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Adsorption and desorption behavior of silver ions onto valonia tannin resin

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Abstract: Valonia tannin (VT) was gelated through polymerization with formaldehyde to prepare an adsorbent, which was found effective to remove Ag^+ from aqueous solution. The adsorption–desorption behaviors of valonia tannin resin (VTR) were investigated under various initial Ag^+ concentrations, solution temperatures, pH values etc. The applicability of empirical kinetic models was also studied. The pseudo-second-order model studies revealed the Ag^+ sorption was very rapid. VT and VTR were characterized using FTIR and SEM before and after adsorption. The Ag^+ biosorption on VTR increased with a rise in initial concentration of Ag^+ and with a decrease in temperature. Desorption experiments were conducted at low pH values and the solutions of H_2SO_4, HNO_3 and HCl were used for desorption. The VTR shows high adsorption capacity to Ag^+ in a wide pH range of 2.0−7.0, and a maximum adsorption capacity of 97.08 mg/g was obtained at pH 5.0 and 296 K when the initial concentration of Ag^+ was 100.0 mg/L. Ag^+ ion desorption could reach 99.6% using 1 mol/L HCl+1% thiourea (NH_2CSNH_2) solution. By utilizing such characteristics of VTR, it is expected that it can be applied to recovering Ag^+ efficiently and simply with low cost.

Key words: biosorption; desorption; kinetics; silver; Ag^+ ions; absorbent; valonia tannin; resin

1 Introduction

Silver has the highest electrical and thermal conductivity among metals. It exhibits superior corrosion and oxidation resistance. Silver is a nonessential trace metal. The monovalent silver ion is more toxical for fish than copper or mercury, and it is an extremely effective bactericide [1]. Silver is not a dietary requirement for organisms. Antimicrobial agents such as silver are used in commercial textiles and they damage the cell wall or alter cell membrane permeability, denature proteins, inhibit enzyme activity or inhibit lipid synthesis, all of which are essential for cell survival [2]. The presence of pathogen microorganism in water and environment is one of the perennial problems. Recently, nano-silver-containing composite materials have been used in studies to remove bacteria, fungus, viruses and odor from water and environment [3−6]. The experimental studies showed that the dope loaded nano-silver particles have high practicality. In view of these notable properties, the industrial and technical usage of silver in photographic materials, electrical and electronic products, brazing alloys, batteries, silver painted bearings of aircraft, diesel locomotives and gas turbine engines, mirrors and in dental amalgams has exceeded its applications as a decorative and ornamental metal [7].

In literature, many natural organic and inorganic materials have been used as adsorbents. HANZLIK et al [8] studied the removal of Ag(I), Cd(II) and Cu(II) ions by adsorption by "natural carbonaceous materials (spruce wood, pine bark, cork, peat, fusinite, lignite, oxidised lignite, bituminous coal and anthracite)" [8]. Since metal ions have toxic effects on the environment, many researchers suggested cost-effective organic biosorbents such as living [9] and non-living biomass [10,11] for removing dissolved metals from wastewaters.

Recently, various sorbents have been used in studies to remove Ag ions and the heavy metals from water and waste water by sorption. Several studies have been proposed in the literature about the use of new sorbents, in relation with silver ions sorption from water solutions. These materials have some comparative advantages in contrast to common sorbent materials. In the last decade, researches have prepared new Ag sorbents using various materials by miscellaneous methods. Some remarkable studies can be seen in Table 1.

As seen in Table 1, there are researches all over the world, on the understanding of the mechanisms of removing Ag ions through new sorbents. Tannin adsorbents are used for metal sorption as powder or granules in direct use [24], and some studies have used

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Table 1 Silver sorption studies

Sorption material	pH	*T*/K	Ag^+ sorption capacity	Reference
717 anion-exchange resin	2−3		0.58 mol/g	[12]
Calcium alginate beads	4	295	52 mg/g	[13]
Chelamine	6	295	1.2 mmol/g	[14]
Polyurethane foam (PUF)	5	298	65.4 μmol/g	[7]
Carbon adsorbents	6	−	1.06 mmol/L	[15]
Shenfu3^{-1} coal	4.5	353	116.414 mg/g	[16]
Acrylic copolymers functionalized resin (As 14P)	4	298	100 mg/g	[17]
Poly(*o*-phenylenediamine) microparticles	5	303	533 mg/g	[18]
Chemically modified melamine resins	7.2	318	1.140 mmol/g	[19]
Amino/thiol-bearing resin (RIV)	6.5	301	2.86 mmol/g	[20]
6-mercaptopurinylazo resin	6	−	0.52 mmol/g	[21]
3-amino-1,2,4-triazole-5-thiol chelating polymers	6.7	328	2.43 mmol/g	[22]
Thiourea-modified chitosan resin	4	298	3.77 mmol/g	[23]
Valonia Tannin resin (VTR)	5	295	97.087 mg/g	This study

them fixed onto a constant membrane. In many studies, developed tannin resins were used for uptake platinum(IV), palladium(II) [25], and bismuth(III) [26] ions as adsorbent on their own and in others adsorbent mechanisms are studied on tannins immobilized collagen fiber membrane.

