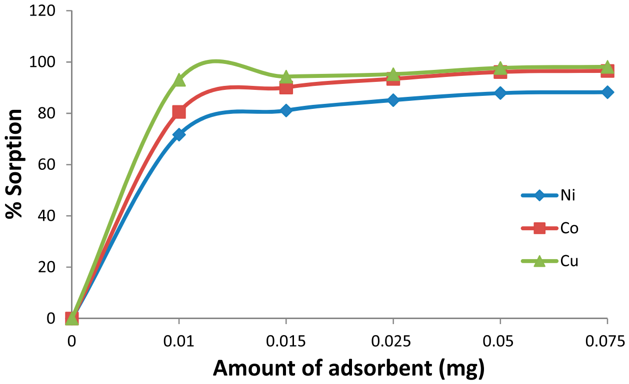

Fig. 5a. The effect of the amount of Cu(II), Co(II), and Ni (II) ions on the amount of sorbent.

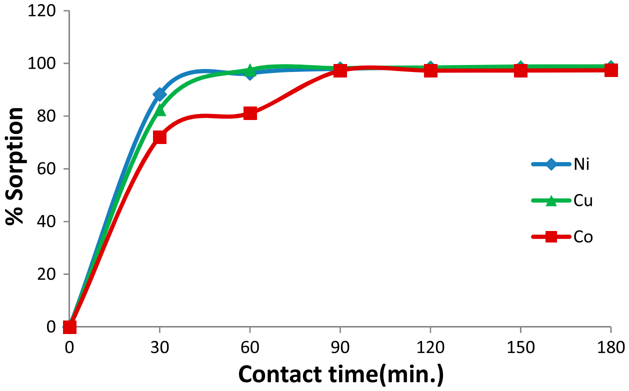

Fig. 5b. The effect of the contact time on the adsorption of Cu(II), Co(II), and Ni(II) ions.

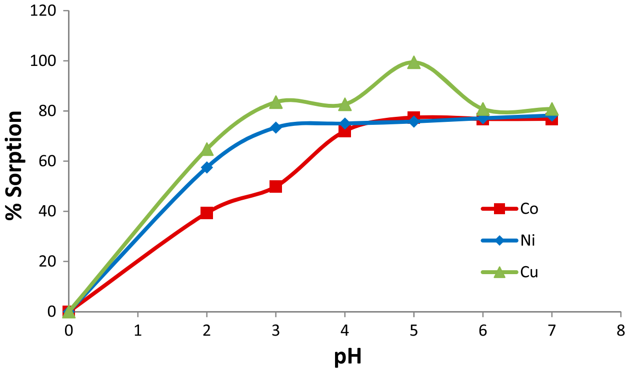

Fig. 5c. The effect of pH on the sorption of pH of Cu(II), Co(II), and Ni(II) ions.

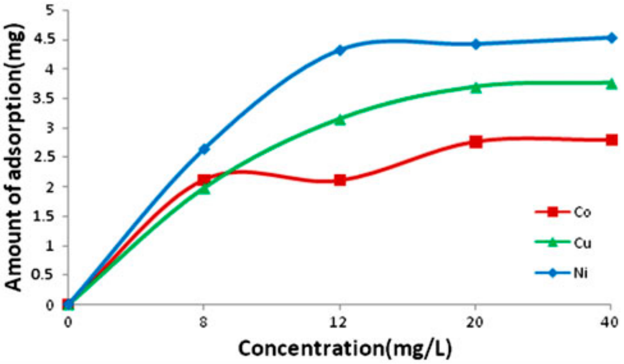

Fig. 5d. The adsorption effect depend on concentration of Cu(II), Co(II), and Ni(II) ions.

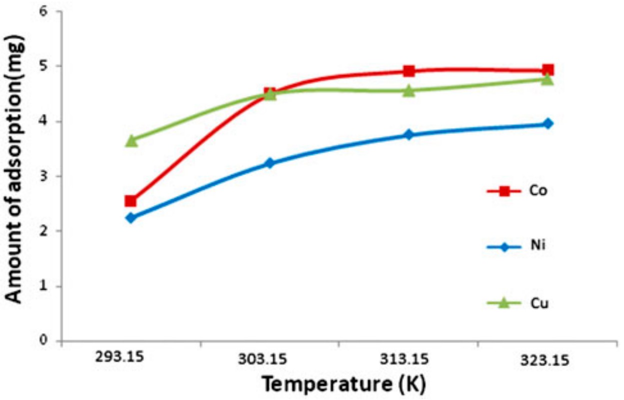

Fig. 5e. The effect of temperature on the adsorption of Cu(II), Co(II), and Ni(II) ions.

