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Silver sorption on acrylic copolymers functionalized with amines. Equilibrium and kinetic studies

Research Article

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Abstract: The sorption capacity of three weak base ion exchangers based on acrylic copolymers functionalized with ethylenediamine, triethylenetetramine and N, N- dimethylamino propylamine for Ag(I) ions was evaluated. Adsorption experiments were carried out by batch method. The effect of pH, crosslinking degree of copolymers, amount of sorbent, initial ion concentration, contact time and temperature was studied. The parameters which characterize the retention process were estimated using Langmuir and Freundlich isotherm models, the best fitting being for the first model. Kinetic data were fitted to pseudo-first order, pseudo-second order and intraparticle diffusion models. Experimental data were in good agreement with the pseudo second order.

Keywords: *Silver • Sorption • Chelating resin • Equilibrium and kinetic study*

1. Introduction

Silver and its compounds have a variety of applications in electronics, photography, mirrors, medicine, food or clothing production and also as catalysts. The increasing use of silver compounds and silver-containing products has increased its prevalence in the environment because of waste water discharge. At low concentrations (50 – 200 μg L^{-1}) silver can be useful as a disinfectant for drinking water by controlling microbial activity with no risk to human health [1]. The line between indispensable and harmful is usually fine and determining the right level in food and water can be difficult [2]. Moreover the interaction of silver with essential nutrients [3] has brought attention to its potential toxicity. Considering the toxicity and relative accessibility of Ag(I) [4], sensitive determination and treatment methods have been widely developed.

The low concentration range (less than 10 mg L^{-1}) of heavy metals in environmental samples requires separation and preconcentration steps. Conventional methods of silver separation / preconcentration such as liquid - liquid extraction [5,6], co-precipitation [7] are still in use but they are less advantageous when dealing with a large volume which contains heavy metal ions in low concentration. For this reason they are preferred as a step in modern laboratory analysis techniques. For industrial separation and recovery of toxic metals, adsorption is considered more effective and less expensive than other technologies. Solid phase extractions [8,9] and

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ion exchangers are possible alternatives. Heavy metal sorption is an attractive option because of the basic simplicity of the application. Moreover a large number of suitable adsorbents such as activated carbon, polymeric resin or various low cost adsorbents may be used. Activated carbon finds wide applications but it is expensive and its adsorption properties are strongly influenced by the physicochemical nature of precursor material and the thermal history during the manufacturing process. Polymeric resins can provide selective removal of heavy metals and they are used for purification and for treatment of final wastewaters. The typical chelating sorbent for silver separation contains ligands with sulphur [10-15], but as soft cations Ag(I) also react with sorbent functionalized with N containing groups [16-20]. Besides functionalized synthetic resins, many studies report the use of different biosorbents as a low cost technology for removal of heavy metals (including silver) from water [21-23]. The cost advantage of biosorbents is often annihilated by the low reproducibility of the experiments and by the clogging effect in the column system.

There are many determination methods for silver such as potentiometric and voltametric [24-27], but flame atomic absorption spectrophotometry is frequently used because of its simplicity, sensitivity, selectivity, speed and fairly low operational cost. Complex samples and the generally low concentrations of silver require an additional preconcentration step for this method [28-31].

The main objective of this study was to investigate the equilibrium and kinetic parameters of silver(I) sorption onto different crosslinked acrylic copolymers functionalized with amines. For attaining maximum adsorptive silver(I) removal of the tested resins the experiments were conducted in a manner as to optimize "one factor at a time" .

The synthesis of the weak base resins used as adsorbents was previously detailed [32] as well as some studies on the sorption of Zn(II) [33], Co(II) [34] and Ni(II) [35] with the polymers of interest.

