



Isotherms and thermodynamics for the sorption of heavy metal ions onto functionalized sporopollenin

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ABSTRACT

In this study, sporopollenin of *Lycopodium clavatum* spores was used for the sorption experiment. Glutaraldehyde (GA) immobilized sporopollenin (Sp), is employed as a sorbent in sorption of selected heavy metal ions. The sorbent prepared by sequential treatment of sporopollenin by silanizing compound and glutaraldehyde is suggested for sorption of Cu(II), Zn(II) and Co(II) from aqueous solutions. Experimental conditions for effective sorption of heavy metal ions were optimized with respect to different experimental parameters using batch method in detail. Optimum pH range of Cu(II) has occurred at $\text{pH} \geq 5.5$ and Zn(II), Co(II) at $\text{pH} \geq 5.0$, for the batch method. All of the metal ions can be desorbed with 10 cm^3 of 0.5 mol dm^{-3} of ethylenediaminetetraacetic acid (EDTA) solution. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm equations were applied to the experimental data. Thermodynamic parameters such as free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) were also calculated from the sorption results used to explain the mechanism of the sorption. The results indicated that this sorbent is successfully employed in the separation of trace Cu(II), Zn(II) and Co(II) from the aqueous solutions.

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1. Introduction

The increasing level of heavy metals in water represents a serious risk to human health and ecological systems [1]. Heavy metals, such as lead, cadmium and mercury, are harmful to living organisms. Indeed, even in very small quantities, some of these metal ions, especially mercury ions, may harm flora, fauna and other living beings. Their accumulation in humans causes kidney failure, nervous system damage and bone softening, as well as other serious illnesses [2]. Sorption is widely used for elimination of the heavy metal ions. Metal sorption through precipitation and complexation is a common approach to reduce metal toxicity in the environment.

Several materials such as activated carbon, resins, clays, silica gel, and biological materials [1] have been studied for sorption of heavy metal ions. Support structure plays a dominant role in mechanical, chemical and thermal stability of sorbent materials. One of the materials is sporopollenin which possesses a high content of functional groups available for modification [3].

The outer wall of spores and pollen contains a highly resistant biomacromolecule, sporopollenin, occurs naturally as a component of spore walls *Lycopodium clavatum* has a stable, cross-linked structure and has an aromatic character that contains carbon, hydrogen, and oxygen with a stoichiometry of $\text{C}_{90}\text{H}_{144}\text{O}_{27}$, which can survive in geological strata over millions of years with full

retention of morphology. Sporopollenin is produced by 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 and the detailed chemical structure of sporopollenin is as yet unknown [4].

Recently, surface modification of sorbents has garnered intense interest in order to be used as solid supports due to its large surface area, fast sorption kinetics and due to specifications of sorbent [5]. Modification of sporopollenin can be achieved via chemisorptions of the active species onto the sporopollenin surface. In this process, organic reagents or synthesized organic molecules containing the desired organic functional group are directly attached to the supports [6].

Sporopollenin with its polymeric structure would be a candidate sorbent for removal of heavy metal ions from aqueous solutions due to its low cost. However, 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 *Lycopodium clavatum* as support for immobilization of glutaraldehyde. The objective of this work was to investigate the Cu(II), Zn(II) and Co(II) sorption performance of Sp-APT-GA as a new sorbent. The focus in the present study is on characterizing the sorption properties of this material. Surface structure of the immobilized sporopollenin was examined by Fourier Transformed Infrared Spectroscopy (FTIR), thermal analysis (TGA), and elemental analysis. Several factors, including solution

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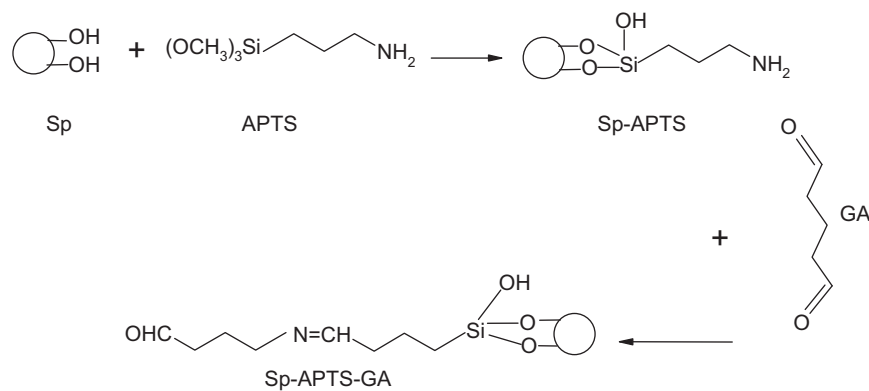


