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Adsorptive removal of Co(II), Ni(II), and Cu(II) ions from aqueous media using chemically modified sporopollenin of *Lycopodium clavatum* as novel biosorbent

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ABSTRACT

In this study, sporopollenin of *Lycopodium clavatum* spores was used for sorption experiments. (E)-4-((2-hydroxyphenylimino) methyl) benzoic acid (HPBA) immobilized sporopollenin (Sp) was employed as a sorbent in sorption of selected heavy metal ions in aqueous solutions. The sorbent material was prepared with sequential treatment of sporopollenin with silanazing compound and HPBA. Experimental conditions for effective sorption of heavy metal ions were optimized with respect to different experimental parameters using the batch method in detail. pHs for maximum sorption of Cu(II) ≡ Ni(II) and Co(II) ions were found in six and five, respectively. Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm equations were applied to the experimental data. Thermodynamic parameters such as free energy (ΔG^o), entropy (ΔS^o), and enthalpy (ΔH^o) were also calculated from the sorption results and were used to explain the mechanism of the sorption. The results indicated that this sorbent is successfully employed in the separation of trace Cu(II), Ni(II), and Co(II) from the aqueous solutions.

Keywords: Chemical immobilization; Sporopollenin; Adsorption; Metal ion

1. Introduction

The increasing level of heavy metals (such as nickel, cobalt, and copper) in water represents a serious risk for human health and ecological systems. The elevated level of nickel and cobalt in the environment is a cause for alarm owing to its allergic, carcinogenic, and toxic effects. Although copper is an essential element for life in minute amounts, at higher levels of exposure it shows mutagenic and carcinogenic effects such as nickel and cobalt. As a result of heavy metal ions, such as nickel, cobalt, and copper, release from industrial wastewater and water pollution has become a more serious problem [1–3]. Several materials, such as activated carbon, resins, clays, silica gel, sporopollenin (Sp), and biosorbents [4,5] have been studied for the removal of heavy metal ions. The sorption technique is widely used for removal of heavy metal ions from wastewater. Metal sorption through precipitation

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and complexation is a common approach to reduce metal toxicity in the polluted waters [5–12].

For the approach, the support structure plays an important role in mechanical, chemical, and thermal stability of sorbent materials. One of the structures is Sp, which possesses a high content of functional groups available for modification [13–15]. Sporopollenin [16], with its polymeric structure, would be a candidate sorbent for the removal of heavy metal ions from aqueous solutions, thanks to its low cost [17–21].

Sporopollenin of *Lycopodium clavatum* spores is preferred because it has a stable aromatic structure and contains carbon, hydrogen, and oxygen. Sporopollenin is produced by the oxidative polymerization of carotenoids and carotenoid esters, which leads to proposed monomer structures of the macromolecular sporopollenin. At present, sporopollenin is generally considered to be a biopolymer, but the detailed chemical structure of sporopollenin is yet unknown [7–19]. In the recent years, studies shows that the surface modification of sorbents onto the solid support materials provide a larger surface area and rapid sorption kinetics [17–26]. The modification of sporopollenin was achieved via chemical immobilization of the appropriate organic groups onto its surface. In this process, organic reagents are directly attached to the support surfaces [26–30].

Conversely, the literature search indicates that the studies which comprehensively intensify the ability of sporopollenin-based materials in complexation process are very few. To the best of our knowledge, there exists no report on the use of sporopollenin from *L. clavatum* a support for the immobilization of HPBA. The objective of this work was to investigate the Cu (II), Ni(II), and Co(II) sorption performance of Sp-HPBA (Sporopollenin HPBA) as a new sorbent. The paper focused on the characterization and sorption properties of this material. The surface of the immobilized sporopollenin was examined by Fourier transformed infrared spectroscopy (FTIR), thermal analysis (TGA), and elemental analysis. Several factors including solution pH, solution concentration, and reaction temperature were studied for kinetic parameters. Thermodynamics of the sorption process was also studied and thermodynamic parameters such as ΔG^o, ΔS^o, and ΔH^o were calculated for the systems.

2. Materials and methods

2.1. Materials

All of the chemicals used were analytical grade; ultra pure water was used. A series of standard metal solutions with the appropriate dilution of the stock metal solution was prepared. The dilute NaOH and HNO_3 solutions were used for pH adjustments.

2.2. Apparatus

The infrared spectra were obtained in the 650–4,000 cm^{-1} range by a Perkin–Elmer 100 FTIR spectrometer. Thermogravimetric (TG) curves were obtained on a Setaram TG Analyzer/Setsys analyzer at a temperature range of 298–1,073 K. The pH values were monitored with a Jenway 3010 model digital pH meter with glass and saturated calomel electrode, calibrated on the operational stage using a 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 (ContrAA 300, Analytikjena). All aqueous solutions were prepared with ultra pure water obtained from a Millipore Milli-Q Plus water purification system.