2. Experimental Procedures

2.1 Reagents

Acrylic crosslinked copolymers-based on divinyl benzene (DVB), ethyl acrylate (EA) and acrylonitrile (AN) - functionalized with ethylenediamine (EDA) As 13P, triethylenetetramine (TETA) As 14P, N,N-dimethylaminopropylamine (DMAPA) As 15. For the resin syntheses the following materials were used: divinylbenzene (DVB) C=80 wt%; and ethylvinylbenzene - 20 wt% Merck; acrylonitrile AN), C=99 wt%, Fluka; ethylacrylate (EtA), C>99 wt%, Fluka; benzoyl peroxide (POB) with 25 wt% water, Fluka; styrene-ammonium maleate copolymer (SAM), C=20 wt% aqueous solution; ethylenediamine (EDA), C=99 wt%, Fluka; triethylenetetramine (TETA), C=99 wt%, Fluka; N,N-dimethylaminopropylamine (DMAPA), C=98 wt%, Fluka; toluene C=99.9 wt% Fluka; aqueous solution of NaOH and HCl of 1 N concentration. The properties of the resins are given in Table 1.

$AgNO_3$ volumetric standard 0.1 N solution in water from Aldrich was used (by diluting with double distilled water) to obtain solution model of metal ion pollution. Merck standard solution of Ag(I) (1000 mg L^{-1} in HNO_3) was used for calibration.

HNO_3 and NaOH (analytical grades) were used for adjusting pH.

NH_4OH and Merck standard solution of Cu(II) (1000 mg L^{-1} in HNO_3).

2.2 Methods

2.2.1 Sorbents preparation

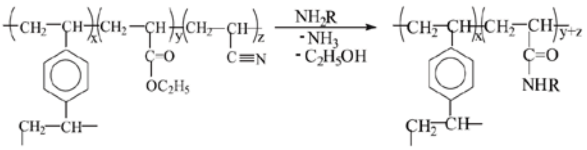
The crosslinked acrylic copolymers were obtained using water suspension radical polymerization of DVB (2 wt%), AN (20 wt%) and EtA (78 wt%) in the presence of toluene as an inert component (D=0.4), initiator was benzoyl peroxide (1 wt%) and 0.5 wt% a styrene-ammonium maleate copolymer aqueous solution as the continuous phase. The copolymers were then aminolysed with

Table 1. Characteristic data of tested acrylic copolymers.

Characteristics	As 13P	As 14P	As 15P
Grade	laboratory	laboratory	laboratory
Matrix	Cross-linked polyacrilate DVB:AE:AN	Cross-linked polyacrilate DVB:AE:AN	Cross-linked polyacrilate DVB:AE:AN
Active group	EDA	TETA	DMAPA
Chemical form	Free base	Free base	Free base
Physical form	Spherical beads	Spherical beads	Spherical beads
Mean particle size, mm	0.3 - 0.8	0.3 - 0.8	0.3 - 0.8
Total exchange capacity	0.53 mEq mL^{-1} 7.217 mEq g^{-1}	0.908 mEq mL^{-1} 14.664 mEq g^{-1}	0.243 mEq mL^{-1} 6.657 mEq g^{-1}
pH range	1-14	1-14	1-14
Operational temperature	Until 80°C	Until 80°C	Until 80°C
Chemical stability	Good in acid and basic media	Good in acid and basic media	Good in acid and basic media

EDA, DMAPA and TETA for 16 h using the copolymer/amine wt-ratio of 1/3 and temperatures of 110, 125 and 180°C, respectively.

The aminolysis-hydrolysis reactions of DVB:AN:EtA copolymer are presented in Scheme 1.



R: $-(CH_2)_2-NH_2$; $-(CH_2)_2-NH-(CH_2)_2-NH-(CH_2)_2-NH_2$; $-(CH_2)_3-N(CH_3)_2$

Scheme 1. The aminolysis - hydrolysis of acrylic copolymers

2.2.2 Adsorption experiments

The effect of important parameters such as pH, contact time, initial metal ion concentration, adsorbent dose and temperature on the adsorptive retention of silver ions was investigated in a series of kinetic and equilibrium experiments.