Fig. 1. Possible structure of the sporopollenin bonded glutaraldehyde molecules.

pH, solution concentration, and reaction temperature were studied. Thermodynamics of the sorption process was also studied and thermodynamic parameters such as ΔG^0 , ΔS^0 and ΔH^0 were calculated for the systems.

2. Materials and methods

2.1. Materials

Lycopodium clavatum spores (sporopollenin) with 20 μm particle size obtained from Fluka Chemicals. All the chemicals used were of analytical grade and ultra pure water was used throughout. Toluene (Merck) was distilled and dried. 3-Aminopropyltrimethoxysilane (APTS), glutaraldehyde (25%), EDTA, and Co(II), Cu(II) and Zn(II) nitrates were also obtained from Merck. A series of standard metal solution by appropriate dilution of the stock metal solution were prepared. Solutions of 0.01 M NaOH and HNO₃ were used for pH adjustment.

2.2. Apparatus

An infrared spectrum was obtained in the 400–4000 cm^{-1} range, by Perkin Elmer 100 FTIR spectrometer. Thermogravimetric curves were obtained on a Setaram Termogravimetrik Analyzer/Setsys analyzer at temperature range of 25–800 °C. Elemental analysis was performed with a Leco CHNS 932 microelemental analyzer.

The pH value was 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. Selecta-Ivmen 100D thermostatic shaker was used for the sorption experiments. Metal concentration of the supernatant was 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 firstly converted into Sp-OH through described elsewhere [7]. Immobilization of the APTS onto sporopollenin was performed as follows: sporopollenin (15.0 g) was suspended in dry toluene (100 cm^3) and 3-aminopropyl trimethoxysilane (APTS) (9 cm^3) was added. The mixture was then refluxed for 72 h and conditioned under vacuum to prevent the reaction between the immobilized amine groups and CO₂ present in the atmosphere [8].

In the next step, approximately 10 g Sp-APTS was treated with 25% of GA solution (33 cm^3) and stirred at 308 ± 2 K for 15 h. After filtration of the suspension, the residue was washed and dried

under vacuum at 313 ± 1 K for 72 h to obtain the Sporopollenin-Silanzing compound-Glutaraldehyde (Sp-APTS-GA). Fig. 1 shows a schematic diagram of proposed products of organic compounds anchored on the sporopollenin surface.

2.4. Sorption studies

Sorption studies were carried out by batch process. 20 mg of sorbent with 10 cm^3 of sorbate of various concentration and pH was shaken in a temperature controlled shaker incubator till equilibrium was reached (90 min). The sorption experiment the temperature was controlled at 298 ± 1 K. After extraction, the solid phase was separated by filtered. Residual metal concentration of the supernatant was determined by an AAS. All experiments were performed in triplicate. The amount of cations sorbed by sorbent was calculated as

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

where q is the amount of metal ion sorbed onto unit amount of the adsorbent (mmol g^{-1}), C_0 and C_e are the initial and equilibrium concentrations of the metal ions in aqueous phase (mmol dm^{-3}), V is the volume of the aqueous phase (dm^3), and W is the dry weight of the adsorbent (g).

2.4.1. Optimum pH studies

The acidity of a solution has two effects on metal sorption. Firstly, protons in acid solution can protonate binding sites of the chelating molecules. Secondly, hydroxide in basic solution may complex and precipitates many metals. Therefore pH of a solution is the first parameter to be optimized [9].

A total of 20 mg of Sp-APTS-GA sorbent was suspended with constant stirring in 10 cm^3 of 10 mmol dm^{-3} of Cu(II), Zn(II) and Co(II) at different pH (2.0, 3.0, 4.0, 5.0, 5.5, 6.0, 6.5, 7.0) values and the mixture was shaken for 90 min at 298 ± 1 K to attain equilibrium. After the equilibrium, the concentrations of the metal ions in solution were directly determined by AAS.

