

Synthesized of Sporopollenin-Immobilized Schiff Bases and Their Vanadium(IV) Sorption Studies

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Abstract This study investigated the potential use of a biologic polymer *Lycopodium clavatum* spores (Sporopollenin) for removal of vanadium ions (V(IV)) from aqueous solution. Three Schiff base derivative compounds immobilized sporopollenin were prepared and characterized. Immobilized sporopollenin was characterized via a scanning electron microscope, elemental analysis, infrared spectroscopy and thermal analysis techniques. The sorption capacities of the immobilized surfaces toward V(IV) ions were investigated by batch sorption experiments. V(IV) concentration, initial pH and the temperature effects were studied. The isotherm data of V(IV) ions were correlated reasonably well both Langmuir, Freundlich sorption isotherm. The thermodynamic studies showed that the V(IV) sorption onto immobilized sporopollenin derivatives is a spontaneous, endothermic and a chemical reaction.

Keywords Schiff base · Immobilization · Sporopollenin · Sorption · Characterization

1 Introduction

Many researchers are interested in heavy metals such as vanadium, in natural waters due to their potential use as geochemical tracers and high toxicity to environment. Vanadium is widely distributed in the earth's crust and has

been recognized as a potentially dangerous pollutant in the same class as mercury, lead and arsenic [1]. Removal of toxic metal ion from aquatic environment is therefore considered important and serves as an attractive case study. There are several physicochemical methods available for removal of heavy metal ions concentration in industrial wastewater, including chemical precipitation, ion-exchange, reverse osmosis, filtration, solvent extraction and electro deposition [2, 3]. Sorption is considered a simple and effective method to remove contaminants within water and wastewater [4]. Although several sorption studies have associated metals, such as lead, cadmium, copper, zinc, mercury and arsenate with toxic effects but there are few publications addressing studies to remove vanadium from contaminated waters. Under aqueous conditions vanadium exists in the oxidation states III, IV and V. In natural waters the chemistry of vanadium is dominated by vanadium(IV) and vanadium(V) [5]. Vanadium is known as an essential trace element for plants and animals. Although vanadium is important for biological system at low concentrations, it is toxic at high concentrations [6]. Vanadium has an electronic configuration of $[\text{Ar}]3d^34s^2$ and can exist in eight oxidation states ranging from -3 to $+5$, but with the exception of -2 . Only the three highest, $+3$, $+4$ and $+5$, are important in biological systems. Under ordinary conditions, the $+4$ and $+5$ oxidation states are the most stable [6, 7]. The $+4$ oxidation state, which is generally the most stable one for vanadium, is best represented by the vanadyl ion, VO^{2+} , which is stable in aqueous solution and under complexation with a wide range of ligands. Although most oxovanadium(IV) complexes are blue green, certain Schiff base complexes may vary from yellow to maroon (reddish purple), and (2) a strong $\text{V}=\text{O}$ stretching band in the IR in the range $950\text{--}1,000\text{ cm}^{-1}$ [8]. Several processes can be used to remove vanadium from

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aqueous solution, but adsorption is a relatively inexpensive, non-hazardous, rapid and versatile technique that may permit recovery of metals from the sorbing media [1].

Schiff bases, named after Hugo Schiff, are formed when any primary amine reacts with an aldehyde or a ketone under specific conditions. Structurally, a Schiff base (also known as imine or azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (C=O) has been replaced by an imine or azomethine group [9]. Schiff base ligands coordinate to a metal through the imine nitrogen and another group, usually oxygen, situated on the original carbonyl compound [10].

Immobilized Schiff bases and their metal complexes have various application area such as separation and purification of proteins, removal of heavy metal ions or toxic organic substances from wastewater or different solvent systems, catalyzed organic reactions as hydrogenation, oxidation, isomerization and epoxydation, and specific processes as purification of hydrocarbons from sulphur compounds [11]. Transition metal Schiff base complexes that bound to different types of inert supports, such as modified silica gel, zeolite and carbon materials, natural or synthetic organic polymers, have been reported but very few reports are available on sporopollenin, anchored Schiff bases metal complexes and their possible application on ligand adsorption. The biopolymer sporopollenin is the main component of the outer walls of spores and pollen. This substance is extremely resistant to non-oxidative chemical and biological degradation procedures [12]. Some advantageous of sporopollenin as a solid support are as follows: (a) it has high resistance to chemicals (many of organics and inorganics) (b) it occurs naturally as a component of spore walls so it is easily obtained (it is not cosefficient) (c) it has a high capacity (d) it possesses suitable functional groups for further modifications (e) it exhibits relatively low swelling and straining properties [11].