2.3. Synthesis of the sorbent

Sporopollenin was selected as a support material for this study and was first converted to Sp-OH, though described elsewhere [22]. The immobilization of the (3-Chloropropyl)trimethoxysilane [CPTS] onto sporopollenin was carried out as follows: sporopollenin (15.0 g) was suspended in dry toluene (100 cm^3) and CPTS (9 cm^3) was added. The mixture was then refluxed for 72 h and conditioned under a vacuum [9]. In the next step, approximately 10 g of Sp-CPTS was treated with 25% of HPBA solution (33 cm^3) and stirred for 15 h. After the 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 Sp-HPBA. The scheme of target structure is given in Fig. 1.

2.4. Sorption studies

20 mg of sorbent with 10 cm^3 of sorbate of various concentration and pH was shaken in a temperature controlled shaker incubator until equilibrium was reached (90 min). The temperature of the sorption experiments was controlled at 298 ± 1 K. After extraction, the solid phase was separated by filtration. The residual metal concentration of the supernatant was determined by an atomic absorption spectrometer (AAS). The amount of cations adsorbed was calculated as,

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

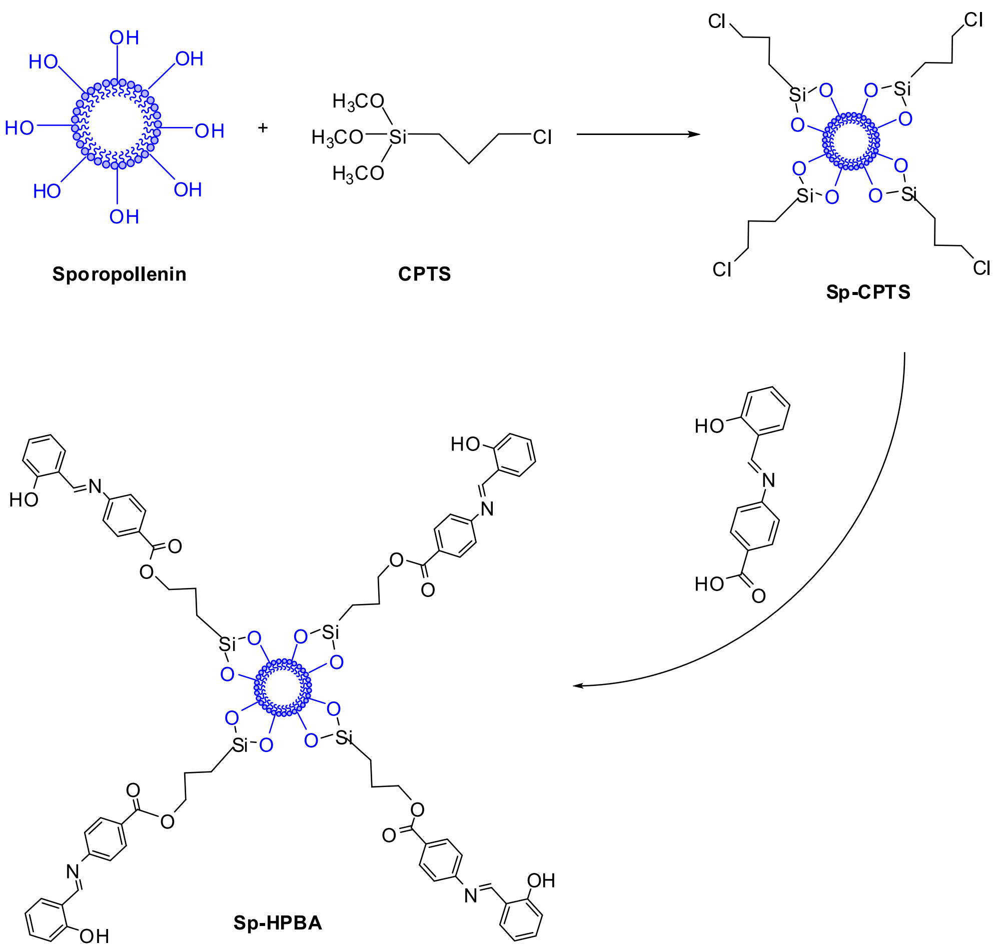

Fig. 1. Possible structure of sporopollenin bonded (E)-4-((2-hydroxyphenylimino)methyl)benzoic acid (HPBA) molecules.

where q is the amount of metal ion adsorbed onto unit amount of the adsorbent (mmol g^{-1}), C_o and C_e are the initial and equilibrium concentrations of the metal ions in aqueous phase (mmol dm^{-3}), respectively, V is the volume of the aqueous phase (dm^3), and W is the dry weight of the adsorbent (g) [9].

2.4.1. Optimum pH studies

The pH of a solution has two different effects on metal sorption (as acidity or basicity). The binding sites of the chelating molecules can be protonated by protons of the acid solution, or the metal cations can give a complex reaction with the hydroxide ions in basic medium. Therefore, the pH of a solution must be optimized for the best results (range pH = 2–16) [30]. 20 mg of Sp-HPBA was stirred in presence of 10 cm^3 of Cu(II), Ni(II), and Co(II) solutions in 10 $mmoldm^{-3}$ concentration and studied to different pH values (2.0, 3.0, 4.0, 5.0, 6.0, and 7.0). The mixture was shaken for 90 min at 298 ± 1 K.