For removal of many elements such as Hg^{2+}, Zn^{2+}, Pb^{2+}, Cr^{2+}, Cd^{2+}, Ni^{2+}, Bi^{3+}, Th^{4+}, V, U and precious metals such as Au^{3+}, Pt^{4+}, Pd^{2+}, tannin sorbents have been employed in literature [27]. However, no studies on Ag^+ removal with the tannin biosorbents were found. Recovery of silver as a precious metal from industrial wastewater is important from economical and environmental perspectives. The aim of the present work was to study the detailed sorption isotherms and kinetics of less-researched Ag(I) metal from aqueous solutions by tanin resins and the desorption behavior. Experiments were performed as a function of adsorption time, initial Ag^+ concentration in the solution, and the temperature. Our objectives were (i) to determine and compare the isotherms of Ag^+ adsorption on VTR with various physico-chemical properties, (ii) to determine and compare the sorption kinetics and mechanism of Ag^+ adsorption on VTR, and (iii) to investigate the sorption–desorption hysteresis phenomena and its possible mechanism.

2 Materials and methods

2.1 Preparation of VTR

Valonia tannin was selected as the raw material to synthesize the resin. Tannin was provided from the Tuzla Organized Leather Industry (Turkey). A certain amount of tannin powder was dissolved in ammonia solution at room temperature. Then, tannin was gelated through polymerization with formaldehyde (37%) at 343 K. After gelation at 343 K for 14 h, the obtained tannin resin was crushed and sieved to produce particles of 38−53 μm in diameter. They were washed successively with distilled water and HNO_3 solution (0.5 mol/L) to remove unreacted substances, and finally rinsed with distilled water again.

2.2 Batch equilibrium studies

The concentration of the silver solution was determined by an atomic absorption spectrophotometer (Shimadzu, AA-6200 type). The adsorbed Ag^+ concentrations were obtained from the difference between total initial Ag^+ concentration and finally detected Ag^+ concentration. The maximum adsorption capacity (Q_m) was calculated from isotherm data. The amount of Ag^+ ion sorption onto VTR can be calculated by [28]

$$q_e = \frac{C_i - C_e}{m} V \quad (1)$$

where q_e is the silver ion adsorbed onto the VTR (mg/g); C_i is the initial silver ion concentration (mg/L); C_e is the final silver ion concentration in the solution (mg/L), V is the volume of the solution (L); m is the mass of used VTR adsorbent (g). Batch adsorption studies were conducted to determine the relationship between adsorbent and adsorbate, varying the amounts of adsorbate. In the study, VTR particle size of 38−53 μm was used. Agitation rate on the Ag uptake was studied by using 350 r/min stirring speed. All experiments were repeated three times and the results given here are the average of there values.

In the all batch experiments, contact time was 180 min. Parameters such as temperature and pH are quite important on adsorption. The pH of the solution was adjusted to desired values with 0.1 mol/L HNO_3 and 0.1

mol/L NaOH. Adsorption studies were performed by mixing 1 g VTR with various initial Ag solution concentrations ranging from 10 to 150 mg/L at (296±2) K and pH 5.0.

2.3 Physical and chemical characterization of adsorbent

Characterization of the adsorbents was performed in four ways: raw VT, VTR and Ag adsorbed VTR were analyzed by scanning electron microscopy (SEM), infrared spectroscopy (FT-IR) by determining of multi-point surface area and Zeta potential measurement. The SEM enables the direct observation of the changes in the surface structures of the resin due to the modifications. In order to understand the surface structure of VTR, morphological analysis of the VT and VTR was performed by SEM using a Jeol JSM-6060LV. Energy dispersive spectrophotometry (EDS) analysis was performed with EXRF SYSTEMS İnc 500 Digital processing. Fourier transform infrared (FTIR) spectra of VT and VTR were obtained by using a FTIR spectroscope (Mattson 60R). The dry beads (about 0.1 g) were thoroughly mixed with KBr and pressed into a pellet and then the FTIR spectrum was recorded. Surface area is a main characteristics that shows the adsorption ability of an adsorbent. The multi-point BET surface area analysis of VTR powder was performed with quantachrome autosorb automated gas sorption system (Vers.1.27). The analysis was carried out through an adsorption of N_2 gas (gas effluent temperature=75 °C; bath temperature=77.35 °C). Zeta potential was measured with a Zeta potential-mobility measurement system (MALVERN Nano ZS90).