Polymer-supported vanadium Schiff base complexes have been considered as versatile catalytic reagents for a wide range of oxidation reactions like, oxidation of olefins and allylic alcohols, benzene/alkylaromatic compounds, sulfides and alcohols. In the presence of inexpensive oxidants such as O₂, H₂O₂ or hydroperoxides, catalysts work efficiently in homogeneous conditions [13].

The aim of the present study is to prepare a three Schiff bases immobilized sporopollenin sorbent for the determination of V(IV) in aqueous solutions. The sorbent was characterized using several techniques such as SEM, elemental analysis, TGA and FTIR. The sorption behavior of the sorbents towards V(IV) ions was investigated through batch-type sorption experiments. In the sorption study, process parameters such as sorbent weight, pH, metal concentration and temperature on the sorption properties are investigated.

2 Experimental

2.1 Chemicals

Lycopodium clavatum spores (sporopollenin) with 20 µm particle size obtained from Fluka Chemicals. Metal salts, 2-hydroxybenzaldehyde, 2,4-dihydroxybenzaldehyde, 2,5-dihydroxybenzaldehyde, 3-aminopropyltriethoxysilane (APTS), Vanadium acetylacetonate (VO(acac)₂) and solvents were obtained Fluka, Sigma-Aldrich and Merck Companies. All of the chemicals and solvents were of reagent grade and used without further purification. All aqueous solutions were prepared with deionized water which is purified with Millipore Milli-Q Plus water purification system.

2.2 Instrumentation

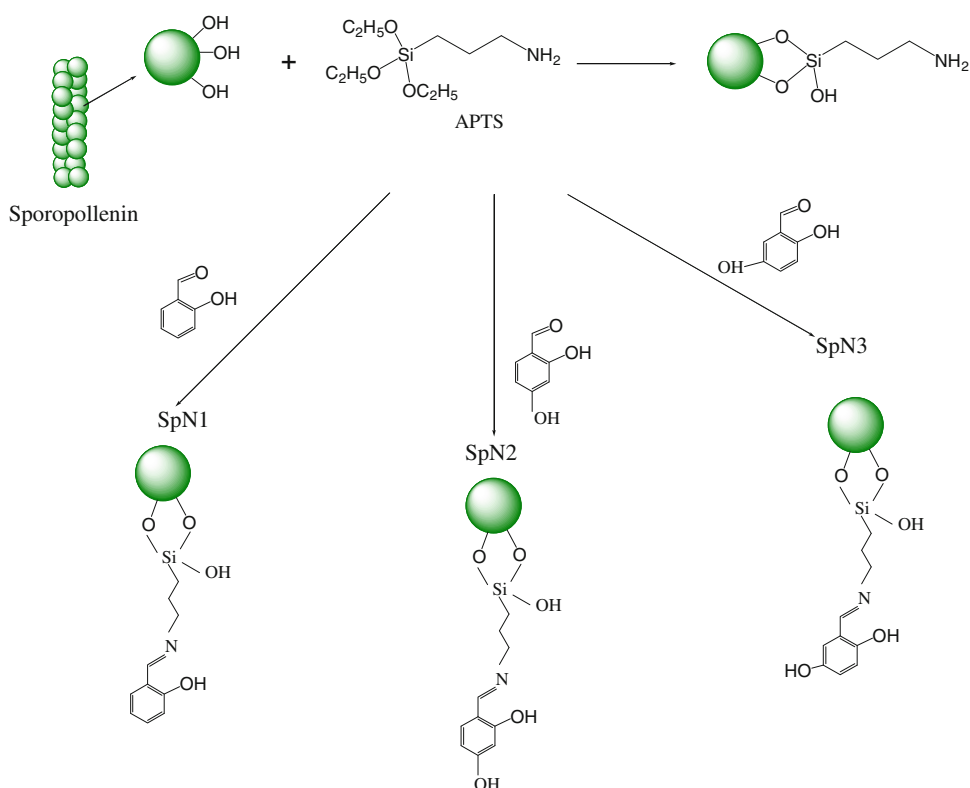
In order to determine the melting and decomposition point of these synthesized materials, Buchi Melting Point, B-540 device was used. These synthesized materials were dried in vacuum drying ovens marked as VacuCell 22. For the characterization of these structures, FTIR Spectrophotometer (Perkin Elmer Spectrum 100/ATR Sampling Accessory), elemental analysis (CHNS-932, LECO), thermal analysis (Shimadzu TA60) and SEM (JSM 5600) were used. 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. The concentration of metals in the solution was determined by using an atomic absorption spectrometer (ContrAA 300, Analytikjena). Sorption studies were executed by using thermostatic shaker (Selecta-Ivmen 100D).