2.4.2. Effect of concentration

The sorption was investigated for aqueous solution of divalent cobalt, copper and nickel nitrates at 298 ± 1 K. For these sorption measurements, 20 mg of the functionalized sporopollenin was suspended in 10 cm^3 of aqueous solution containing various amounts of each cation. These suspensions were shaken in concentrations between 8.0 and 40.0 ± 0.01 mmol dm^{-3} in a shaker thermostated for 90 min [24]. After equilibrium was established, the amounts of metallic cations remaining in solution were determined by AAS.

2.4.3. Temperature studies

The metal sorptions depent on temperature 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 [11,12].

3. Results and discussion

3.1. Characterization

There are two main stages for the organofunctionalization of the sporopollenin surface, as given in Fig. 2. The functionalized sporopollenin is characterized by FTIR, TGA, and elemental analysis.

The infrared spectra of the synthesized products are compared with pure sporopollenin which is shown in Fig. 2. For pure sporopollenin, the peak between 3,400 and 3,200 cm^{-1} is attributed to the presence of the OH stretching frequency of the surface and also to adsorbed water molecules (Table 1). The peaks at 2,924 and 2,854 cm^{-1} are C–H stretching vibration, the peaks at 1,100–1,200 cm^{-1} are –C–OH stretching vibrations; the peak at 1,709 cm^{-1} can be attributed to C=C stretching vibration due to convertion from C=C–OH form to CH–C=O form in sporopollenin structure; and the peak at 1,445 cm^{-1} is attributed –C–H asymmetric in-plane bending vibration. The spectrum of CPTS immobilized sporopollenin shows that the characteristic adsorption bands of Si–O–Si, siloxane stretching of CPTS appears a broad peak at 1,111 cm^{-1}. Frequency of OH stretching vibration in Sp-CPTS is shifted to 3,372 cm^{-1} from 3,312 cm^{-1} (Sp). The frequency of –C=N stretching vibration is 1,676 cm^{-1} and the frequency of –CH stretching vibration is 1,600–1,450 benzene groups in Sp-HPBA. The appearance of a peak related to the siloxane stretching frequency, Si–O–Si, is observed at 1,054 cm^{-1}. Moreover, the large peaks at 1,110 and 996 cm^{-1} may be attributed to esteric groups obtained when HPBA binding to Sp-CPTS [16].

The TG curves of Sp, Sp-CPTS, and Sp-HPBA enable the establishing of information on thermal stability and also confirm the amount of compounds immobilized as shown Fig. 3. The results of TGA are also summarized in Table 2. The curves show that the SP-HPBA has more thermal stability than the other surfaces and distinct mass losses, reflecting the molar mass of the pendant groups covalently bonded to inorganic phase.

According to the TGA curves of the the synthesized materials, Sp decomposes in three steps, while Sp-CPTS and Sp-HPBA decompose in a two steps. Physically absorbed water initially bonded on pure sporopellennin (Sp) was lost at low temperature in the first step (7.80%). An icrease in temperature caused condensation of surface groups that gives a second mass loss step (80.50%, between 312 and 450℃). The immobilized surfaces (Sp-CPTS) showed a mass loss due to physically absorbed water (7.60%). The first mass loss step is in the range of 147–185℃ is due to release of immobilized molecules (7.60%). An abrupt loss in mass detected in the third mass loss region (46.80%), from 185 to 460℃, suggesting the progressive release of the sporopellenin attached silane molecules (Sp-CPTS) [20].