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

where q_e is the amount of solute sorbed on the surface of the sorbent (mMg^{-1}), C_e is the equilibrium ion concentration in the solution (mML^{-1}), q_0 is the maximum surface density at monolayer coverage, and b is the Langmuir adsorption constant (LmM^{-1}). The plot of C_e/q_e vs. C_e for the sorption gives a straight line of slope $1/bq_0$ and intercepts $1/q_0$ (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 [23]. 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 (mMg^{-1}), the equilibrium concentration of the solute (mML^{-1}), the *Freundlich constant*, respectively. According to Eq. (3), the plot of ln q_e vs.

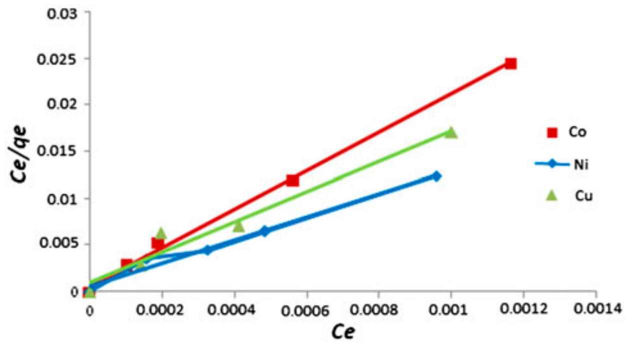

Fig. 6a. *Langmuir isotherms* of Cu(II), Co(II), and Ni(II) removal by *Si-PHTA*.

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 [24].

The values of $1/n$ for *Si-PHTA* are <1 is an indication of high sorption intensity [20]. The K_F values showed that immobilized silica gel has higher adsorption capacity for Ni(II) and Cu(II) (0.10, 0.50 mMg^{-1}) compared to Co(II) (0.03mMg^{-1}) [25]. Values of $n > 1$ represent favorable adsorption conditions [26]. 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 *D–R isotherm* was chosen to estimate the adsorption energy. The model is expressed as Eq. (4):

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

where ε (Polanyi potential) is $[RT\ \ln(1 + \ (1/C))]$, q_e is the amount of solute adsorbed per unit weight of adsorbent (mol g^{-1}), k is a constant related to the adsorption energy ($\text{mol}^2\,(\text{kJ}^2)^{-1}$) and q_m is the adsorption capacity (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. 6(c)). The mean free energy (E), calculated by the *D–R isotherm*, is presented in Table 4. The energy values were calculated with using Eq. (5):

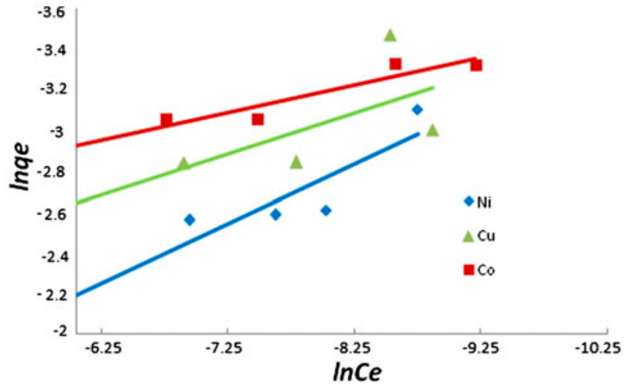

Fig. 6b. *Freundlich isotherms* of Cu(II), Co(II), and Ni(II) removal by *Si-PHTA*.