The adsorption experiments were performed by a bath method where the copolymer (0.05–0.2 g) was suspended in 10–50 mL solution containing 5–125 mg L^{-1} Ag(I) under precise experimental conditions (8–40°C, pH=1–8, contact time 15 minutes - 24 hours).

The sorption capacity was evaluated by the amount of metal ion adsorbed onto the resin (Eq. 1), the percent of metal ion removal (Eq. 2) and the distribution constant (Eq. 3).

$$q_e = (C_o - C_e)\ V\ 10^{-3} / m \qquad (1)$$

$$R\ \% = (C_o - C_e)\ 100 / C_o \qquad (2)$$

$$K_d = q_e / C_e \qquad (3)$$

where: q_e is the amount of Ag(I) adsorbed per unit weight of adsorbent at equilibrium, mg g^{-1}; C_o and C_e are initial and equilibrium concentration of Ag(I) in solution, mg L^{-1}; m is the amount of adsorbent, g; V is the volume of solution, mL; K_d is the distribution constant, (mg g^{-1})/(mg L^{-1}).

2.3 Aparatus

The pH was varied from 1 to 8 and measured with a RADELKIS pH - meter, OP 211/2 using a combined-glass electrode.

The excess of Ag(I) was determined in an aliquot of supernatant by flame atomic absorption spectrometry on a PERKIN-ELMER 3300 spectrophotometer. The measurements were repeated three times. The equation of the calibration curve was determined to be:

$y = 0.0789\ x - 0.0026$ with an $R^2 = 0.9991$.

3. Results and discussions

3.1 Batch equilibrium studies

3.1.1 Influence of different parameters

3.1.1.1 Testing of copolymers

A preliminary selection was made using ~0.05 g resin and 10 mL Ag(I) solution with a concentration of 5 mg mL^{-1} and 24 hours contact time. The retention is dependent on the nature of the functionalized copolymer and of the cross linking degree of the resin. Thus the resins with 2% DVB As 14P and As 15P retain more than 90% Ag(I) and As 13P has a maximum of 60%. For corresponding resins with 8% DVB the adsorbed quantity is less by half for the investigated concentration. The subsequent studies were made on copolymers with 2% DVB.

3.1.1.2 Effect of pH

pH is one of the most important factors controlling the adsorption of heavy metals cations. The investigated copolymers are weak bases and pH influences the protonation and deprotonation of the amine group that is involved in the heavy metal removal.

The solutions with pH varying from 1 to 8 and concentrations of 5 mg L^{-1} Ag(I) were left in contact with 0.05 g resin for 24 hours. The results (Figs. 1a-1c) proved that the amount adsorbed at equilibrium is pH dependent. The low metal adsorption at low pH (<3) could be explained as a competition between protons and Ag(I) ions for the same functional group. On the other hand, the protonation of amine groups would lead to a strong electrostatic repulsion between the silver positive cations. The increase in pH up to 6 considerably decreases of the positive surface charge and, as a result, Ag ions may reach the active site and coordinate to it. At higher pH values other processes such as hydrolysis and/or precipitation may occur.

Systematic studies were done for As 14P and As 15P.

Effect of contact time and initial Ag(I) concentration 50 mL of Ag(I) solution with 16 mg L^{-1}; 50 mg L^{-1}; 83 mg L^{-1} and 125 mg L^{-1} , respectively, pH=4, were slowly stirred with 0.1g resin (previously tested for 24 hours in 10 mL double distilled water) for 600 minutes. 0.5 mL aliquots were removed at different times and were analyzed. The results are presented in Figs. 2a and 2b and indicate that the removal efficiency increased with an increase in contact time before equilibrium is reached.