2.3 Synthesis of Sporopollenin-Immobilized Schiff Bases

2.3.1 Preparation of the Amino Functionalized Sporopollenin (SpN)

For the activation of sporopollenin surfaces, Sp (*L. clavatum*) particles (15 g) were suspended in acetone (150 mL) and stirred under reflux for 4 h. The suspension (activated sporopollenin) was then filtered and dried overnight in vacuum at 60 °C. This process was repeated four times. Immobilization of the APTS onto sporopollenin was performed as follows: activated sporopollenin (10.0 g) was suspended in dry toluene (100 mL) and 3-aminopropyl trimethoxysilane (APTS) (9 mL) 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. After filtration,

Fig. 1 Reaction mechanism for the modification of sporopollenin with three Schiff base compound



the resulting aminopropyl sporopollenin (SpN) were washed with 100 mL toluene and 100 mL acetone and then dried in an oven at 60 °C for 24 h. The resulting product may be stored for later use (Fig. 1)[14].

2.3.2 Preparation of the SpN-1

3.2 g min functionalized sporopollenin (SpN) was suspended in 100 mL of dry toluene under a gentle heating, and 0.43 mL (4 mmol) salicylaldehyde was added dropwise to a stirred suspension. The mixture was refluxed for 72 h, left to cool and the product was filtered off under vacuum, washed with ethanol and thoroughly to remove unreacted salicylaldehyde. The light yellow product was dried in a vacuum at 50 °C overnight (Fig. 1).

2.3.3 Preparation of the SpN-2

3.2 g SpN was suspended in 100 mL of dry toluene under a gentle heating. 2,4-dihydroxybenzaldehyde (0.56 g, 4 mmol) dissolved in methanol was carefully added with stirring to a suspension of activated sporopollenin. The resulting mixture was allowed to stir magnetically under reflux for 72 h. The resulting precipitate was filtered, washed with ethanol and thoroughly to remove unreacted 2,4-dihydroxybenzaldehyde. The orange product was dried in a vacuum at 50 °C overnight (Fig. 1).

2.3.4 Preparation of the SpN-3

3.2 g SpN was suspended in 100 mL of dry toluene under a gentle heating. 2,5-dihydroxybenzaldehyde (0.56 g, 4 mmol) dissolved in methanol was carefully added with stirring to a suspension of activated sporopollenin. The resulting mixture was allowed to stir magnetically under reflux for 72 h. The resulting precipitate was filtered, washed with ethanol and thoroughly to remove unreacted 2,5-dihydroxybenzaldehyde. The dark yellow product was dried in a vacuum at 50 °C overnight (Fig. 1).

2.4 Sorption Studies

For sorption studies, 0.02 g each of the dried sorbent (SpN-1, SpN-2 and SpN-3) were equilibrated separately with 20 mL solutions containing different V(IV) concentrations (5–20 mg/L) in a 50 mL joint-stopper conical flask. For the concentration and pH study, batch equilibrium sorption experiments were performed at 298 ± 1 K. For the thermodynamic study, the contents were shaken thoroughly at the temperatures of 293, 298, 303, 313, and 323 K using a thermostatic shaker rotating at 200 rpm. The solutions were then filtered and the equilibrium concentrations of V(IV) concentrations were determined using the flame atomic absorption spectrometer. The amount of solute sorbed at equilibrium was calculated as:

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

where q is the amount of metal ion sorbed onto unit amount of the sorbent (mmol g^{-1}), C_o and C 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 pH Effect of the Sorption

The pH of the V(IV) solution plays an important role on the sorption capacity, where it affects both the degree of ionization of the metal ions as well as the surface properties of the sorbent. To evaluate the influence of pH on sorption, studies of V(IV) sorption onto SpN1, SpN2, and SpN3 were conducted within pH range of 2.0–6.0 at room temperature.