2.4.2. Effect of concentration

The sorption was carried out batch wise in aqueous solution for divalent cobalt, copper and zinc nitrates at 298 ± 1 K. For these sorption measurements, samples of 20 mg of sporopollenin derivatized were suspended in 10 cm^3 of aqueous solution containing variable amounts of each cation, whose concentrations varied over 3.5–25.0 ± 0.01 mmol dm^{-3} range, in a shaker thermostated for 90 min [10]. After equilibrium was established, the suspension was eluted and the amounts of metallic cations remaining in solution were determined by AAS. A scheme given by Fig. 2 shows metal ions sorbed Sp-APTS-GA.

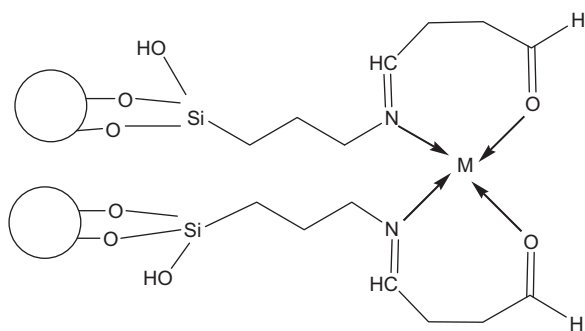


Fig. 2. Suggested model of the possible mode of metal ion (M) complexation by the SP-APTS-GA.

2.4.3. Temperature studies

Temperature experiments were carried out between 297 and 323 ± 1 K at optimum pH values for each metal ion. The amount of sorbed metal ion was calculated from the change in the metal concentration in the aqueous solution before and after equilibrium and weight of the dry sporopollenin [11].

2.4.4. Desorption studies

Desorption studies were performed by stirring the EDTA solution and all desorption experiments were carried out at room temperature. The desorbent EDTA, which can bind metals via the formation of covalent bonds by electron pairs in four acetate and two amine groups, is a chelator with six coordination sites. The metal ion adsorbed Sp-APTS-GA was thoroughly washed with deionized water and dried at room temperature, and then added to a flask containing 0.5 mol dm^{-3} EDTA solution (10 cm^3). The flask was mechanically stirred for 90 min at 298 ± 1 K. Following desorption, the solid was filtered and the metal ion concentration of the filtrate determined as AAS. The metal desorbed sorbent was used in the next cycle of adsorption and desorption. The above procedure was employed for three consecutive cycles. The ratio of desorption

Table 1

Assignments of IR bands of sporopollenin samples from the spores of *Lycopodium clavatum*.

Wave number [cm^{-1}]	Assignment
3400	OH-stretching vibrations
2925, 2850	CH-stretching vibrations of saturated carbons
1625	N-H bending vibration
1705	C=O-stretching vibrations
1450	$\text{CH}_2 + \text{CH}_3$

was calculated using the relation:

$$\text{Desorption (\%)} = \frac{\text{amount of desorbed ion}}{\text{amount of sorbed ion}} \times 100 \quad (2)$$

3. Results and discussion

3.1. Characterization

There are two main stages for the organofunctionalization of the sporopollenin surface, as given in Fig. 1. 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. 3. For pure sporopollenin, the peak between 3400 and 3200 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 2924 and 2855 cm^{-1} are C-H stretching vibration, the peak at 1706 cm^{-1} C=O stretching vibrations, the peak at 1188 cm^{-1} C-N stretching vibration and the peak at 1439 cm^{-1} CH_2 and CH_3 groups. The spectrum of APTS immobilized sporopollenin is shown that the characteristic adsorption bands of Si-O-Si, siloxane stretching of APTS appear at 1113 cm^{-1} . Sp-APTS-GA materials, presented the same set of bands related to the sporopollenins morphology. It is shown that, after the GA immobilization onto sporopollenin surface, FTIR spectrum was changed. The spectrum of Sp-APTS-GA indicated the appearance of C=O stretching at 1705 cm^{-1} , in addition to the other characteristic features associated with the main pendant carbon chain. The -CO and -NH groups can also be seen from Fig. 3 at around