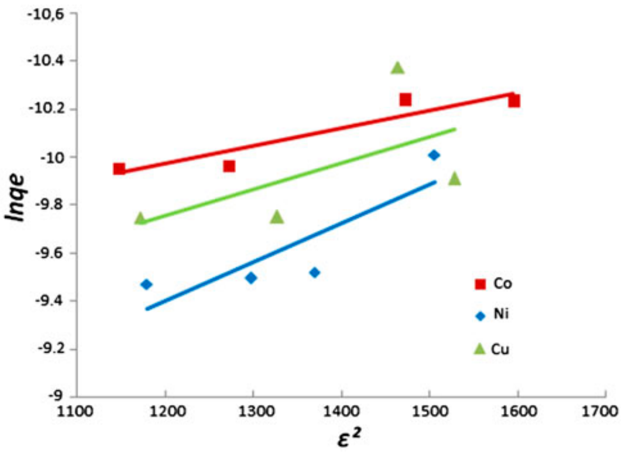

Fig. 6c. *D–R isotherms* of Cu(II), Co(II), and Ni(II) removal by *Si-PHTA*.

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

The mean free energy was between 18.26 and 22.36 kJ mol^{-1} for the three metal ions (Table 4). The adsorption 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 mol^{-1} [27,28]. The value of energy in the range of 8–16 kJ mol^{-1} referred to adsorbed species.

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.

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

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

Table 4
Isotherms parameters for Cu(II), Co(II), and Ni(II) ($T = 298$ K)

Freundlich isotherm				Langmuir isotherm			D–R isotherm			
Metal	$1/n$	K_F	R^2	Q_o (mM)	b (L/mM)	R^2	K (mol^2/kJ)	Q_m (mM/g)	E (kJ/M)	R^2
Cu(II)	0.18	0.20	0.734	0.060	25,451	0.988	0.0010	0.160	22.361	0.273
Ni(II)	0.31	0.68	0.847	0.081	18,826	0.977	0.0017	0.552	17.150	0.523
Co(II)	0.29	0.72	0.8975	0.093	23,419	0.981	0.0015	0.592	18.257	0.567

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

where K_D is the *adsorption distribution coefficient*, 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^{-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 enthalpies and entropies values for the sorption of metal ions on to *Si-CPTS-PHTA* 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 listed in Table 5 [19]. Fig. 7 shows value of logarithmic plot of distribution coefficient K_D against 1/T.

The positive value of ΔH°, as shown in Table 5, 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 used sorbent has a complexing capability, and so complex formation must be the predominant mechanism. Positive enthalpy values also support this argument. The values of ΔG° decreased with an increase in temperature, suggesting that the spontaneous nature of adsorption was inversely proportional to temperature. The positive value of entropy change (ΔS°) reflects the increased randomness at the solid–solution interface during sorption, and it also indicates that ion replacement reactions occurs. When a metal ion, which is coordinated with water molecules in solution, binds to the sorbent through coordination covalent bond formation, some of these water molecules leave the compounds. Due to the released water molecules, the degree of randomness increases the magnitude of ΔH°, related to the sorption energy indicate 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^{-1} are required by London, Van der Waals interactions compared from 8 to 40 kJmol^{-1} for hydrogen bond. In contrast, the enthalpy associated with chemical sorption is about 40 kJ mol^{-1}, a value that has been recognized as the transition boundary between both types of sorption processes [29]. ΔH°

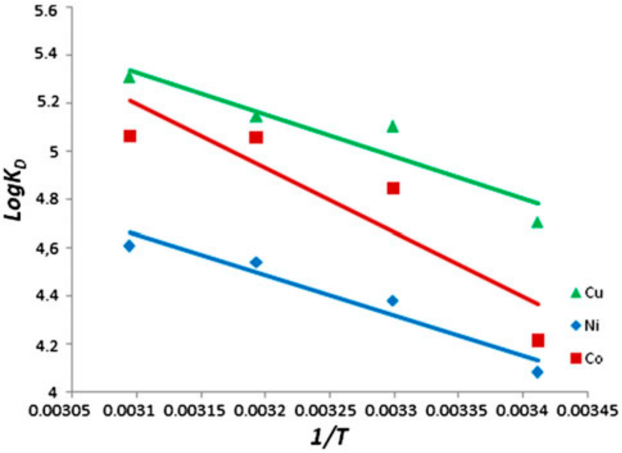

Fig. 7. Plots of log K_D vs. $1/T$ for Cu(II), Co(II), and Ni(II) removal by *Si-PHTA*.