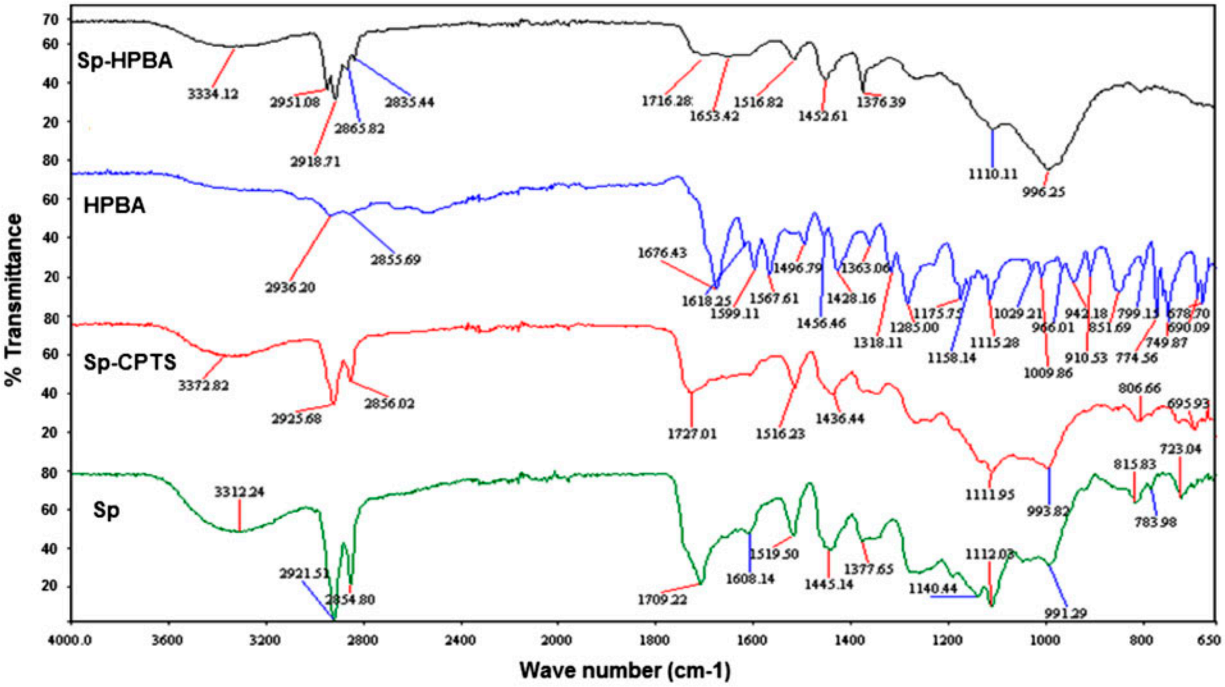

Fig. 2. FTIR spectra of Sp (a) Sp-CPTS (b) HPBA (c) and Sp-HPBA (d).

Table 1
Assignments of IR bands of sporopollenin samples from the spores of *L. clavatum*

Wave number [cm^{-1}]	Assignment
3,312	OH-stretching vibrations
2,924	CH-stretching vibrations of saturated carbons
1,625	C=C-stretching vibration
1,112	C–OH-stretching vibrations
1,445	$CH_2 + CH_3$

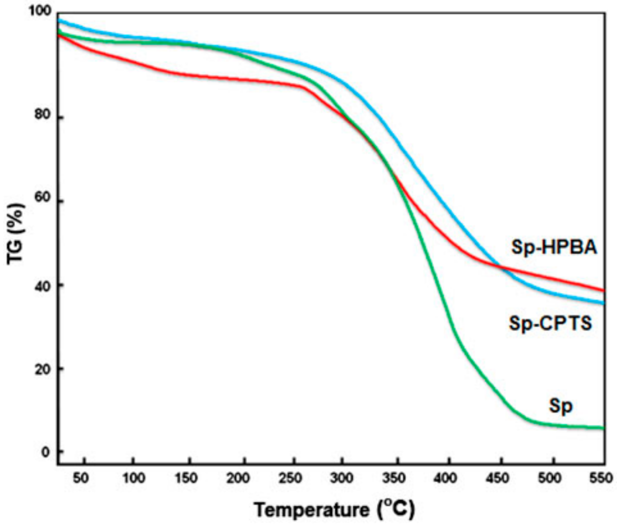

Fig. 3. TG curves of Sp, Sp-CPTS and Sp-HPBA.

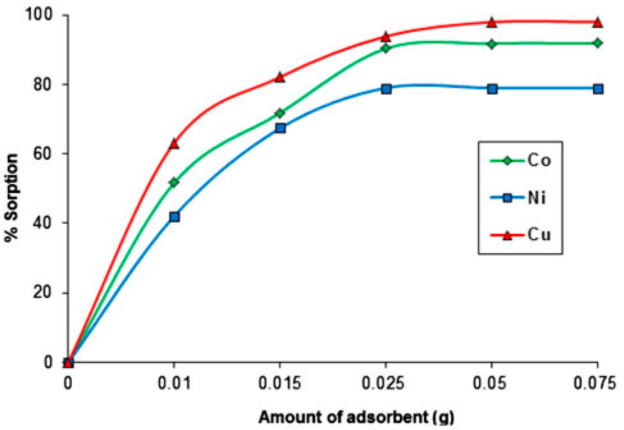

Fig. 4. The effect of the amount of Cu(II), Co(II) and Ni(II) ions on sorption.

3.2. Adsorption studies

3.2.1. Effect of the amount of adsorbent

Fig. 4 shows the effect of the amount of Cu(II), Co(II), and Ni(II) ions on the amount of sorbent. The adsorption ratios change depending on increase of adsorbent. When the amount of adsorbent increased, the total amount of absorbing metal ions also increased and reached steady state values. The maximum amount of adsorbent for Cu(II), Ni(II), and Co(II) ions was found as 0.05, 0.025, and 0.05 g, respectively. The excess of the metal ion will be absorbed by the adsorbent owing to the increase of the active surface. The effect of amount of adsorbent on sorption of Cu(II), Co(II), and Ni(II) ions by Sp-HPBA can be attributed to more chelating effect.

3.2.2. Effect of contact time

Fig. 5 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 the amount of sorption for the studied metal ions and reached the steady state values. The adsorbent with the best effect is defined as its having hydrophilic groups of modified sporopollenin. 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 sporopollenin.