3 Results and Discussion

3.1 Characterization

3.1.1 FTIR

The obtained sorbents named SpN-1, SpN-2, and SpN-3 were characterized by FTIR spectra. The significant infrared bands of the Sp, SpN, SpN-1, SpN-2, and SpN-3 are given in Table 1. The FTIR spectra of pure sporopollenin, modified sporopollenin (SpN) and immobilized Schiff base compound (SpN-1, SpN-2, SpN-3) are shown in Fig. 2. SpN-1, SpN-2, and SpN-3 shows a strong absorption in the $1,633\text{--}1,640\text{ cm}^{-1}$ range in their IR spectra which are characteristic of the azomethine $\nu(\text{C}=\text{N})$ group [15, 16]. In the Schiff base complexes; this absorption has been shifted to the $1,626\text{--}1,615\text{ cm}^{-1}$ region indicating the coordination of the Schiff bases through the nitrogen atom [17, 18]. The strong broad band observed at $3,333\text{--}3,301\text{ cm}^{-1}$ in the spectra of the free ligands is

assigned to $\nu(\text{OH})$. The OH stretching frequency appearing in the spectra of all complexes studied as a broad band in the range $3,370\text{--}3,328\text{ cm}^{-1}$ is due to the presence of water of hydration and/or coordinated water [19]. The new less intense bands in the regions of $415\text{--}435$ and $510\text{--}580\text{ cm}^{-1}$ are due to $\nu(\text{M} \rightarrow \text{N})$ and $\nu(\text{M} \rightarrow \text{O})$, which indicates the coordination of the ligand to the metal ion. These bands were absent in the spectra of the uncomplexed Schiff bases, thus confirming participation of the O and N atoms in the coordination [20]. The band which appeared at $940\text{--}998\text{ cm}^{-1}$ is assigned to $\nu(\text{V}=\text{O})$. This band is observed as a new peak for the complexes and is not observed in the spectrum of free ligands [21].

The surface morphology of the immobilized and pure sporopollenin is shown in Fig. 3a–d. The SEM image indicates that the immobilized surfaces have spherical shape and its surface is contains many pores. For the pure Sp particle has a large internal cavity. Also, it can be seen from this figure that the diameter of the pure sporopollenin was around $5.5\text{ }\mu\text{m}$ (Fig. 3a). After immobilization, the surface cavity of the sporopollenin was filled with Schiff base (Fig. 3b–d) [22].

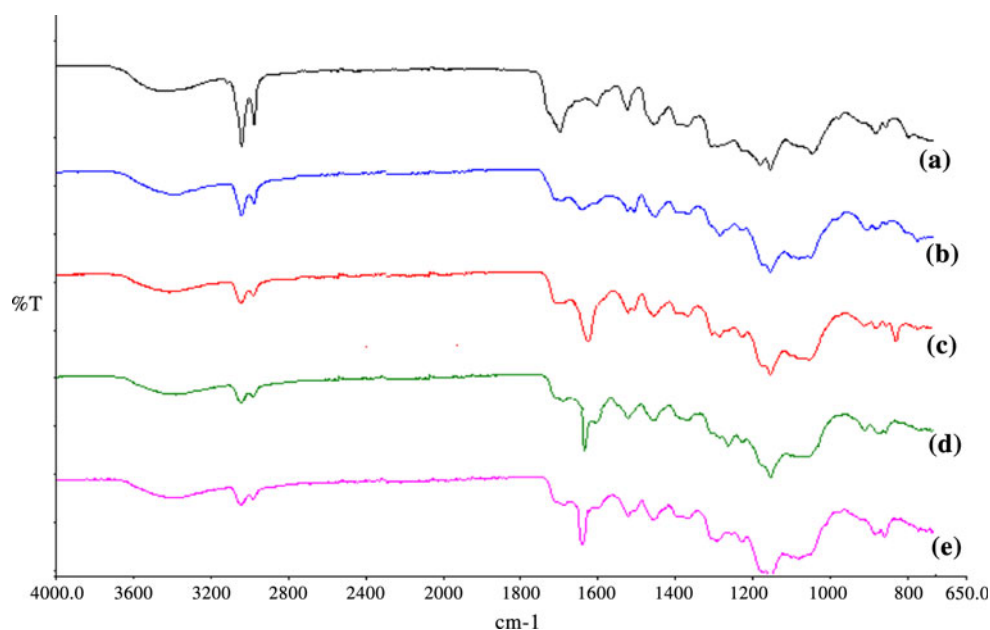
The atomic percentages of the elemental composition of the prepared pure sporopollenin and immobilized materials were given in Table 2. In view of sporopollenin results, the nitrogen contents in the SpN-1, SpN-2, and SpN-3 were roughly increased while hydrogen and carbon contents were decreased in all materials. The results revealed that the immobilized materials contain mainly C, N, and H. As expected, no apparent change was observed in main elements of all the immobilized materials. The results indicated that Schiff base derivatives were successfully immobilized on the sporopollenin [23].

