



Investigation of rhenium adsorption isotherm from two-component solutions by Dowex 21K and desorption tests using alkaline solutions

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Review History:

Received: Jul. 15, 2021

Revised: Apr. 24, 2022

Accepted: Aug. 06, 2022

Available Online: Aug. 27, 2022

Keywords:

Rhenium

Molybdenum

Dowex 21K resin

Isothermal equations

Desorption tests, Ammonium acetate

ABSTRACT: Nowadays, solutions and effluents resulting from the activities of mineral processing plants and related industries can be considered one of the most important resources for the production of valuable elements. Examining the extraction method and improving it, in addition to reducing the needs of modern industries, can be considered one of the effective methods in controlling wastes and reducing environmental concerns. In this study, in the presence of molybdenum the adsorption behavior of rhenium on the Dowex 21K resin from pregnant solutions, in conditions very close to copper-containing solutions resulting from heap leaching, was investigated by Freundlich, Temkin, Dubinin – Radushkevich and Langmuir isothermal equations. The results showed that in the case of one-component solutions, the fit of the data obtained from static experiments on the mentioned equations is most consistent with the Freundlich equation and in the case of two-component conditions with its expanded form. Examination of resin capacity changes in the two conditions showed that due to the presence of the second component, competition between the existing ions, the resin capacity is reduced by about 47%. Also, the examination of ammonium acetate (0.5 M) on desorption of adsorbed ions from seven resin samples loaded showed that after 7 hours, more than 92% of molybdenum was released from the resin, while during this period, the amount of rhenium desorption no more than 13% was obtained.

1- Introduction

One of the main problems in recovering rhenium is its low concentration and its interaction with molybdenum anionic compounds. In general, rhenium-molybdenum solutions always have higher molybdenum than rhenium, and these ions can be absorbed by the resin and reduce the loading of rhenium [1, 2]. In general, it can be said that perhenate ions can be absorbed by strong basic resins, but in the step of elution a large volume of corrosive and toxic solutions such as 6 normal nitric acid, 1 normal perchloric acid, is necessary to release the percentage of rhenium from the charged resin [3]. After absorbing rhenium on each of the resins, it is usually washed using sodium or ammonium hydroxide solutions, which finally results in sodium or ammonium perhenate solutions [4]. In order to increase the efficiency of rhenium washing from non-porous resins, the effect of operating parameters can also be investigated [5]. The results of research on the effect of temperature changes, the concentration of ammonia solution and replacing part of the washing solution with ethanol on the efficiency of washing rhenium from A172 resin (in both fully saturated and semi-saturated conditions) showed that washing rhenium from this type of resin is optimized and increased only by chemical changes of the desorbed solution (decrease of dielectric

constant and other cases) [6, 7].

In this research, in order to determine the behavior pattern of rhenium adsorption from two-component rhenium-molybdenum solutions on alkaline resin with gel structure, Dowex 21K, first by isothermal models, the behavior of rhenium adsorption in single-component static conditions and then in the presence of the most effective competing ions (Mo⁶⁺) was investigated, then for the first time, desorption experiments were performed on charged rhenium-molybdenum resins, using an accessible compound with relatively high alkaline strength (ammonium acetate = 4.8 pKa).

2- Methodology

Equilibrium isotherm adsorption tests in a discontinuous system and by 100 ml erlenmeyer flasks containing 0.05 grams (gr) of adsorbent and 50 ml (ml) of rhenium metal ion solution with concentrations of 25, 80, 120, 150 and 250 mg/L (ppm) absorption were performed. In order to reduce the effect of the most serious competitor in the process of rhenium absorption and also to approach the conditions of industrial solutions, the concentration of molybdenum ions is always considered five times the concentration of perhenate ions, the pH of the environment in each series of experiments

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is adjusted by sulfuric acid at an approximate value of 0.5, and also the stirrer speed was set at 200rpm.

To determine the capacity of the resin, the amount of absorbed metal ions was determined from the difference between the initial and final concentration of the solution, and the following equation was used in all experiments:

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

where C_0 is the initial ion concentration in the solution (ppm), C_e is the equilibrium concentration measured after the absorption process (ppm), V is the total volume of the solution in the system (l), and W is the weight of the adsorbent or dry resin used in the process (gr) [8, 9].

For desorption tests, at first, 7 samples of resins were charged in the same conditions as the competitive absorption tests in the industry, especially the solutions obtained in the washing of copper minerals ($Mo/Re = 5$), and then after washing the resins with distilled water, desorption tests were performed using 50 ml of 0.5 M ammonium acetate.

Equilibrium data after analyzing the concentration of the element involved (rhenium or molybdenum) in the examined samples, on the linear form of Freundlich, Temkin, Dubinin-Radushkevich and Langmuir models, were fitted and after deriving the equation of the fitting line, the corresponding constants were calculated and determined[6].

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max} K_L} \quad (2)$$

$$\text{Freundlich: } \log q_e = \log k_f + \frac{1}{n} \log C_e \quad (3)$$

$$\text{Temkin: } q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \log C_e \quad (4)$$

$$\text{D-R: } \ln q_e = \ln q_m - \beta \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \quad (5)$$

$$, E = \frac{1}{\sqrt{2\beta}}$$

Where C_e concentration in the liquid phase in equilibrium with the concentration in the solid phase (mg/g); q_e concentration in the solid phase in equilibrium with the concentration in the liquid phase (mg/g); q_m final adsorption capacity (mg/g); k equilibrium constant in (L.mg); Freundlich constant K_F related to adsorption capacity ($L \cdot mg^{-1}$); $1/n$ heterogeneity factor; The surface adsorption energy constant β (mol^2/j^2) is proportional to the average adsorption energy per mole of adsorbent that is transferred to the solid surface over an unlimited distance in the solution. A Temkin's constant is equivalent to the bond constant related to the maximum bond energy between the adsorbed substance and the adsorbent (L/mg), and b is the constant related to the heat of adsorption ($Jmol^{-1}$) [9].