2.4 Desorption studies

Desorption of the adsorbed silver ions from the VTR was studied in a batch system. Firstly, 1 g of VTR was used for adsorbing Ag^+ ions in 1000 mL of Ag^+ solution (50 mg/L) at pH 5 and then the Ag adsorbed VTR was used for desorption studies. Ag^+ binding on VTR was washed with deionized water to remove any unabsorbed Ag^+ ions. Then, desorption experiments were carried out using various concentrations of H_2SO_4, HNO_3, HCl, thiourea (NH_2CSNH_2) and thiourea–HCl solutions with a constant stirring (130 r/min) at room temperature for 30 and 10 min. Thiourea is an alternative nonpolluting reagent for extracting precious metals such as silver, gold, etc [29]. It is possible to take advantage of different fundamental parameters for the separation of Ag^+ and Cu^{2+} in the presence of thiourea [30], and indeed it works in the optimal conditions. The desorption ratio was calculated from the number of metal ions adsorbed on the VTR and the final metal ion concentration in desorption medium, according to the following equation:

$$\text{Desorptionratio} = \frac{\text{amount of metal ions desorbed}}{\text{amount of metalions adsorbed}} \times 100\% \quad (2)$$

3 Results and discussion

3.1 Characteristics of resin

3.1.1 Microscopic analysis of VTR

Scanning electron micrographs were obtained on raw tannin and resin samples either before or after sorption of Ag ions (Fig. 1). As shown in Figs. 1(a) and (b), many small pores and particles with diameter <1 μm are seen on the surface of raw VT and VTR. In Fig. 1(c) the pores of VTR are partially covered with bright Ag ions.

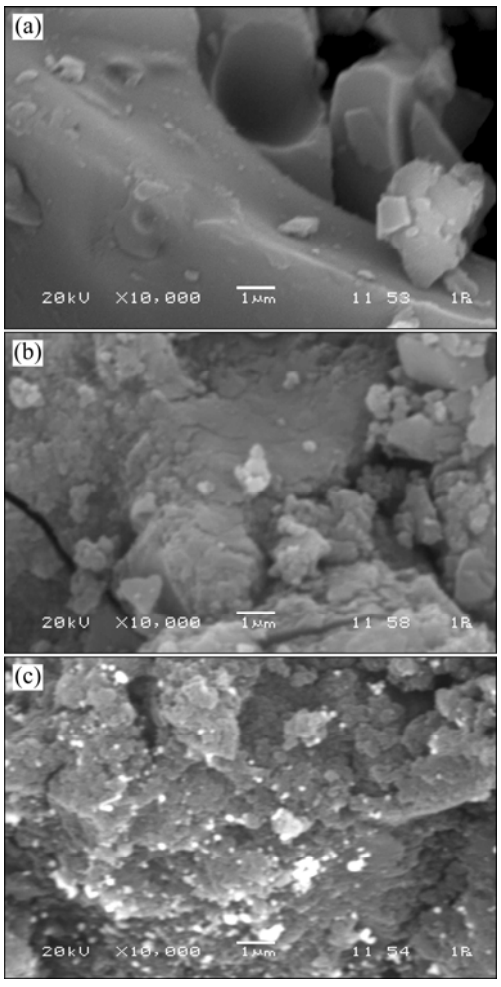


Fig. 1 SEM images of raw VT (a), VTR (38−53 μm in particle size) (b), Ag adsorbed VTR at (366±2) K (38−53 μm in particle size, ρ_o=30 mg/L) (c)

A look at Table 2 indicates that VT is not pure and it involves 9.77% impurity (S, Na, Mg and Ca ions) according to EDS (energy dispersive spectrophotometry) results. When valonia tannin is transformed into VTR,

the impurity of S, Na, Mg and Ca ions decreases to 4.01%. This may be due to the chemicals added when tannin is turned into resin.

Table 2 Average surface components of raw VT and VTR by using EDS

Material	x(C)/%	x(O)/%	x(Ag)/%	Impurity/%
Raw VT	44.28	45.94	−	9.77
VTR	64.28	31.70	−	4.01
Ag adsorbed VTR	60.27	33.83	5.62	0.27

3.1.2 Fourier transform infrared spectroscopy

FT-IR spectra of raw VT and VTR are shown in Fig. 2. Bold line in Fig. 2 illustrates the spectrum of the raw tannin before VTR. When looking at IR bands, it is seen that wide peaks in the range of 3200−3600 cm^{-1} show that phenolic —OH groups are intensively present within the nature of raw tannin. In VTR, it is seen that this wide band has undergone some changes and broadened extensively. This suggests the existence of intense hydrogen bonds. Between 3000−3200 cm^{-1} aromatic C—H peaks have decreased in contrast to raw valonia tannin. Conversely, between 2900−3000 cm^{-1} aliphatic C—H groups in VTR have increased. The peaks between 1740−1750 cm^{-1} show the presence of ketone. The peaks between 1600−1650 cm^{-1} indicate the —C═C— bonds in aromatic nature. The peak around 1190 cm^{-1} shows the presence of ether (C—O—C) groups.