TGA curves of the three sorbent are presented in Fig. 4. The thermal stability of immobilized materials is also presented for comparison. The weight loss curve for unmodified sporopollenin is characterized by three stages. The first one, at $95\text{ }^\circ\text{C}$, which corresponds to a mass loss of 5.54%, can be assigned to the loss of water, followed by another loss of 38.10% in the $220\text{--}400\text{ }^\circ\text{C}$ intervals and

Table 1 Important FTIR bands of sporopollenin and its derivatives

Compound	Colour	Yield (%)	$\nu(\text{O-H})$	$\nu(\text{C-H})$ aliph	$\nu(\text{CH}=\text{N})$	$\nu(\text{V}=\text{O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
Sp		–	3,376	2,857–2,924	–	–	–	–
SpN			3,309	2,857–2,930	–	–	–	–
SpN-1	Light yellow	89	3,333	2,861–2,932	1,633	–	–	–
SpN-2	Orange	95	3,301	2,861–2,928	1,637	–	–	–
SpN-3	Dark yellow	92	3,317	2,855–2,942	1,640	–	–	–
SpN 1(VO)	Yellow	85	3,370	2,840–2,945	1,615	976	510	415
SpN 2(VO)	Orange	87	3,350	2,857–2,937	1,620	940	567	418
SpN 3(VO)	Yellow	90	3,328	2,860–2,950	1,626	998	580	435

Fig. 2 IR spectra of compounds; *a* Sp, *b* SpN, *c* SpN-1, *d* SpN-2, *e* SpN-3



finally mass loss of 23.52% at 400–900, this corresponds to the main degradation of sporopollenin with the elimination of volatile products. Similarly, three stage decomposition mechanisms have been observed for three immobilized materials (SpN-1, SpN-2, and SpN-3). The first step of this decomposition can be attributed to the release of water physically adsorbed on surfaces. In the second stage, it has been observed that SpN-1, SpN-2, and SpN-3 exhibit a clear mass loss of 34.90, 23.66 and 23.69% within the 200–400 °C temperature range, respectively. This event is associated with the dehydrogenation of Schiff base compound. Finally, mass loss of 35.80, 29.91, and 25.87% corresponds to degradation sporopollenin molecules associated with the final product, respectively. Considering the potential application, it was found that all three sorbents have a good thermal stability [24].

3.2 Effect of the pH

The initial pH value of the solution is an important factor that must be considered during sorption studies. The pH has two kinds of influence on metal sorption: an effect on the solubility and speciation of metal ions in solution, and on the overall charge of the sorbent. As mentioned in introduction section, vanadium can be found in $+4$ oxidation states as vanadyl cation, VO^{2+} , in reducing media and is stable in acidic solution below pH 2 [6]. However, it is known that vanadium exists in different hydrolyzed forms depending upon its concentration and the pH of the system [1]. The experimental results are shown in Fig. 5, where the V(IV) removal is plotted against the solution pH. As, the concentration of H^+ ions decreases with increasing pH of the medium, more number of V(IV) get exchanged and

hence observed a higher sorption near pH 5.5. At pH value higher than 5.5, the sorption studies could not be carried out because of the precipitation of V(IV) as $\text{V}(\text{OH})_2$. As seen the Fig. 5, the sorption capacity of SpN-1, SpN-2, and SpN-3 increases as pH rises 2.00–5.50, reaches maximum sorption in the pH range 5.00–5.50 and then decreases linearly as pH increases from 5.50 to 6.00. The maximum sorption yield was found to be 62.52, 56.10 and 67.88% at pH 5.50, respectively SpN-1, SpN-2, and SpN-3. Therefore, all the sorption experiments were carried out at pH 5.5. Low pH value of V(IV) solution contains high concentration of H^+ ions that may compete effectively with metal ions for exchangeable cations on the surface active sites of modified surfaces. This could be also due to the protonation of the functional groups on sorbent surfaces, inducing an electrostatic repulsion of metal ions and the surface active sites of modified structures [4].