The sorption profile was different for the two investigated resins. For As 14P the sorption process was faster in the first stage: up to 70% of the Ag(I) present in solution was removed after 15 minutes, followed by a

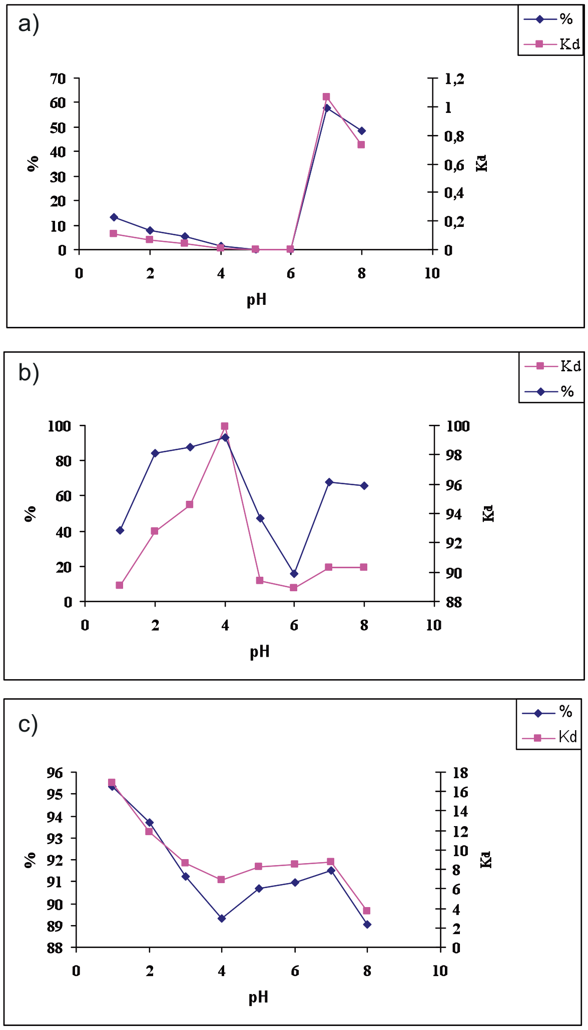


Figure 1. pH effect of Ag(I) sorption on a) As 13P, b) As 14P and c) As 15P (0.01 g resin, C_o=5 mg L^{-1}, T=25°C, 24 hours contact time).

slower stage until 180 minutes when another 20% was removed. For the studied concentration range studied, equilibrium was established after 600 minutes. For As 15P the sorption process was slower and weaker, and it might be explained by the smaller number of amines on the adsorbent surface and by lower hydrophilic character of DMPA compared to TETA.

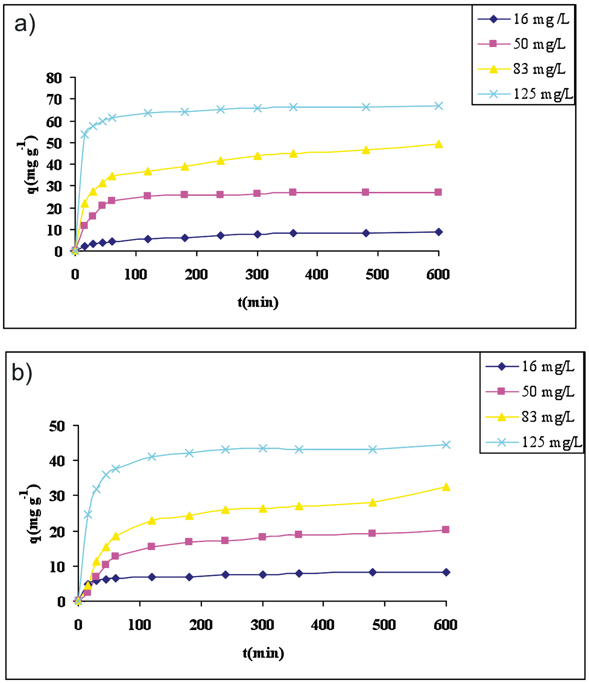


Figure 2. pH effect of Ag(I) sorption on a) As 13P, b) As 14P and c) As 15P (0.01 g resin, C_o=5 mg L^{-1}, T=25°C, 24 hours contact time).

3.1.1.3 Effect of temperature

The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate across the external boundary layer, and this is due to a decrease in the viscosity of solution. In addition, the change of temperature modifies the capacity of the adsorbent for the particular adsorbate [36].