Table 2
Thermal degradation values of the synthesized compounds

Compounds	First degradation temperature (°C)				Second degradation temperature (°C)				Third degradation temperature (°C)					
	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 600°C
Sp	176	160	275	7.80	275	394	450	80.50	450	452	550	3.90	7.80	5.60
Sp-CPTS	147	155	185	7.80	185	312	460	46.80	460	460	550	37.80	7.60	26.40
Sp-HPBA	145	151	191	7.50	191	275	425	40.20	425	425	550	39.70	12.60	38.70

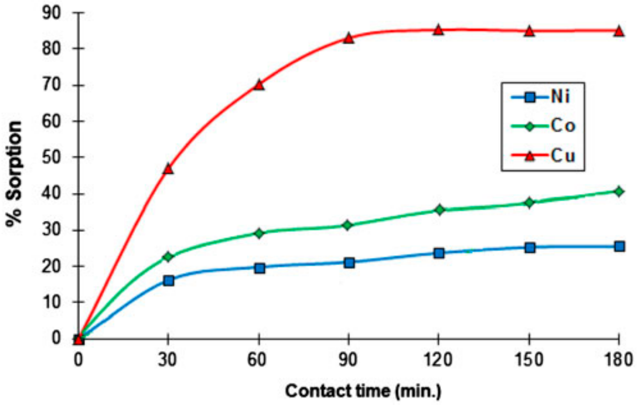

Fig. 5. The effect of the contact time on the adsorption of Cu(II), Co(II) and Ni(II) ions.

3.2.3. Optimum pH studies

The effect of pH on the sorption was studied for Cu(II), Co(II), and Ni(II) ions as shown in Fig. 6. The results show 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 is enhanced due to the increased concentration of H_3O^+ ions in medium [18]. The pH for maximum sorption of Cu(II) ≡ Ni(II) and Co(II) ions was found as 6 and 5, respectively. This can be explained by the different binding affinities of the binding sites. The experimental faults caused to little shifts. Optimum pH's are between 5 and 6 for all metal ions.

3.2.4. Effect of concentration

Fig. 7 shows that the adsorption effect depends on the concentration of metal ions. The curves of the graph show 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.

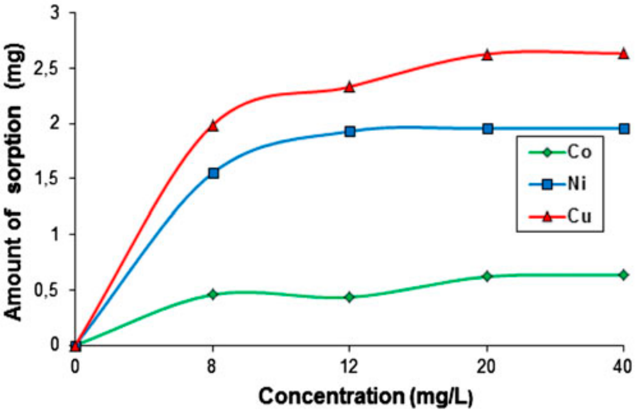

Fig. 7. The adsorption effect depend on concentration of Cu(II), Co(II) and Ni(II) ions.

3.2.5. Effect of temperature

Fig. 8 exhibits the effect of temperature on the adsorption. The amount of adsorption increased with temperature and reached steady state values. It was observed that thermodynamic parameters values changed with increase/decrease in temperature depending on endothermic nature of sorption.

3.3. Adsorption Isotherms

As known, chemisorption is a kind of adsorption which involves a chemical reaction between the surface and the adsorbate, and new chemical bonds are generated at the adsorbent surface. The interaction between

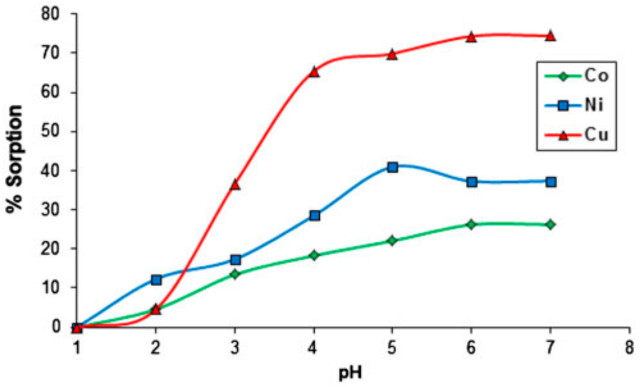

Fig. 6. The effect of pH on the sorption of pH of Cu(II), Co(II) and Ni(II) ions.