3.3 Sorption Isotherm

Sorption isotherm is critical to determine the sorption capacity of sorbents as well as to understand the nature of sorbate–sorbent interactions [25]. Sorption isotherms depend on certain parameters, whose values express the surface properties and the affinity of the sorbent. They can also be used to compare the sorptive capacity for different metal ions [26]. The Langmuir and Freundlich models are often used to describe equilibrium sorption isotherms. The Langmuir isotherm is based on the assumption that all sorption sites are equivalent and adsorption in an active sites is independent of whether the adjacent active sites is occupied or not. It can be described by the linearized form [27]:

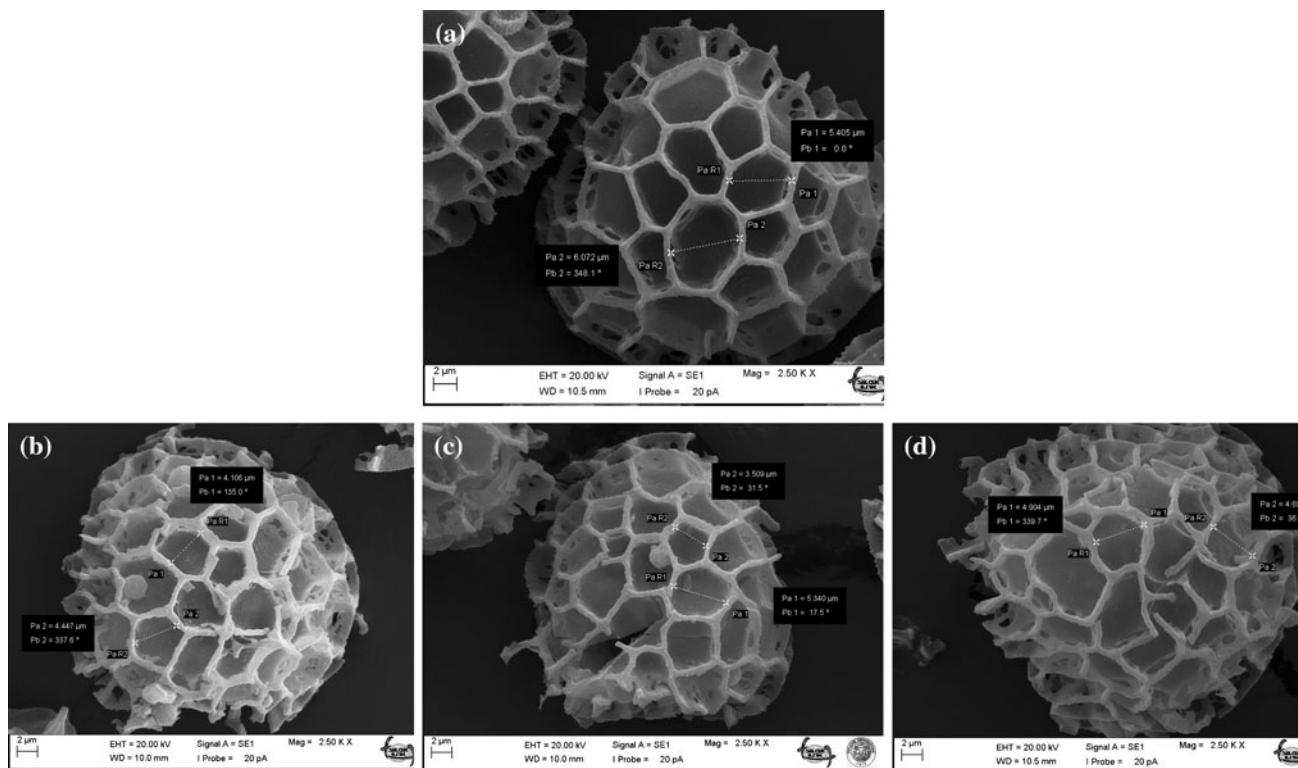


Fig. 3 SEM image of the sporopollenin: Sp (a), SpN-1 (b), SpN-2 (c) and SpN-3 (d)

Table 2 Percentages (%) of hydrogen (H), carbon (C) and nitrogen (N) for the matrices Sp, SpN-1, SpN-2, and SpN-3

Surface	Nitrogen (%)	Carbon (%)	Hydrogen (%)
Sp	1.00	66.7	8.62
SpN-1	2.42	44.81	4.56
SpN-2	2.55	41.86	4.85
SpN-3	2.46	40.10	4.67

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

where q_e is the amount of solute sorbed on the surface of the sorbent (mmol g^{-1}), C_e is the equilibrium ion concentration in the solution (mmol dm^{-3}), q_0 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 $1/bq_0$ and intercepts $1/q_0$.