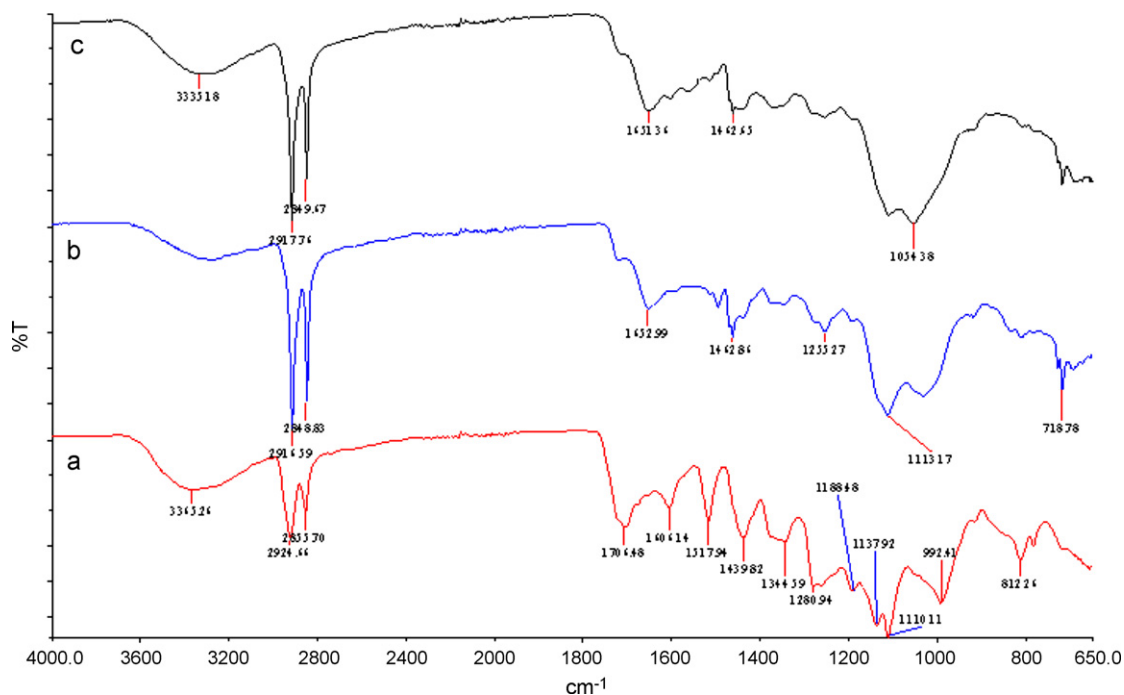


Fig. 3. FTIR spectra of Sp (a), Sp-APTS (b), and Sp-APTS-GA (c).

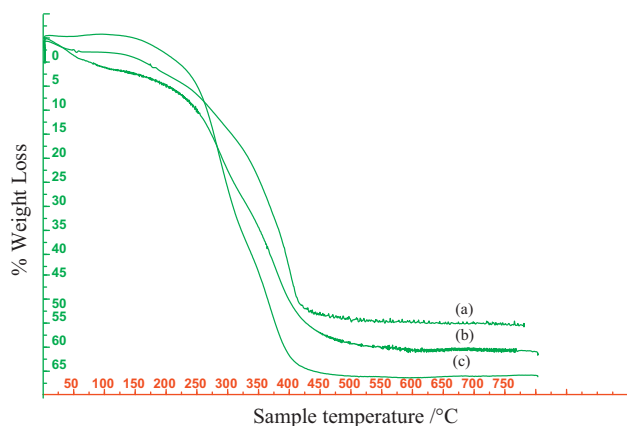


Fig. 4. Thermogravimetric curves of Sp (a), Sp-APTS (b), and Sp-APTS-GA (c) samples.

1651 and 1462 cm^{-1} , respectively. Some of the group vibrations were of lesser intensity, which could be due to the accumulation of the molecules or groups of atoms on the surface. The appearance of a peak related to the siloxane stretching frequency, Si–O–Si, is observed at 1054 cm^{-1} [12,13].