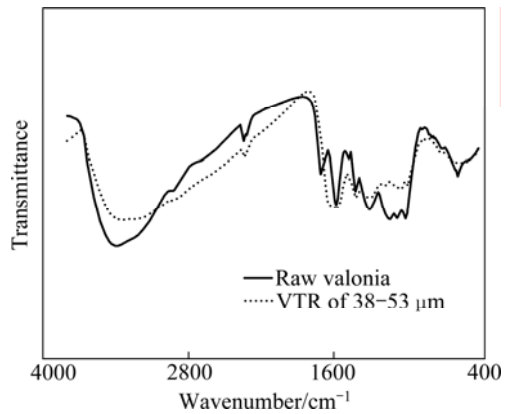


Fig. 2 FTIR spectra of raw VT and VTR

3.1.3 BET surface area

The BET specific surface area of VTR was measured to be 3.821 m^2/g. In comparing the surface area of VTR and common activated carbon, it is seen that the VTR is smaller in size. The surface area of activated carbon ranges between 200−1500 m^2/g [31]. Though the surface area of resin is not large, its adsorption capability to metal ions is high. This shows that functional groups in resin are more efficient than surface area in sorption process.

3.1.4 Zeta potential

Figure 3 shows Zeta potential measured in certain pH range. As seen in Fig. 3, the isoelectric point of resin corresponds to very low pH (pH=2.20). The resin has a negative surface when it is high above its pH 2 value.

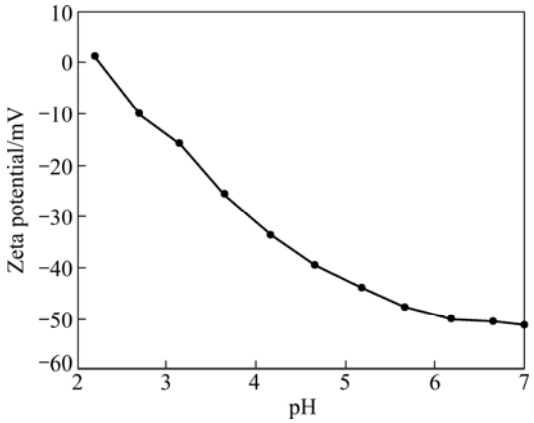
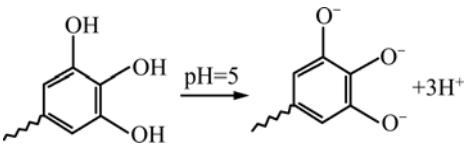


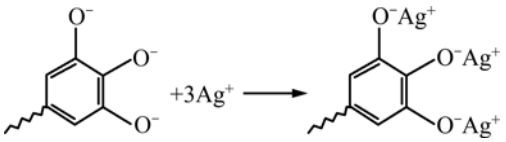
Fig. 3 Isoelectric titration graph of VTR

3.2 Influence of initial pH

In sorption study, knowledge of pH is important because the pH of solution strongly affects the sorption capacity of the resin regarding metal ions. The effect of pH on the Ag^+ removal of VTR was determined over the pH ranging 2 to 7. Figure 4(a) indicates the effects of pH on the silver adsorption onto VTR. Since the surface charge of an adsorbent could be modified by changing the pH of the solution, pH is one of the most important parameters affecting the adsorption process of Ag^+ ions. In order to understand the influence of this parameter on the adsorption, VTR was contacted with Ag metal ion solution at different pH values changing from 2 to 7 for 3 h. Following the equilibrium, remaining metal concentrations were determined for each solution. The results of pH experiments are presented in Fig. 4(a). It may be seen from Fig. 4(a) that adsorption of Ag^+ ions increased by pH on VTR. Clearly, the maximum lead uptake by the VTR was found at pH 5. VTR contains three adjacent hydroxyl groups for binding of metal ions. Ag^+ ions react with phenolic groups of the tannin resins to release protons with their anion sites to displace an existing Ag^+. The adsorption of silver ions onto VTR is a pH-dependent process due to both the chemistry of silver ions in solution and the protonation of functional groups. The VTR has a negative surface at pH 5 (Eq. (3)). Silver ions can be adsorbed onto VTR by ionic interaction (Eq. (4)).



(3)



(4)

3.3 Influence of temperature and thermodynamic considerations

VTR was contacted with Ag metal ion solution at various temperatures for 3 h. Temperature studies were performed at about 296, 306, 326, 346 and 366 K. The results are shown in Fig. 4(b). Figure 4(b) shows the effect of temperature on adsorption of Ag^+ ions onto VTR at pH 5.0 with an initial Ag^+ concentration of 30 mg/L. It can be seen from Fig. 4(b) that the adsorption capacity of Ag^+ ion decreases as the temperature rises, thus the Ag sorption process on VTR is exothermic.