The Freundlich expression is an empirical model based on sorption onto a heterogeneous surface. The linearized form of the Freundlich isotherm [28] is expressed as:

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

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}), K_F is the Freundlich constant

(mmol g^{-1}) which indicates the sorption capacity and represents the strength of the absorptive bond and n is the heterogeneity factor which represents the bond distribution. The plot of $\ln q_e$ versus $\ln C_e$ should give a straight line with a slope of $1/n$ and the intercept of $\log K_F$.

To deepen the understanding of sorption mechanism, Dubinin–Radushkevich (D–R) isotherm model was chosen to apply on sorption study. The D–R isotherm can be used to describe sorption on both homogenous and heterogeneous surfaces [29]. A linear form of D–R isotherm is:

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

where ε (polanyi potential) is $[RT \ln(1 + 1/C)]$, q_e is the amount of solute adsorbed per unit weight of adsorbent (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.

The mean free energy (E), calculated by the Dubinin–Radushkevich isotherm, is presented in Table 3. The energy values were calculated using the equation:

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

From the Table 3, the values of E values are found 8.64, 8.00, and 8.16 kJ mol^{-1} for SpN1, SpN2, and SpN3, respectively. The value of this parameter can give

Fig. 4 Thermogravimetric curves for Sp, SpN1, SpN2, and SpN3 surfaces

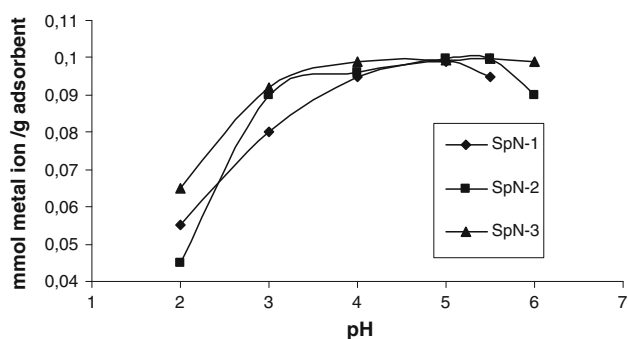
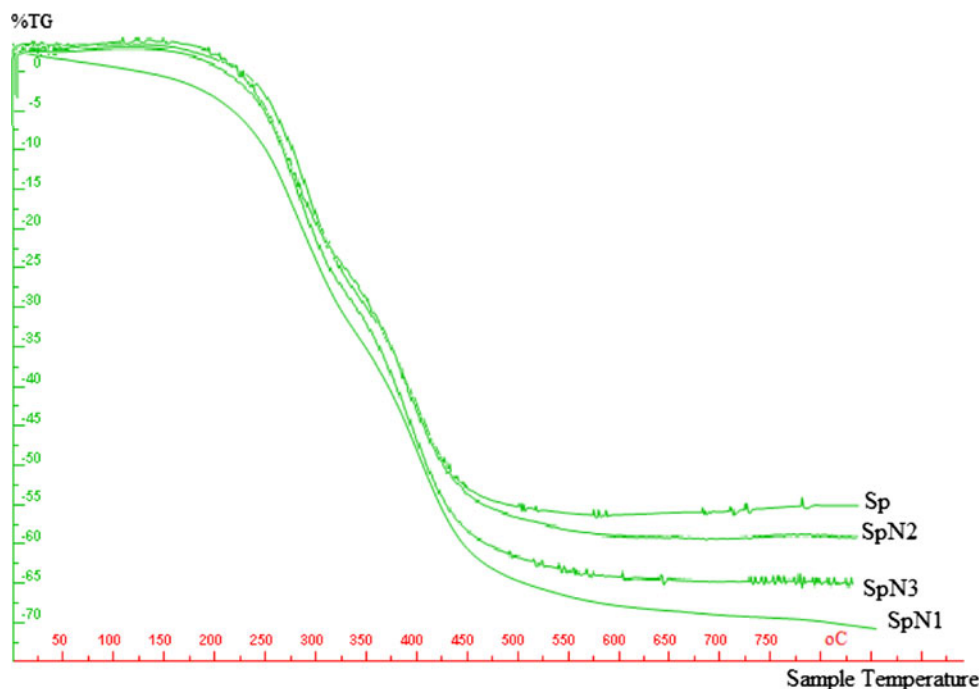


Fig. 5 Influence of pH on the sorption of V(IV) ions onto SpN-1, SpN-2, and SpN-3 surfaces

information about sorption mechanism. E value is between 8 and 16 kJ mol^{-1} , which indicate the sorption process follows by ion-exchange, while its value in the range of 20–40 kJ mol^{-1} is indicative of chemisorption [27]. So, it seems that ion-exchange mechanism is dominating in the adsorption process.