The percentage of carbon, hydrogen and nitrogen for Sp and Sp-APTS and Sp-APTS-GA are found to be 61.07, 8.36, 2.34; 61.65, 9.29, 5.98 and 62.40, 8.81, 4.19, respectively. Based on the nitrogen content, the pendant chains in the final compound, Sp-APTS-GA ($\text{Sp-C}_8\text{H}_{15}\text{O}_4\text{SiN}$) was calculated as 2.99 mmol g^{-1} of nitrogen atoms, which showed the incorporation of nitrogen donor atoms in the pendant chains of the synthesized materials [14].

The thermogravimetric curves for all materials enable the establishing of information on thermal stability and also confirm the amount of the compounds immobilized, as shown in Fig. 4. The curves show that the Sp-APTS-GA has more thermal stability than other surfaces and distinct mass losses, reflecting the molar mass of the pendant groups covalently bonded to inorganic phase.

The TG curves of the Sp (a), Sp-APTS (b), and Sp-APTS-GA (c) are shown in Fig. 4. Physically adsorbed water initially bonded on pure sporopollenin was lost at low temperature in the first step (2.66%). An increase in temperature caused condensation of surface groups that gives a second mass loss step (20.56%, 200–400 °C). The immobilized surfaces (Sp-APTS and Sp-APTS-GA) showed a mass loss due to the physically adsorbed water in the first step, near the same range as observed for the pure sporopollenin. The first mass loss step is in the range of 25–110 °C. In the second step loss of anchored molecules and also loss of water from the surface is included. The second mass loss step, in the range of 150–400 °C, is due to release of immobilized glutaraldehyde molecule (24.14%). An abrupt loss in mass detected in the third mass loss region (28.40%), from 400 to 700 °C, suggesting the progressive release of the sporopollenin-attached silane molecules (APTS). Sp-APTS-GA was more thermally stable than Sp-APTS and Sp and showed three decomposing transitions [15,16].

3.2. Optimum pH studies

The pH of the solution was buffered between the pH values of 2.0 and 7.0. In the pH study, 0.1 mmol dm^{-3} of acetic acid-sodium acetate buffer solution was used at a pH in the range of 4.0–5.5 and phosphate buffer solution was used at a pH from 2.0 to 7.0, in order to maintain a pH of the working solutions. Fig. 5 shows the effect of pH on divalent metal ions sorption on GA immobilized sporopollenin. The optimum pH for maximum sorption of Co(II) and Zn(II) were occurred at $\text{pH} \geq 5.0$ and Cu(II) at $\text{pH} \geq 5.5$. This can be explained by the different binding affinities of the binding sites,

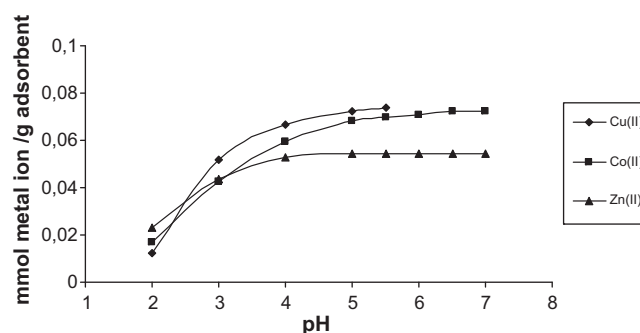


Fig. 5. Effect of solution pH on sorption of 10 mmol dm^{-3} of Co(II), Cu(II) and Zn(II).

which was attributed to deprotonation of the sorbed surface [17]. With increasing pH of the medium the metal adsorption increases significantly (Fig. 5). Increasing pH beyond 8.0 was discouraged due to possibility of hydrolysis of metal ions.

3.3. Sorption isotherm

The sorption data were evaluated by 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:

$$\frac{C_e}{q_e} = \frac{C_e}{q_o} + \frac{1}{q_o b} \quad (3)$$

where q_e is the amount of solute sorbed on the surface of the sorbent (mmol g^{-1}), C_e is the equilibrium ion concentration in the solution (mmol dm^{-3}), q_o is the maximum surface density at monolayer coverage and b is the Langmuir adsorption constant ($\text{dm}^3\text{ mmol}^{-1}$). The plot of C_e/q_e versus C_e for the sorption gives a straight line of slope $1/bq_o$ and intercepts $1/q_o$ (Fig. 6).