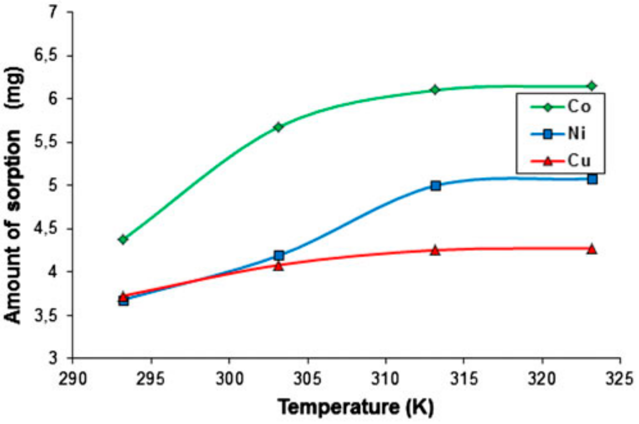

Fig. 8. The effect of temperature on the adsorption of Cu(II), Co(II) and Ni(II) ions.

the adsorbate and the substrate surface (with heterogeneous catalysis) creates new types of energy. Therefore The sorption data were evaluated with different sorption isotherms namely 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 is often expressed as:

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

where q_e is the amount of solute sorbed on the surface of the sorbent (mmolg^{-}1), C_e is the equilibrium ion concentration in the solution (mmoldm^{-3}), q_o is the maximum surface density at monolayer coverage, and b is the Langmuir adsorption constant (dm^3 mmol^{-1}). The plot of C_e/q_e vs. C_e for the sorption gives a straight line of slope 1/bqo and intercepts $1/q_o$ (Fig. 9).

The isotherm equation further assumes that the adsorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a metal ion occupies a site, no further adsorption can take place at that site. Theoretically, the sorbent has finite capacity for the sorbate. The Langmuir isotherm assumes that metal ions are chemically adsorbed at a fixed number of well defined sites, where each site can hold only one ion, and all sites are energetically equivalent without any interaction between the ions [23].

The Freundlich isotherm is an empirical isotherm model used for adsorption on heterogeneous surfaces or surfaces supporting sites of varied affinities [19]. The Freundlich isotherm can be written as,

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

where q_e is the equilibrium solute concentration on adsorbent (mmolg^{-1}), C_e is the equilibrium concentration of the solute (mmolL^{-1}), K_F is the Freundlich constant that indicates the sorption capacity and represents the strength of the absorptive bond, and n is the heterogeneity factor that represents the bond distribution. According to Eq. (3), the plot of ln q_e vs. ln C_e gives a straight line, and K_F and n values can be calculated from the intercept and slope of this straight line [9].

The values of $1/n$ for Sp-HPBA are <1 indicative of high sorption intensity. The K_F values were calculated for Cu(II), Co(II), and Ni(II) as 0.14, 0.13, and 0.12, respectively [19]. Values of $n > 1$ represent the favorable adsorption conditions [14]. Values of K_F and n are calculated from the intercept and slope of the plot (Fig. 10) and are listed in Table 3. The Dubinin–Radushkevish (D–R) isotherm was chosen to estimate the adsorption energy. The model is often 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 (molg^{-1}), k is a constant related to the adsorption energy (mol^2(kJ^2)$^{-1}$), and q_m is the adsorption capacity (molg^{-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. 11). The mean free energy (E), calculated by the Dubinin– Radushkevich isotherm, is presented in Table 3. The energy values were calculated using the equation:

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

If the value of E is between 8 and 16 kJ mol^{-1} [11,12] the adsorption process can be explained by a sorption process that is chemical in nature. Table 3 shows that the mean free energy was between 18.90

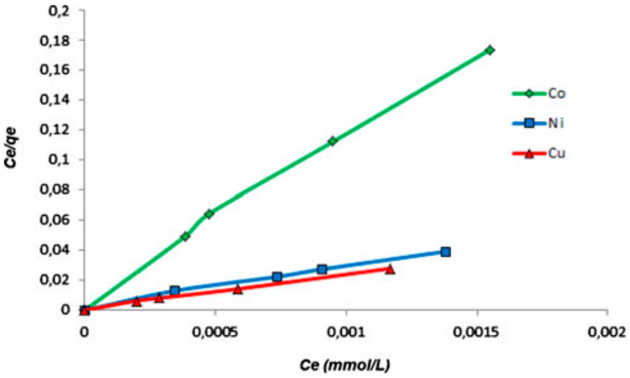

Fig. 9. Langmuir isotherms of removal of Cu(II), Co(II) and Ni(II) by Sp-HPBA.

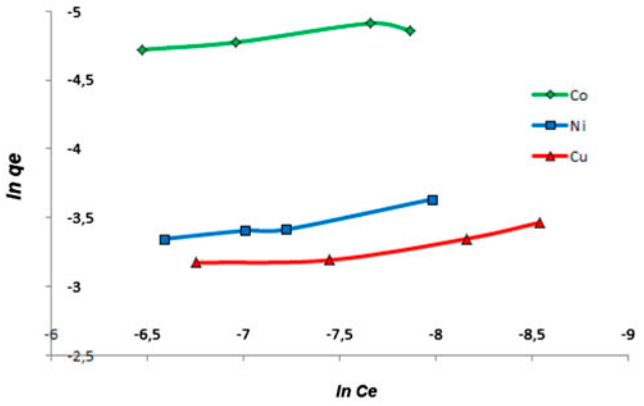

Fig. 10. Freundlich isotherms of removal of Cu(II), Co(II) and Ni(II) by Sp-HPBA.