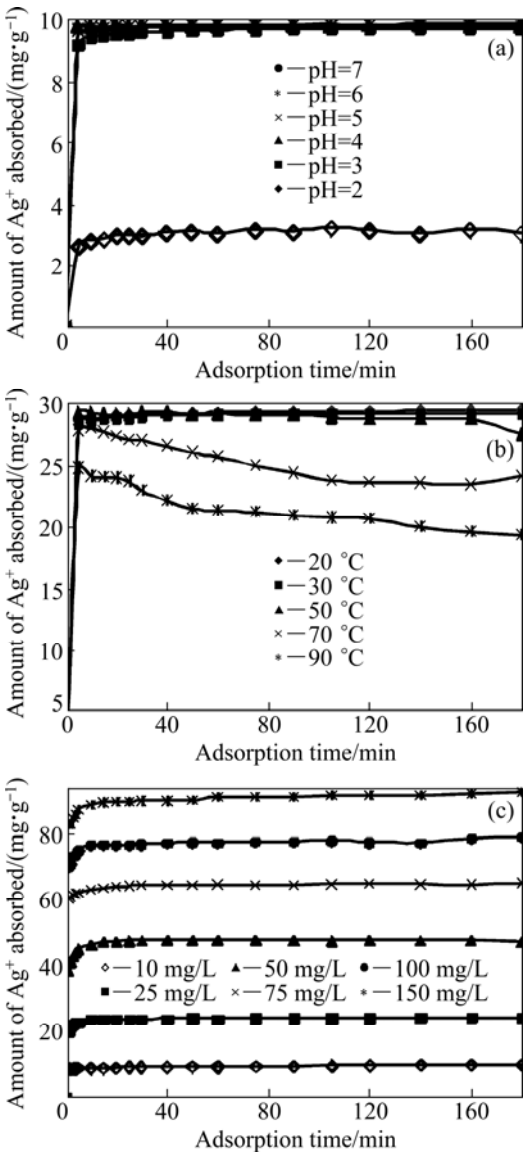


Fig. 4 pH influence (a), temperature influence (b), initial concentration influence (c) on Ag^+ biosorption (ρ_0=30 mg/L, particle size=38−53 μm, pH=5, VTR dose of 1 g/L)

The knowledge of the relevant thermodynamic parameters is needed to establish if the removal process would be able to occur spontaneously or not. Hence, the standard changes of Gibbs free energy ΔG^Θ (kJ/mol), enthalpy ΔH^Θ (kJ/mol), and entropy ΔS^Θ (J·mol^{-1}·K^{-1}) have been estimated to evaluate the feasibility of the adsorption process. If enthalpy (ΔH^Θ) is negative, the reaction is exothermic, that is the overall decrease in enthalpy is achieved by the generation of heat. A negative value of entropy (ΔS^Θ) indicates a decrease in entropy, and the system becomes less random. The Gibbs free energy change of the process is related to the K_c by the following equations [32]:

$$\Delta G^\Theta = -RT\ln K_c \tag{5}$$

$$K_c = \frac{C_a}{C_e} \tag{6}$$

where K_c is the distribution coefficient for the adsorption, C_a is the amount of adsorbate (mg) adsorbed on the adsorbent per liter of the solution at equilibrium and C_e is the equilibrium concentration (mg/L) of solution.

The thermodynamic parameters such as ΔG^Θ, ΔH^Θ and ΔS^Θ were determined by using the following equation:

$$\ln K_c = \frac{\Delta S^\Theta - \Delta H^\Theta}{R} \times \frac{1}{T} \tag{7}$$

To determine thermodynamic parameters, batch experiments were carried out at different temperatures in the range of 296−366 K for Ag^+ adsorption. The values of ΔH^Θ and ΔS^Θ were calculated from the slope and intercept of the plots of ln K_c versus 1/T. The obtained values are given in Table 3. The Gibbs free energy change (ΔG^Θ) values are found to be decreasingly negative with temperature [33], which indicates the feasibility and spontaneity of the adsorption process of Ag^+ ions on VTR. The negative standard enthalpy and the entropy changes showed the exothermic nature of Ag^+ adsorption.

Table 3 Thermodynamic parameters for Ag^+ adsorption on VTR (ρ_o=30 mg/L, pH=5, particle size of 38−53 μm and agitation rate of 350 r/min)

Temperature/ K	K_c	ΔG^Θ/ (kJ·mol^{-1})	ΔH^Θ/ (kJ·mol^{-1})	ΔH^Θ/ (J·mol^{-1}·K^{-1})
296	51.9	−9.59	−42.17	−113.90
306	34.27	−8.90		
326	11.05	−6.45		
346	4.12	−4.04		
366	1.81	−1.79		

3.4 Influence of initial Ag^+ concentration

The effect of initial silver ion concentration in the solution for six different concentrations of Pb (10, 25, 50,

75, 100 and 150 mg/L) on the adsorption is shown in Fig. 4(c). It can be seen from Fig. 4(c) that there was decrease in adsorption of silver with increasing silver ion concentration. Within the first 10 min, a rapid increase in Ag adsorption took place because of the large number of sites available for the sorption, and no less than 90% of total Ag^+ ion was removed. After this period, owing to a reduction in the number of available sites, the silver ions took more time to access the least accessible sites. So, the sorption decelerated and reached the equilibrium approximately after 20 min.