The isotherm equation further assumes that 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 a 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 [18].

$$y(\text{Cu}) = 23.48x + 0.0035 \quad y(\text{Zn}) = 6.5476x + 0.0016 \quad y(\text{Co}) = 7.7091x + 0.0027$$

$$R^2 = 0.9921 \quad R^2 = 0.9895 \quad R^2 = 0.9766$$

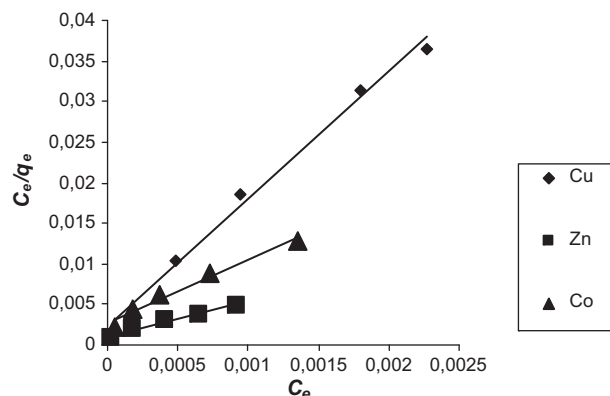


Fig. 6. Langmuir isotherms of Cu(II), Co(II) and Zn(II) removal by Sp-APTS-GA.

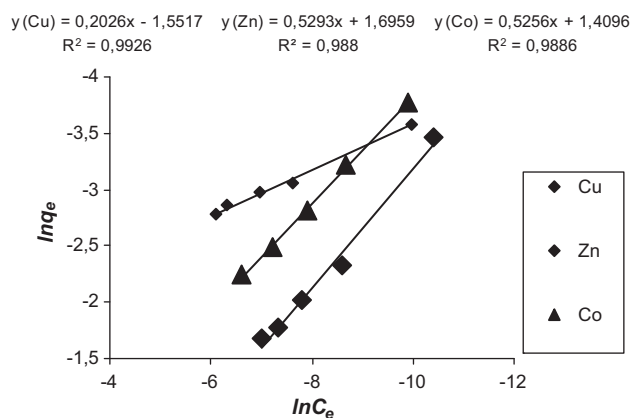


Fig. 7. Freundlich isotherms of Cu(II), Co(II) and Zn(II) removal by Sp-APTS-GA.

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

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

where q_e is the equilibrium solute concentration on adsorbent (mmol g^{-1}), C_e is the equilibrium concentration of the solute (mmol L^{-1}), K_F is the Freundlich constant which indicates the sorption capacity and represents the strength of the absorptive bond and n is the heterogeneity factor which represents the bond distribution. According to Eq. (4) the plot of $\ln q_e$ versus $\ln C_e$ gives a straight line and, K_F and n values can be calculated from the intercept and slope of this straight line [20,21].

The values of $1/n$ for Sp-APTS-GA are <1 indicative of high sorption intensity. Smaller value of $1/n$ and larger value of K_F indicates that the adsorbent has greater affinity for a particular metal ion over another. The K_F values showed that immobilized sporopollenin has higher adsorption capacity for Co(II) and Zn(II) (1.90 , 1.89 mmol g^{-1}) compared to Cu(II) (0.21 mmol g^{-1}) [22]. Values of $n > 1$ represent favorable adsorption condition [23]. Values of K_F and n are calculated from the intercept and slope of the plot (Fig. 7) and they are listed in Table 2.

The Dubinin-Radushkevich (D-R) isotherm was chosen to estimate the adsorption energy. The model is often expressed as:

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

where ε (polanyi potential) is $\left| RT \ln(1 + (1/C)) \right|$, 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 $\ln q_e$ versus ε^2 it is possible to generate the value of q_m from the intercept, and the value of k from the slope (Fig. 8).

The mean free energy (E), calculated by the Dubinin-Radushkevich isotherm, is presented in Table 2. The energy values were calculated using the equation:

$$E = (2k)^{1/2} \quad (6)$$

Table 2
Isotherms parameters for Cu(II), Co(II) and Zn(II) by Sp-APTS-GA ($T = 298 \text{ K}$).