Table 3
Isotherms parameters for Cu(II), Co(II) and Ni(II) by Sp-HPBA ($T = 298$ K)

Freundlich isotherm			Langmuir isotherm		D–R isotherm		
Metal	$1/n$	K_F	Q_o (mmol)	b (L mmol^{-1})	k (mol^2 K^{-1} J^{-1})	q_m (mmol g^{-1})	E (kJ mol^{-1})
Cu(II)	0.18	0.14	0.043	28,829	0.014	0.243	18.90
Ni(II)	0.14	0.12	0.036	37,092	0.002	0.135	20.41
Co(II)	0.16	0.13	0.039	31,743	0.001	0.020	26.73

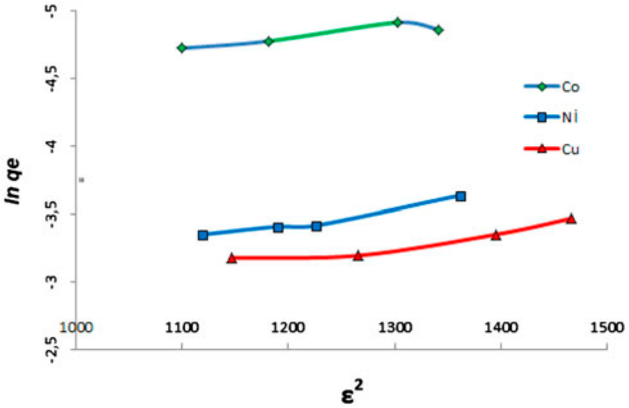

Fig. 11. D–R isotherms of removal of Cu(II), Co(II) and Ni(II) by Sp-HPBA.

and 26.72 kJ mol^{-1} for the three studied metals, which suggests that the sorption of Co(II), Cu(II), and Ni(II) occurs via a chemisorption mechanism in which the sorption energy lies within 8–16 kJ mol^{-1} [27]. Finally, the magnitude of the mean free energy indicates that the sorption of selected divalent metal ions occurs via chemisorption [21].

3.4. Thermodynamic studies

Thermodynamic parameters such as enthalpy change (ΔH^o), entropy change (ΔS^o), and free energy change (ΔG^o) are crucial and must be taken into consideration in order to determine the spontaneity of a process. The effect of temperature on the sorption on immobilized sporopollenin was investigated at temperatures (293–323 K) under optimized conditions of pH values for each ion.

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

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

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

where K_D is the adsorption equilibrium constant, V is the volume of the aqueous phase (dm^3), and W is the dry weight of the sorbent (g). Also, in Eq. (6) ΔG° is the change in Gibbs free energy (kJmo^{-1}), ΔH° is the change in enthalpy (kJmol^{-1}), ΔS° is the change in entropy (J mol^{-1} K^{-1}), T is the absolute temperature (K), and R is the gas constant (8.314×10^{-3}, kJmol^{-1}K^{-1}).

The enthalpies and entropies values for the sorption of metal ions onto Sp-HPBA were evaluated from the van't Hoff plots: log K_D vs. $1/T$. ΔG° was also calculated by using Eq. (7) and the results are listed in Table 4 [12]. Fig. 12 shows the value of logarithmic plot of distribution coefficient K_D against $1/T$.

The positive value of ΔH^o as shown in Table 4 indicates the endothermic nature of adsorption. The negative values of ΔG^o for three cations indicate that adsorption onto the adsorbents is a feasible and spontaneous process, and energy input from outside of the system is required. The sorbent used has a complexing capability, and so complex formation must be

Table 4
Thermodynamic parameters for sorption of metal ions of Sp-HPBA (metal ion concentration 10mmoldm^{-3})

Metal	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	$-\Delta G^\circ$ (kJ mol^{-1})			
			297	303	313	323
Cu(II)	54.53	225.01	11.62	12.30	13.87	14.33
Ni(II)	36.66	162.40	11.01	11.82	13.14	13.69
Co(II)	51.58	213.52	10.94	12.58	13.71	14.26

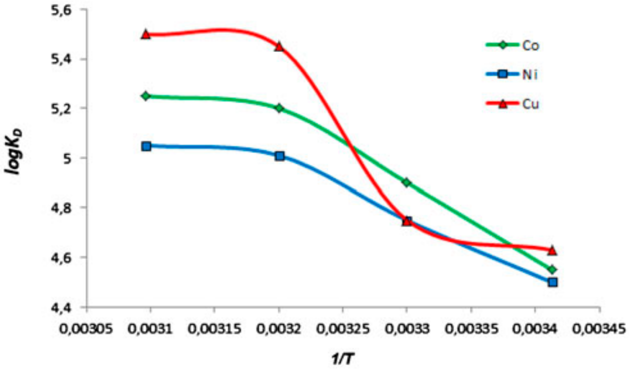

Fig. 12. Plots of log K_D vs. $1/T$ for removal of Cu(II), Co(II) and Ni(II) by Sp-HPBA.

the predominant mechanism. Positive enthalpy values support this argument. The values of ΔG^o 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^o) reflects the increased randomness at the solid/solution interface during sorption, and also indicates that ion replacement reactions occurred. When a metal ion, which is coordinated with water molecules in solution, binds to a sorbent through formation of a covalent bond, some of these water molecules leave to the metal ion. Due to the released water molecules, the degree of randomness increases.