3.5 Isotherm models for Ag^+ biosorption by VTR

Four isotherm equations have been applied for this study: Langmuir [34], Freundlich [35], Temkin [36] and Dubinin-Radushkevich [37] isotherms.

The well-known linearized isotherm equation of Langmuir was reported below [34]:

$$\frac{C_e}{q_e}=\frac{1}{K_L}+\frac{a_L}{K_L}C_e \tag{8}$$

where q_e is the amount of Ag(I) adsorbed at equilibrium (mg/g), and $C_{e\ is}$ the equilibrium concentration of the adsorbate (mg/L). The empirical constants K_L and a_L for Langmuir model are related to the maximum capacity (L/g) and bonding strength (L/mg), respectively. The theoretical monolayer capacity is Q_o and numerically equal to K_L/a_L.

In addition to the experimental data, the linearized form of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms were used for Ag ion removal by VTR. The outcome values of parameters a_L, K_L, Q_o, K_F, n, B, A, q_m, ε and R^2 for all the experiments with pH of solution equal to 5 for removal of Ag^+ are presented in Table 4.

The Langmuir constants can be seen from Table 4. The isotherm data fits the Langmuir equation well (R^2=0.998). The value of maximum monolayer adsorption capacity (Q_o) of the VTR which was used at 296 ± 2 K was found to be 97.087 mg/g. The Langmuir equation is valid for monolayer sorption onto a completely homogeneous surface with a finite number of identical sites. The results suggested that the Langmuir model was the best choice among the other isotherm models to describe the adsorption behavior of Ag^+ onto VTR.

3.6 Kinetic modeling of Ag^+ biosorption by VTR

In kinetic studies, intra particle diffusion model [38], Lagergren pseudo-first-order [39], Pseudo-second-order [40] and Elovich [41] models were used to test the experimental data and their formulas.

The second-order equation [40] is in the following form:

$$\frac{t}{q_t}=\frac{1}{k_2{q_e}^2}+\frac{1}{q_e}t \tag{9}$$

where k_2 is the rate constant of the second-order equation ($g\cdot mg^{-1}\cdot min^1$); q_t the amount of adsorption at time t (mg/g); q_e is the amount of adsorption equilibrium (mg/g).

The calculated q_t values were not in agreement with the experimental q_e values, suggesting that the adsorption of silver ion does not follow the intra particle diffusion

Table 4 Langmuir, Freundlich Temkin and Dubinin-Radushkevich isotherm constants for Ag^+ adsorption onto VTR (at (296±2) K, pH=5)

Langmuir isotherm				Freundlich isotherm			Temkin isotherm			Dubinin-Radushkevich isotherm		
a_L/ ($L\cdot mg^{-1}$)	K_L/ ($L\cdot g^{-1}$)	Q_o/ ($mg\cdot g^{-1}$)	R^2	K_F/ ($L\cdot g^{-1}$)	n	R^2	B	A/ ($L\cdot g^{-1}$)	R^2	q_m/ ($mmol\cdot g^{-1}$)	β/ ($mmol^2\cdot J^{-2}$)	R^2
0.263	25.575	97.087	0.998	41.773	1.544	0.925	16.471	5.028	0.997	552.747	-4×10^{-6}	0.788

Table 5 Kinetic parameters for sorption of Ag^+ on VTR

ρ_o/ ($mg\cdot L^{-1}$)	q_e/ ($mg\cdot g^{-1}$)	Intra particle diffusion model		Lagergren pseudo-first-order kinetic model		Pseudo-second-order kinetic model		Elovich equation		
		k_{int}/ ($mg\cdot g^{-1}\cdot min^{1/2}$)	R^2	k_1/($L\cdot min^{-1}$)	R^2	k_2/ ($g\cdot mg\cdot min$)	R^2	α/ ($mg\cdot g\cdot min$)	β/ ($g\cdot min^{-1}$)	R^2
10	9.672	0.0993	0.958	0.0151	0.884	0.0580	0.9992	2.106×10^{14}	4.2105	0.850
25	23.985	0.1931	0.517	0.0196	0.753	0.0929	1.0000	1.409×10^{15}	1.6683	0.774
50	46.736	0.4310	0.448	0.0072	0.265	0.7491	0.9999	7.640×10^{12}	0.7106	0.741
75	64.957	0.3178	0.722	0.0142	0.681	0.0539	1.0000	3.543×10^{28}	1.0894	0.934
100	78.656	0.4794	0.644	0.0106	0.649	0.0260	0.9999	1.276×10^{22}	0.7103	0.861
150	92.197	0.6359	0.766	0.0143	0.847	0.0186	0.9999	2.251×10^{20}	0.5580	0.944

model, pseudo-first-order, and Elovich kinetics. In order to find a more reliable description of the kinetics, a pseudo-second-order kinetic model was applied to the experimental data. R^2 and several parameters obtained from the kinetic models are shown in Table 5. The experimental data fitted well to the pseudo-second-order kinetic model with a high correlation coefficient, which indicates that the external mass transfer limitations in the system can be neglected and the chemical sorption is the rate-limiting step. Hence, the adsorption kinetics could be approximated more favorably by pseudo-second-order kinetic model for Ag^+ onto VTR. A similar trend was observed in similar systems [17].