As-fitted Langmuir and Freundlich isotherm parameters for the sorption of V(IV) onto immobilized three sorbent are listed in Table 3. As shown in Table 3, both the Langmuir and Freundlich models correlated the sorption isotherms on all three sorbent quite well, with all R^2 values higher than 0.98. The Langmuir equation is derived from the assumption of monolayer sorption on specific homogenous sites, while the Freundlich model represents sorption on heterogeneous surfaces. The good application of both models implied that besides adsorption onto specific sorption sites through chemical interactions such as surface complexation and cation bridging, sorbate–sorbate interaction may also play

Table 3 Langmuir, Freundlich, and D–R isotherm parameters

Sorbent	Freundlich isotherm		Langmuir isotherm		D–R isotherm		
	$1/n$	K_F	q_0	b	k	q_m	E
SpN1	0.77	13.59	3.70	0.00082	0.0067	2.04	8.63
SpN2	0.92	36.23	1.66	0.0054	0.0079	3.69	7.96
SpN3	0.90	48.91	1.56	0.0037	0.0075	4.84	8.16

an important role in the sorption process by sorbents. Thus, the Freundlich and the Langmuir isotherms are the most suitable equations to describe the adsorption equilibrium of V(IV) onto modified surfaces at 25 °C [30].

3.4 Thermodynamic Study

Thermodynamic parameters such as enthalpy change (ΔH°), entropy changes (ΔS°), and Gibbs free energy change (ΔG°) must take into consideration in order to determine the spontaneous of a process. The apparent thermodynamic parameters ΔH° and ΔS° changes for the V(IV) sorption onto SpN1, SpN2, and SpN3 at 10 mmol dm^{-3} initial metal ion concentrations are calculated from the slopes and intercepts of the linear variation of $\log K_D$ versus $1/T$ by the equation (Table 4) [14]:

$$\log K_D = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (6)$$

where 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), R is the gas constant ($8.314 \times$

Table 4 Thermodynamic parameters

Sorbent	ΔH (kJ mol ⁻¹)	ΔS (JK ⁻¹ mol ⁻¹)	$-\Delta G$ (kJ mol ⁻¹)				
			293	298	303	313	323
SpN1	41.22	192.62	15.24	16.20	17.16	19.09	21.02
SpN2	22.12	127.71	15.29	15.93	16.57	17.58	19.12
SpN3	60.23	261.37	16.49	17.80	19.11	21.73	24.35

10⁻³ kJ mol⁻¹ K⁻¹). Gibbs free energy (ΔG°) is calculated from the Eq. 7:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

where ΔG° is the change in Gibbs free energy (kJ mol⁻¹). The negative values of ΔG° obtained in each case indicate the feasibility and spontaneous nature of the sorption processes under standard conditions. It is also observed that in each case, ΔG° becomes more and more negative with increasing temperature, indicating thereby greater sorption at higher temperatures. The positive values of ΔH° confirm the endothermic nature of the sorption process, while the positive ΔS° values reflect a good affinity of SpN1, SpN2, and SpN3 towards V(IV) (Table 4).

4 Conclusion

This study is revealed that Schiff base immobilized sporopollenin can be used as an alternative sorbent for V(IV) ions removal in aqueous solution. The sorption of V(IV) onto three sorbent was affected by pH, adsorbent concentration and temperature. The pH of the medium has an influence on the sorption of V(IV) onto modified sporopollenin and a maximum sorption was observed at pH 5.5. The sorption data follows Freundlich and Langmuir isotherms. The nature of sorption process is spontaneous and endothermic. The mechanism of vanadium sorption onto all the modified forms of sporopollenin is governed by sorption and ion-exchange. Thermodynamic constants were also evaluated using thermodynamic equations (Eqs. 6, 7). The negative values of ΔG° indicated the spontaneity of V(IV) adsorption process and the positive values of ΔH° and ΔS° showed the endothermic nature.

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