The magnitude of ΔH^o, related to the sorption energy, can 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 and Van der Waals interactions, compared with 8–40 kJ mol^{-1} for hydrogen bonding. In contrast, the enthalpy associated with chemical sorption is about 40 kJ mol^{-1}, a value that has been recognized in literature as transition boundary between both types of sorption processes [31]. High ΔH^o values were observed for Cu (II) (54.53 kJ mol^{-1}) and Co(II) (51.58 kJ mol^{-1}) in the temperature range of 293–323 K. The calculated ΔH° values for Ni(II) sorption were lower than 40 kj mol^{-1}, indicative of the weak interactions of the compound with the Sp-HPBA surface at this temperature range.

3.5. Mechanism

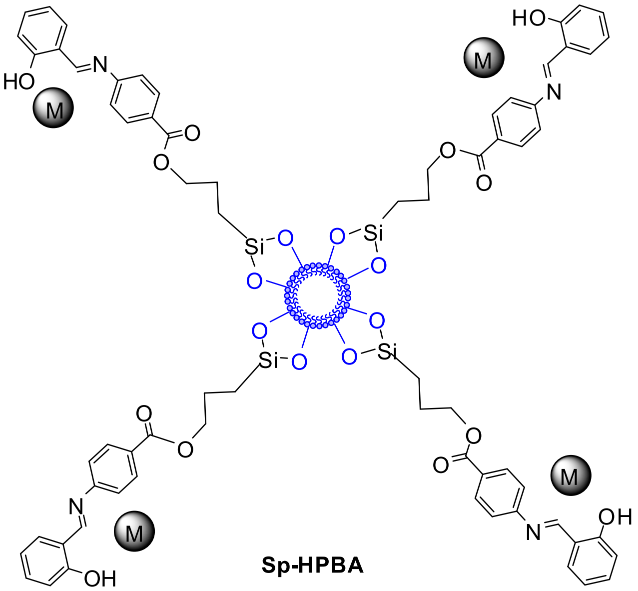

Fig. 13. The estimated perspective of Sp-HPBA-metal ions combination.

The sorption mechanism of Cu(II), Co(II), and Ni(II) metal ions on Sp-HPBA can be explained with an ion exchange process. However, the chelating effect of the Schiff base functional group on Sp-HPBA 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 Sp-HPBA-metal ions combination can be estimated as given in Fig. 13.

4. Conclusions

In this study, the chemical modification of sporopollenin was attempted with HPBA by using the immobilization method to yield the chelating material Sp-HPBA. The optimum pH range for the sorption of the metal ions is from 5.0 to 6.0. The effect of metal ion concentration is studied in the range of 8–40.0 ± 0.01 mmol dm^{-3} for the uptake, and the behavior of the chelating materials was studied. The metal sorption followed the order $Cu^{2+} > Co^{2+} > Ni^{2+}$ for the removal of metal ion. The adsorption of Cu^{2+}, Co^{2+}, and Ni^{2+} onto the immobilized material obeyed Langmuir and Freundlich adsorption models. Also, according to regeneration studies, immobilized sporopollenin can be used several times for the sorption of metal ions from aqueous solutions. The efficient modification of HPBA by CPTS on sporopollenin surfaces are confirmed/verified by FTIR and elemental analysis. Also, according to the result of TG analysis, Sp-HPBA had a higher stability than the other two materials (Sp and Sp-CPTS). The selectivity of the modified sporopollenin towards metal ions depends on various factors such as size of the modified structures, activity of the bonded groups, appropriate functional groups, and interaction of the hard/soft-acid/base [1].

The calculated thermodynamic parameters reflected reactions were endothermic and spontaneous. For spontaneous processes, the values of ΔG^o were negative in the range of 293–323 K, as expected. While temperature increases there is a decrease in ΔG^o value, which indicates that sorption of selected heavy metal ions on Sp-HPBA becomes better at higher temperatures.

Finally, the metal sorption study on Sp-HPBA for HPBA-synthesized compound, used for first time immobilization, is original. Immobilized material can act as chelate, and it is used for the removal of metal ion from aqueous solution [14]. When Sp-HPBA was compared with raw sporopollenin, the chelating effect increased to the sorption of heavy metal ions. Overall, it can be concluded that the proposed sorbent system is practical and efficient for the removal of heavy metals contamination from effluents with the advantages of being inexpensive, largely available, and environmental friendly for the use of waste water effluent. If a literature search is done about the sorption studies related to sporopollenin, a very limited number of manuscripts can be found. Some of them did not give any place to characterization, and some of them attach metal ions on sporopollenin surface by physical forces [2,3,9]. When these are taken into account, this study is very important in providing complete steps of characterization as well as providing effective usage of Sp-HPBA in removing metal.

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