The correlation coefficients, R^2, showed that the pseudo-second-order model fits better the experimental data (R^2=1) than the intra particle diffusion model (R^2 is 0.09−0.635), the pseudo-first-order model (R^2 is 0.265−0.884) and Elovich equation (0.741−0.944).

3.7 Desorption of Ag

Samples prepared for the adsorption studies were used in the desorption studies. Desorption experiments were conducted at low pH values and the solutions of H_2SO_4, HNO_3, HCl and thiourea−HCl were used for desorption. Initial batch desorption experiments were performed using 100 mL of 2.5 mol/L H_2SO_4, 5 mol/L HNO_3, 5 mol/L HCl solutions with constant stirring (130 r/min) at room temperature for 30 minutes. Then the mixture was filtered and the concentration of Ag^+ in filtrate was determined, and then desorption extent was calculated. Figure 5(a) shows the amount of the desorbed Ag^+ in the different acid solutions. Results demonstrate that experiments conducted with 5 mol/L of acid solutions were not more efficient. Next desorption experiments were performed using 100 mL of 1 mol/L HNO_3, 5 mol/L HNO_3, 10 mol/L HNO_3 solutions with constant stirring (130 r/min) at room temperature for 30 min. Figure 5(b) shows the amount of the desorbed Ag^+ in the different HNO_3 concentrations.

Results show that experiment conducted with 1 mol/L HNO_3 was very efficient.

The last experiments were carried out with different HCl concentrations in the presence of thiourea. Figure 5(c) indicates the amount of the desorbed Ag^+ in the different HCl−thiourea concentrations. It was found that HCl−thiourea solution is very effective for desorption of Ag^+ from VTR. It can be concluded from Fig. 5(c) and Table 6 and Table 7 that 1 mol/L HCl+1% thiourea solution is the most effective solution in this desorption study. Desorption experiments for Ag were fast similar to the adsorption reaction. For all Ag desorption experiments, a greater quantity of Ag was desorbed in the presence of thiourea. In batch experiments, the adsorbed Ag on VTR can be almost completely desorbed by thiourea–HCl solution. Studies reveal that VTR is great potential to be used as low-cost and reusable adsorbent for the removal of Ag from wastewater.