The effect of this parameter on Ag(I) sorption was investigated by carrying out a series of experiments at three different temperatures (8, 25 and 40°C), with 0.1 g adsorbent, for four Ag(I) concentrations and a 10 hour contact time.

The results (Table 2) indicated that the maximum percentage of Ag(I) removal increased for all investigated concentrations for As 14P until room temperature. A similar behavior was observed for the Ni(II) [35], Co(II), Cd(II) and Cu(II) sorption onto this resin (unpublished data). The decrease in sorption at higher temperatures

Table 2. Effect of temperature on removal percentage of Ag(I) using As 14P and As 15P (0.1 g resin, pH=4, C1=16 mg L^{-1}, C2=50 mg L^{-1}, C3=83 mg L^{-1}, C4=125 mg L^{-1}, 10 hours contact time).

Temperature °C	Percent of Ag(I) removal							
	As 14P				As15P			
	C1	C2	C3	C4	C1	C2	C3	C4
8	93.5	83.4	77.2	70.9	92.1	74.6	70.5	63.8
25	99.2	97.2	94.3	93.1	93.9	69.2	67.4	61.9
40	96.4	88.6	87	83.5	95.4	71.8	77.2	65.7

may suggest that the sorption is complex, and the result of both chemical and /or physical processes. Moreover, the Ag(I) – resin complex might have a higher stability at a lower temperature.

The sorption on the As 15P was not significantly influenced by temperature in the tested range.

3.1.1.4 Effect of NH_4OH

Preliminary tests showed the possibility of silver removal by polyamine functionalized resins from ammonia media. In order to establish the influence of NH_4OH on silver sorption, 0.1 g resin was left in contact with 10 and 100 mg L^{-1} Ag(I) solutions for 24 hours.

The presence of NH_4OH is unfavorable for the sorption process as outlined in Table 3; K_d and the retention percentages decrease with increasing NH_4OH concentrations. The effect is more intense at lower concentrations of Ag(I); *i.e*. for As 14 P, 10 mg L^{-1} Ag(I) initial concentration and 10^{-4}M NH_4OH the retention percentage decreases to 9.71. The decrease in sorption can be assumed to be due to blocking of the silver in the ammonium complex which reaches the active site on the resin more slowly.

Table 3. Influence of NH_4OH concentration on Ag(I) sorption onto As 14P and As 15P resin (m=0.1 g resin, C_0=100 mg L^{-1}, T=25°C, 24 hours contact time).

As 14P		C_{NH4OH}	As 15P	
K_d	%	mol L^{-1}	K_d	%
8.696	99.24	0	3.779	89.92
2.567	86.44	10^{-4}	1.102	72.46
2.1	82.03	10^{-3}	0.845	65.61

3.1.1.5 Effect of Cu(II) ions

Silver may be found in the combined state in nature, *i.e.* in copper mineralization, therefore some experiments of sorption were made in a binary mixture. For this purpose 0.1 g sorbent was stirred with 35 mL solution of 100 mg L^{-1} Cu(II) and 10 mg L^{-1} Ag(I) (pH=4, T=25°C, 600 minutes contact time). The results (Table 4) show that for the As 14P there is no significant variations in the sorption percent for both ions in the experimental conditions. For As 15P, the sorption behavior is different. Ag(I) retention is being drastically decreased (quantity and rate) in the binary mixture. This could be explained by the fast adsorption of Cu(II) ions at the external active sites creating a more hydrophobic surface, and disrupting the diffusion of Ag(I) ions to the internal active sites.

The same behavior was observed for Ni(II) [35]. The ten times higher concentrations in Cu(II) did not have a significant influence on Zn(II), Cd(II), Pb(II) and Mn(II) sorption onto the two investigated resins (unpublished data).