Metal	Freundlich isotherm		Langmuir isotherm		D-R isotherm		
	$1/n$	K_F	q_0 ($\text{dm}^3 \text{ mmol}^{-1}$)	b ($\text{mol}^2 (\text{kJ}^2)^{-1}$)	k (mol g^{-1})	q_m	(kJ mol^{-1})
Cu(II)	0.20	0.21	0.042	0.082	0.016	0.048	17.68
Zn(II)	0.53	1.89	0.153	0.010	0.041	1.038	11.04
Co(II)	0.53	1.90	0.130	0.021	0.038	0.636	11.47

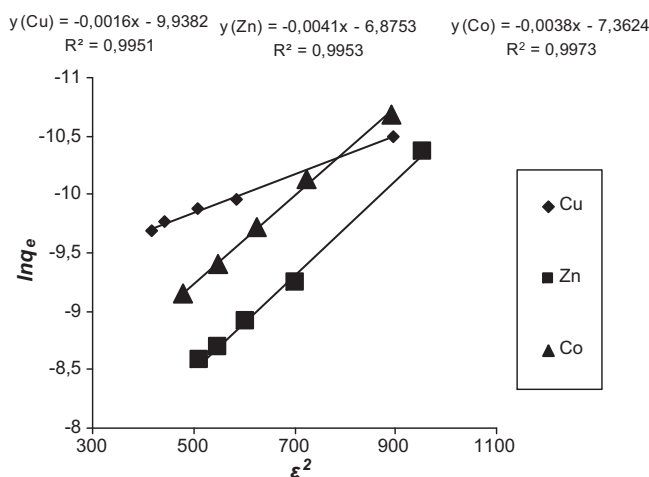


Fig. 8. D-R isotherms of Cu(II), Co(II) and Zn(II) removal by Sp-APTS-GA.

If the value of E is between 8 and 16 kJ mol^{-1} [24], adsorption process can be explained by sorption process is chemical in nature. Table 2 shows that the mean free energy was between 11.04 and $17.68 \text{ kJ mol}^{-1}$ for the three studied metals, which suggests that the sorption of Co(II), Cu(II), and Zn(II) occurs via metal ion complexation mechanism in which the sorption energy lies within 8 – 16 kJ mol^{-1} [25]. Finally, the magnitude of the mean free energy indicates that sorption of selected divalent metal ions occurs via chemisorption [26,27].

3.4. The regenerability of Sp-APTS-GA

Desorption of the loaded metal ions was carried out at optimum pH values for each cations. Three adsorption/desorption cycles, the desorption efficiency was found to be $96.0 \pm 1\%$, $98.0 \pm 1\%$ and $98.0 \pm 1\%$ for Cu(II), Zn(II) and Co(II), respectively. Regeneration of the adsorbent was easy did using EDTA at pH 5.0 reaching efficiency of about 96–97% of all metal complexes

3.5. Thermodynamic studies

Thermodynamic parameters such as enthalpy change (ΔH^0), entropy change (ΔS^0) and free energy change (ΔG^0) 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 (297 – 323 K) under optimized conditions of pH values for each ion.

$$K_D = \frac{(C_0 - C_e)}{C_e} \times \frac{V}{W} \quad (7)$$

$$\log K_D = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (8)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

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. (7) ΔG^0 is the change in Gibbs free energy (kJ mol^{-1}), ΔH^0 is the change in enthalpy (kJ mol^{-1}), ΔS^0 is the

Table 3

Thermodynamic parameters for sorption of metal ions of Sp-APTS-GA (metal ion concentration 10 mmol dm⁻³).

Metal ion	ΔH° (kJ mol ⁻¹)	ΔS° (JK ⁻¹ mol ⁻¹)	$-\Delta G^\circ$ (kJ mol ⁻¹)				
			297	303	307	313	323
Cu(II)	27.21	134.987	12.89	13.70	14.23	15.04	16.39
Co(II)	58.35	242.977	13.81	15.27	16.24	17.70	20.13
Zn(II)	63.60	256.246	12.50	14.03	15.06	16.60	19.16

change in entropy (J (mol K)⁻¹), T is the absolute temperature (K), 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 onto Sp-APTS-GA were evaluated from the van't Hoff plots: $\log K_D$ versus $1/T$. ΔG° was also calculated by using Eq. (8) and results are listed in Table 3 [11]. Fig. 9 shows value of logarithmic plot of distribution coefficient K_D against $1/T$.