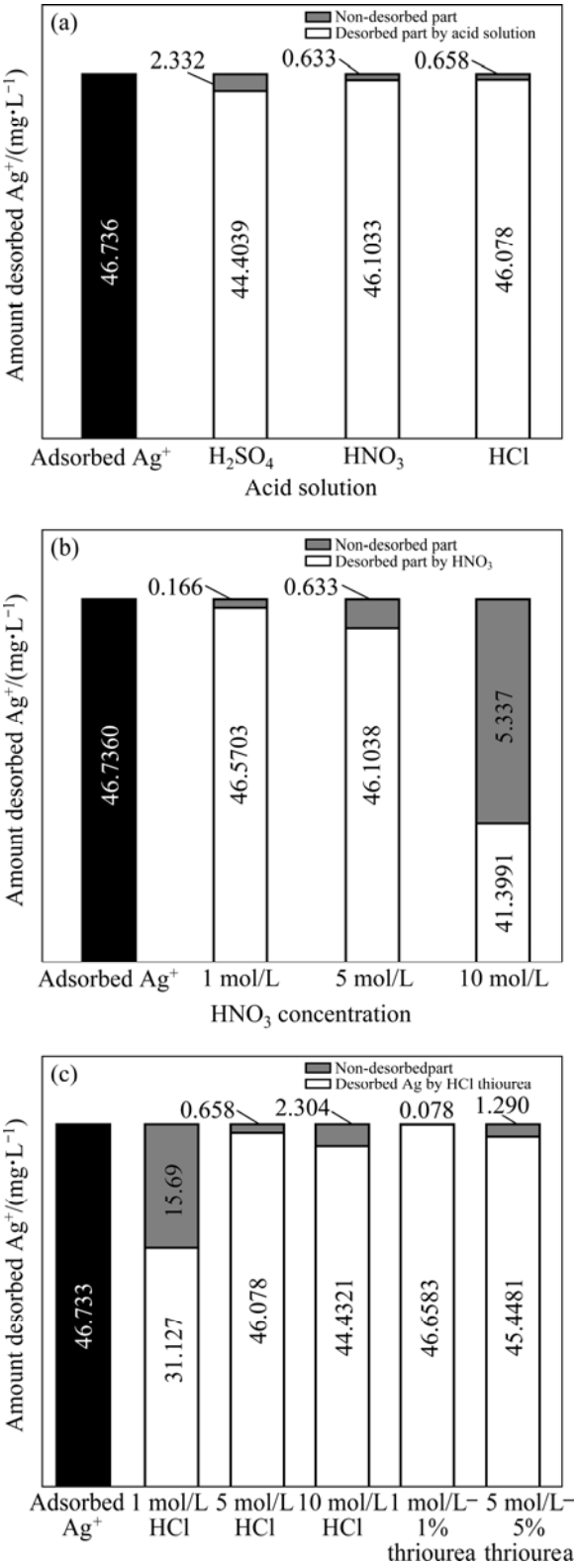


Fig. 5 Ag^+ desorption in different acid solutions (a), in different HNO_3 concentrations (b), in different HCl−thiourea concentrations (c)

Table 6 Ag^+ desorption in 5 mol/L HCl+5% thiourea

Time/min	Desorbed Ag^+/(mg·L^{-1})	Desorption yield/%
1	44.887	96.0
2	46.070	98.6
3	46.096	98.6
5	46.159	98.8
10	46.531	99.6

Table 7 Ag^+ desorption and recovery

Desorbed ion	q_{max}/(mg·g^{-1})	Desorption solution
Ag^+	46.736	1 mol/L HCl+1% thiourea
Desorption time/ min	Desorption yield/%	Recovery from solution/%
30	99.6	93.1

4 Conclusions

1) The adsorption−desorption behaviors of valonia tannin resin (VTR) were investigated under various initial Ag^+ concentrations, solution temperatures, pH values etc. The results suggested that the sorption process was dependent on contact time, initial metal ion concentration, solution pH and temperature. At pH 5 of Ag^+-VTR system, the adsorbent yielded a maximum Ag^+ biosorption. The variation of sorption with temperature yields the values of ΔG^{Θ}=−9.59 kJ/mol at (296±2) K, ΔH^{Θ}=−43.17 kJ/mol and ΔS^{Θ}=−113.90 J/(mmol·K), with a correlation factor R^2=0.998. The negative standard enthalpy and the entropy changes showed the exothermic nature of Ag^+ biosorption. The BET specific surface area of VTR was measured as 3.821 m^2/g. Zeta potential of VTR was measured and the isoelectric point of resin was corresponded to very low pH (pH=2.20). Based on the experimental data, sorption equilibrium and sorption kinetics of Ag (I) removal by VTR followed a Langmuir isotherm and pseudo-second-order kinetics. The maximum adsorption capacity of Ag^+ was obtained as 97.087 mg/g at (296±2) K.

2) Desorption for Ag was fast similar to the adsorption reaction. Desorption experiments were conducted at low pH values. To get low pH values the solutions of H_2SO_4, HNO_3 and HCl were used. It was observed that a greater quantity of Ag was desorbed in the presence of thiourea. The 1 mol/L HCl+1% thiourea (NH_2CSNH_2) solution can effectively desorb Ag^+ ions from the VTR (99.6% efficiency). The results suggest that tannin gel is very useful as an adsorbent in a novel recovery system for silver. As a kind of low-cost, high effective and reusable adsorbent, the practical application of this novel adsorbent can be expected for the removal of Ag^+ from aqueous solution. Investigation with an adsorption column is also recommended before large scale implementation.

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银离子在斛壳丹宁酸树脂表面的吸附和解吸

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摘　要：将斛壳丹宁酸与甲醛聚合来形成的凝胶作为吸附剂能有效地移去水溶液中的银离子。研究了不同银离子初始浓度、溶液温度、pH 值条件下斛壳丹宁酸树脂的附和解吸行为。研究了有关经验动力学模型的适应性。伪二级动力学模型表明银离子的吸附是很快的。用 FTIR 和 SEM 对吸附和解吸银离子后的斛壳彤宁酸和斛壳丹宁酸树脂进行表征。银离子在斛壳宁酸树脂上的吸附随着银离子初始浓度的增加而增加，随着溶液温度的升高而减少。在低 pH 值的 H_2SO_4、HNO_3 和 HCl 溶液中进行解吸实验。斛壳丹宁酸树脂在 pH2.0~7.0 溶液中对银离子表现出高的吸附容量，在银离子初始浓度 100.0 mg/L、温度 296 K 和 pH5.0 的条件下达到最大的吸附量 97.08 mg/g。在 1 mol/L HCl+1%硫脲溶液中银离子的脱吸率达 99.6%。

关键词：生物吸附；解吸；动力学；银；Ag^+离子；吸附剂；斛壳丹宁酸；树脂

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