Table 5
Thermodynamic parameters for sorption of metal ions (metal ion concentration 10mMdm^{-3})

Metal	ΔH° (kJ/M)	ΔS° (JK/M)	$-\Delta G^\circ$ (kJ/M)				
			297	303	313	323	R^2
Cu(II)	31.21	144.73	11.22	12.86	13.40	13.85	0.988
Ni(II)	43.98	185.03	9.95	11.05	11.84	12.99	0.977
Co(II)	51.17	208.52	10.27	12.23	13.18	13.62	0.981

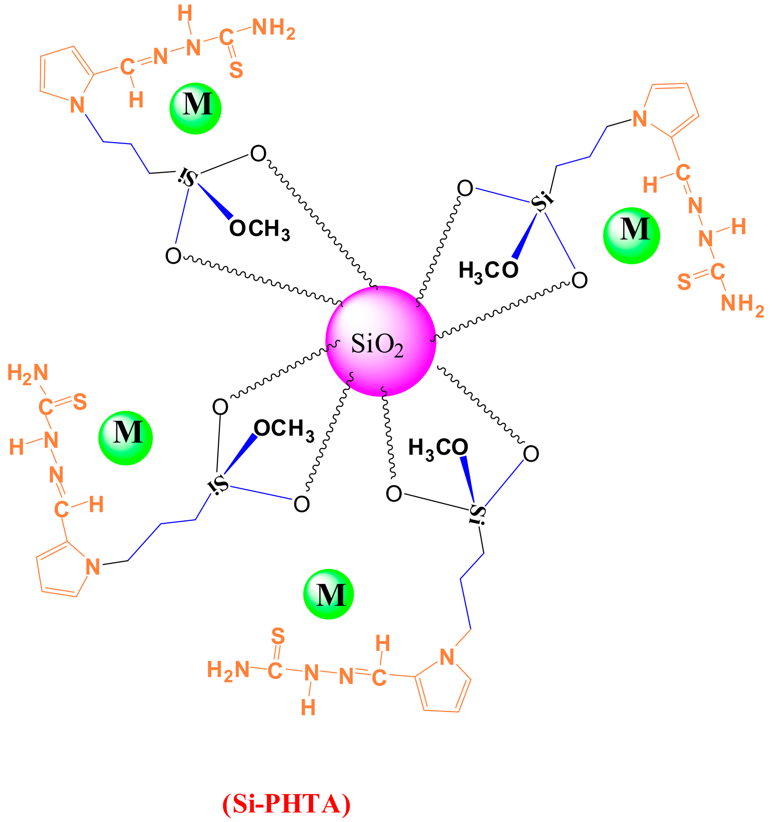

Fig. 8. The estimated perspective of *Si-PHTA*-metal ions combination.

values for Cu(II) (31.21 kJ mol^{-1}), Ni(II) (43.98 kJ mol^{-1}), and Co(II) (51.17 kJ mol^{-1}) were recorded in the temperature range of 293–323 K. The calculated ΔH° values for Cu(II), where sorption was lower than 40 kJ mol^{-1}, indicated the weak interactions of the compound with the *Si-PHTA* surface at this temperature range.

3.5. Mechanism

The sorption mechanism of Cu(II), Co(II), and Ni(II) metal ions on *Si-PHTA* can be explained with a classical chelating effect. However, the chelating effect of the Schiff base functional group is also thought to take part in the sorption process. It is possible to say that donor nitrogens and hydroxyl groups on surface coordinate with the chemisorption of heavy metal ions. The complex perspective of metal ions combination can be estimated as given in Fig. 8.

4. Conclusions

In this study, *PHTA* was immobilized on the surface of silica gel after surface modification by *CPTS*. The optimum pH range for the sorption of the metal ions is 5.0. The metal sorption followed the order Cu(II) > Ni(II) > Co(II) for the removal of metal ion.

The adsorption of Cu(II), Ni(II), and Co(II) onto the immobilized material followed the Langmuir adsorption models. The mean sorption energies for modified silica gel was found 22.361, 17.150 and 18.257 kJ mol^{-1} for Cu(II), Ni(II), and Co(II) respectively, which may correspond to chemical ion-exchange.

The calculated thermodynamic parameters reflected reactions were endothermic and spontaneous. For spontaneous processes, the values of ΔG° were negative in the range of 293–323 K. ΔG° value decreased with increase in temperature, which indicates that sorption of selected heavy metal ions becomes better at higher temperatures.

This study is important in providing complete steps of characterization as well as providing effective usage in removing metal.

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