The positive value of ΔH° as shown in Table 3 indicates the endothermic nature of adsorption, and the negative values of ΔG° 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 the predominant mechanism. Positive enthalpy values 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 occurred. When metal ion, which is coordinated by water molecules in solution, binds to sorbent through coordination covalent bond formation, some of these water molecules leave the metal ion. Due to the released water molecules, the degree of randomness increases.

The magnitude of ΔH° , 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, Van der Waals interactions compared from 8 to 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 the literature as the transition boundary between both types of sorption processes [28]. High ΔH° values were observed for Co(II) (58.65 kJ mol⁻¹) and Zn(II) (63.60 kJ mol⁻¹) in the temperature range of 297–323 K. The calculated ΔH° values for Cu(II) sorption were lower than 40 kJ mol⁻¹, indicative of the weak interactions of the compound with the Sp-APTS-GA surface at this temperature range.

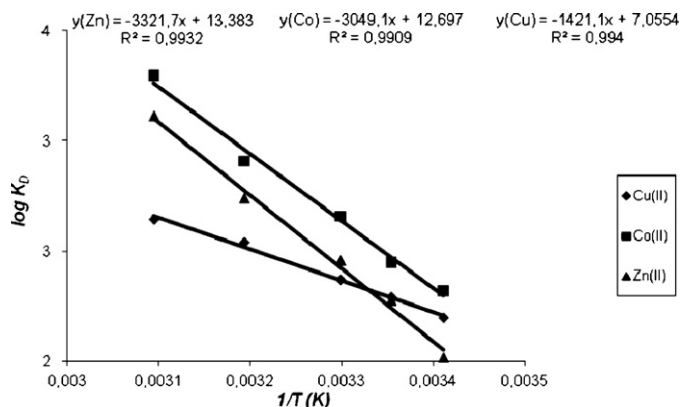


Fig. 9. Plots of $\log K_D$ versus $1/T$ for Cu(II), Co(II) and Zn(II) removal by Sp-APTS-GA.

4. Conclusions

In this study, chemical modification of sporopollenin was attempted with glutaraldehyde by using immobilization method to yield the chelating material Sp-APTS-GA. The optimum pH range for the sorption of the metal ions is from 5.0 to 5.5. The effect of metal ion concentration is studied in the range of $3.5\text{--}25.0 \pm 0.01$ mmol dm⁻³ for the uptake behavior of the chelating materials was studied. Metal sorption followed the order $\text{Co}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$ for removal of metal ion. The Sp-APTS-GA material showed a high adsorption capacity for all the metal ions. The adsorption of Cu^{2+} and Zn^{2+} onto the immobilized material obeyed to both 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. Desorption study showed that metal ions sorbed on the Sp-APTS-GA can be easily and effectively desorbed using 0.5 mol dm⁻³ of EDTA solution.

The efficient modification of glutaraldehyde by APTS on sporopollenin surfaces is confirmed/verified by FT-IR and elemental analysis. Also, according to the result of thermogravimetric analysis, Sp-APTS-GA had higher stability than other two materials (Sp and Sp-APTS).

The calculated thermodynamic parameters reflected reactions were endothermic and spontaneous. For spontaneous processes, the values of ΔG° were negative in the range of 297–323 K as expected. While temperature is increasing, there is a decrease in ΔG° value which indicates that sorption of selected heavy metal ions on Sp-APTS-GA becomes better at higher temperature.

Finally, the metal sorption studies onto Sp-APTS-GA, an original and immobilized material, can act as chelating materials in pollutant metal ion removal from aqueous solution. Overall, it can be concluded from the proposed sorbent system that, it is practical and efficient for the removal of heavy metals contamination from synthetic and industrial effluents with the advantages of inexpensive, large availability and environmental friendly for the use of wastewater effluent. If a literature search is done about the sorption studies related to sporopollenin, a very limited number manuscript can be found. Some of them did not give any place to characterization, and some of them attach metal ions on sporopollenin surface by the physical forces [3,4,29,30]. When these are taken into account, this study is very important due to providing complete steps of characterization as well as providing effective usage of Sp-APTS-GA in metal removing.

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