3.1.2 Adsorption isotherms

The analysis of isotherm data is important in developing of an equation that accurately represents the results and which could be used for the design process [37]. In order to establish the best fit, two isotherm models were tested, the results being judged in terms of correlation coefficients and values of specific parameters.

3.1.2.1 Langmuir isotherm

For the AS-14P and AS-15P resins, the equilibrium results at different concentrations were graphically represented and analyzed (Table 5) using the linear form of the Langmuir equation [38]:

$$1/q_e = 1/\ C_e\ bq_o + 1/q_o = 1/\ C_e\ K_L + 1/q_o \qquad (4)$$

where C_e is the equilibrium concentration of Ag(I) in solution (mg L^{-1}), b is a constant related to the energy of adsorption (L mg^{-1}) and q_o (mg g^{-1}) represents the practical limiting adsorption capacity when the surface is fully covered with metal ions; K_L is the Langmuir constant.

Table 4. Percentages of Cu(II) (C_0=100 mg L^{-1}) and Ag(I) (C_0=10 mg L^{-1}) removal in mono component and bi component system (pH=4, T=25°C, 600 minutes contact time).

System	As 14P		As15P	
	% Cu(II) removal	% Ag(I) removal	% Cu(II) removal	% Ag(I) removal
Cu(II)	90.37	-	76.66	-
Cu(II) + Ag(I)	93.43	92.72	71.02	21.9
Ag(I)	-	89.79	-	78.2

Table 5. Characteristic parameters of Langmuir and Freundlich isotherms.

Sorbent	Langmuir					Freundlich		
	K_L L g^{-1}	q_o mg g^{-1}	b L mg^{-1}	R_L	R^2	K_F L g^{-1}	n	R^2
As 14P	44.247	100	0.442	0.017	0.9923	1.32	1.421	0.9857
As 15P	3.103	49.5	0.0627	0.113	0.9953	0.579	1.698	0.9174

The results indicate that the Langmuir isotherm best fits the experimental data over the experimental range studied for both resins, since it presents the greatest coefficients of correlation.

Comparing the absorption performance in terms of q_o values, As 14P (q_o= 100 mg g^{-1}) seems to be better than As 15P (q_o= 49.5 mg g^{-1}). For the experimental range studied, As 14P did not reach its full saturation.

The separation factor, R_L was calculated with the following relation:

$$R_L = 1 / (1+ bC_o) \qquad (5)$$

where C_o is the highest initial Ag(I) concentration, (mg L^{-1}).

The R_L values (0.017 and 0.113) in the range (0 - 1) express the essential features of Langmuir isotherms; the adsorption behavior of As 14P and As 15P resins is favorable for Ag(I) ions.

3.1.2.2 Freundlich isotherm

The linear form of Freundlich model is represented by the Eq. 6 [39]:

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (6)$$

where K_F (L g^{-1}) and n are the Freundlich constants that point to the relative capacity and adsorption intensity, respectively. The Freundlich constants were calculated from the slope and intercept of the Freundlich plots (Table 5).

It was found that the plots exhibit deviation from linearity for this isotherm type; the data are not well correlated to Freundlich isotherm correlation coefficients compared to the Langmuir model. However, values of 1<n<10 show a preference of the studied absorbents for Ag(I) ions.

3.2 Kinetic studies

Three different kinetic models were used to adjust the experimental data of Ag(I) sorption on the two sorbents.

3.2.1 Pseudo first order model

The kinetics of adsorption was firstly analyzed by the pseudo-first order equation given by Lagergren [40] as:

$$\log (q_e - q) = \log (q_e) - (k_1 / 2.303)\, t \qquad (7)$$

where q_e and q - are the amount of Ag(I) adsorbed on resin at equilibrium and at time t, (mg g^{-1}); k_1 is the rate constant of adsorption, (min^{-1}).

The k_1 values were calculated from the plots of log (q_e - q) *vs.* t, for different concentrations of Ag(I) (Tables 6 and 7). The experimental q_e values did not agree with the calculated values obtained from the linear plots.

3.2.2 Pseudo second order model

The sorption data were also analyzed in terms of pseudo-second order mechanism [41] given in linear form by:

$$(t / q) = (1 / k_2\, q_e^2) + (1 / q_e)\, t = 1/h + (1/q_e)t \qquad (8)$$

where k_2 is the rate constant of pseudo-second-order adsorption, (g mg^{-1} min^{-1}) and h is the initial sorption

Table 6. Kinetic constants for Ag(I) sorption on As 14P.

		Lagergren			Ho				Intraparticle diffusion	
C_o mg L^{-1}	q_{exp} mg g^{-1}	k_1 min^{-1}	q_e mg g^{-1}	R^2	k_2 g mg^{-1} min^{-1}	h mg g^{-1} min^{-1}	q_e mg g^{-1}	R^2	k_{id} mg g^{-1} $min^{-1/2}$	R^2
16	8.538	0.0069	8.22	0.989	0.00152	0.1364	9.47	0.994	0.5119	0.992
50	26.63	0.0041	20.28	0.994	0.00551	4.0241	27.02	0.994	0.7513	0.997
83	49.34	0.0108	5.91	0.973	0.00057	1.4541	50.25	0.995	3.3202	0.996
125	66.91	0.0104	15.11	0.934	0.00243	10.964	67.11	0.999	1.9976	0.979

Table 7. Kinetic constants for Ag (I) sorption on As 15P.

		Lagergren			Ho				Intraparticle diffusion	
C_o mg L^{-1}	q_{exp} mg g^{-1}	k_1 min^{-1}	q_e mg g^{-1}	R^2	k_2 g mg^{-1} min^{-1}	h mg g^{-1} min^{-1}	q_e mg g^{-1}	R^2	k_{id} mg g^{-1} $min^{-1/2}$	R^2
16	2.51	0.0087	7.03	0.996	0.00995	0.0625	2.51	0.987	0.4187	0.871
50	20.15	0.0175	6.96	0.995	0.00101	0.4971	22.22	0.955	2.6893	0.999
83	32.37	0.0138	33.67	0.996	0.0016	0.878	31.42	0.929	3.5885	0.991
125	44.51	0.0191	17.04	0.986	0.00188	3.7835	44.84	0.999	3.374	0.969

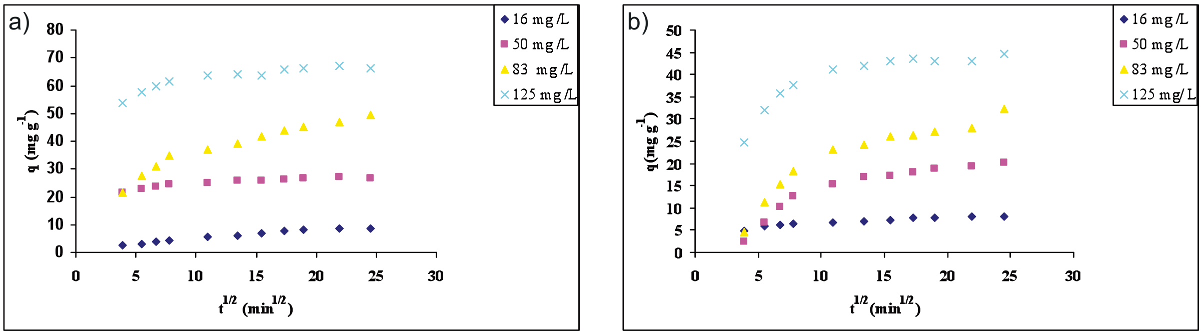


Figure 3. Intraparticle diffusion for Ag(I) sorption onto a) As 14P and b) As 15P (m=0.1 g resin, pH=4, T=25°C).

rate, (mg g^{-1} min^{-1}). The values of h, k_2 and q_e were calculated from the intercept and slope of the linear plots of t/q *vs.* t.

The correlation coefficients were higher than 0.99 for As14P and the estimated values of q_e agree with the experimental ones for both investigated adsorbents (Tables 6 and 7). These resutls suggest that Ag(I) sorption on As 14P and As 15P follows a second order kinetic model which relies on the assumption that this mechanism is predominant and that the overall rate constant chemisorption's process may be the rate limiting step [42].

3.2.3 Intraparticle diffusion

The intraparticle diffusion model based on the theory proposed by Weber and Morris [43] was tested to identify the diffusion mechanism. The rate constant for intraparticle diffusion, k_{id}, is calculated by the following equation:

$$q = k_{id}\, t^{1/2} \qquad (9)$$

where q is the amount of Ag(I) adsorbed on the resin, (mg g^{-1}), at time t (min); k_{id} is the rate constant for intraparticle diffusion, (mg g^{-1} $min^{-1/2}$). The k_{id} values were calculated using the slope of the linear plots of q_t *vs.* $t^{1/2}$ (Figs. 3a, 3b). There are three gradual adsorption stages better defined as the solution concentration increases. The first part of the graph corresponds to the instantaneous adsorption or external surface adsorption. The second part represents the gradual adsorption stage where intraparticle diffusion is the rate limiting step. The last one corresponds to the final equilibrium stage when intraparticle diffusion starts to slow down due to the extremely low adsorbate concentration left in solution [44].

The intraparticle rate constants were determined by linearization of the second parts of the graphical representations (Figs. 3a, 3b). The values of k_{id} (Tables 6 and 7) increased at higher Ag(I) ion concentration. Good correlation coefficients, especially for As 14P at lower concentration, suggest a strong relationship between the parameters and that the intraparticle diffusion has a contribution to the rate of entire sorption process.

3.3 Thermodynamic studies

Variation of Gibbs free energy for the retention of Ag(I) ions on As 14P and As15P was determined from the adsorption constants, b (Langmuir isotherm) using Eq. 10 [45]:

$$\Delta G^0 = -RT \ln b \qquad (10)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature, K.

The obtained values at 281K and 298K are negative and indicate the feasibility as well as the spontaneous nature of the adsorption process. The values lying in the range -20 to -40 kJ mol^{-1} (-23.51 respectively -26.67 kJ mol^{-1} for As 14P and -23.51 respectively -21.83 kJ mol^{-1} for As15P) suggested a superposition of physical and chemical sorption processes.

Enthalpy (ΔH^0) and entropy (ΔS^0) changes were also calculated using Eqs. 11 and 12 [45]:

$$\Delta H^0 = - R\, [T_1T_2 / (T_1+T_2)] \ln b_1/b_2 \qquad (11)$$
$$\Delta S^0 = (\Delta H^0 - \Delta G^0) / T \qquad (12)$$

The ΔH values indicted an endothermic process for As 14P (28.67 kJ mol^{-1}) and an exothermic one for As 15P (-51.34 kJ mol^{-1}).

The positive value of ΔS^0 =185.24 J mol^{-1} K^{-1} for As 14P reflects the affinity of the tested resin for Ag(I) ions.

4. Conclusions

Three resins with differeing degrees of crosslinking (2% and 8% DVB) were investigated for sorption of Ag(I). For the investigated concentration range, the resins with 2% DVB were more efficient (R>60%). The affinity order for Ag (I) sorption is: As 14P> As 15P > As13P.

The maximum Ag(I) recovery was obtained at a pH=3-4, at room temperature. The equilibrium distributions in the resin/metal ion solution systems were described by a Langmuir adsorption isotherm. The sorption is efficient and favorable (R_L= 0.017 and 0.113 for As14P and As 15P respectively).

The retention of Ag(I) onto As 14P and As 15P resins followed a second order kinetics; the decrease in solution concentration increases the effects of intraparticle diffusion.

The adsorption isotherm forms and kinetic data support that the retention of Ag(I) is mainly due to complexation with amine groups on the resins but also other chemical and/or physical adsorption may occur.

The studied sorbents may be used for Ag(I) recovery from dilute solutions.

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