Also, 4 generalized models according to equations (6-9) were used to analyze absorption systems in competitive conditions[10, 11].

$$\text{Extended Langmuir: } q_{e,i} = \frac{q_{\max,i} K_{L,i} C_{e,i}}{1 + \sum_{j=1}^N K_{L,j} C_{e,j}} \quad (6)$$

$$\text{Modified Langmuir: } q_{e,i} = \frac{q_{\max,i} K_{L,i} (C_{e,i} / \eta_i)}{1 + \sum_{j=1}^N K_{L,j} (C_{e,j} / \eta_j)} \quad (7)$$

$$\text{Extended Freundlich: } q_{e,i} = \frac{K_{F,i} C_{e,i}^{n_i + x_i}}{\sum_{j=1}^N C_{e,i}^{x_i} + y_i C_{e,j}^{z_i}} \quad (8)$$

$$\text{Langmuir-Freundlich: } q_{e,i} = \frac{a_i C_{e,i}^{1/m_i}}{\sum_{j=1}^N b_j C_{e,j}^{1/m_j}} \quad (9)$$

where $q_{e,i}$ is the equilibrium value of the i^{th} component in the system, $C_{e,i}$ is the equilibrium concentration of the i^{th} component, $C_{e,j}$ ($j=1, 2, \dots, N$; (N is the number of components in the system), the equilibrium concentration of each component is in the system. $K_{L(i,j)}$ and ($K_{F(i,j),n_i}$) are the constants of the two Langmuire and Freundlich models and $q_{\max,i}$ is the maximum absorption capacity of the i^{th} component.

3- Results and Discussion

Equilibrium adsorption tests of both elements from the single-component systems were performed and after measuring the final concentration, the corresponding data were calculated and extracted with the equilibrium isotherm equations and parameters of each model (Table 1).

According to the values of the maximum absorption capacity (q_m) suggested by this model (Langmuir) for both ions, it is clear that this resin shows a high capacity for molybdenum compared to rhenium due to having a type four amine agent. This tendency is determined by comparing the numerical values of K_1 for two elements, 5 versus 1/2. This difference shows that under the investigated conditions (non-competitive), molybdenum ions show a high affinity for adsorption using Dowex compared to rhenium. As can be seen from the data table of the used models, the value of E in the D-R model for both resins is higher than 8 kJ/mol, which indicates the dominant role of chemical absorption in the process.

In the binary-absorption systems, according to the error values and the calculated correlation coefficient, the results (Table 2) show that the Extended Freundlich model can be used in the competitive system to predict the simultaneous adsorption of rhenium and molybdenum.

In the separation experiments, under completely competitive conditions, in order to investigate the effect of the type of solution on the separation rate, it was tried to use a compound with a relatively strong alkaline power and also available, which ammonium acetate ($pK_a = 4.8$) was selected and then desorption experiments were performed with a concentration of 0.5 M. For absorption tests, as previously described, at first, 7 samples of charged resins using rhenium and molybdenum ions were selected, and then after washing with distilled water, desorption tests were performed using 50 ml of 0.5 M ammonium acetate.

Table 1. Constants of isotherm models for the adsorption of rhenium and molybdenum on Dowex resin from single component system

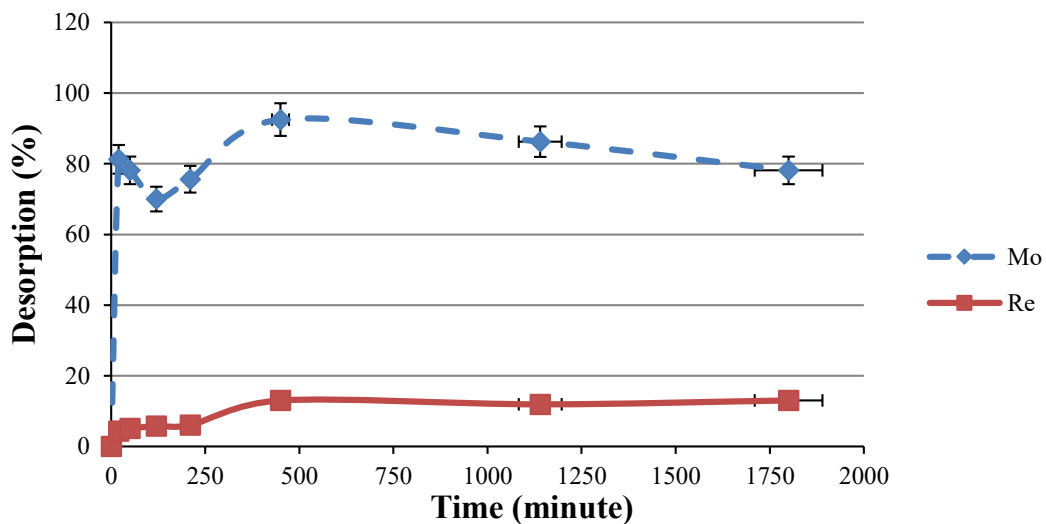
Model	Mo	Re	Cons.
Langmuir	235	147.16	$q_{max} (mg g^{-1})$
	5	2.1	$K_i(L mg^{-1})$
	0.963	0.978	R^2
Freundlich	276.35	69.04	$K_f((mg/g)/(mg/l)^{1/n})$
	1.18	2.16	n
	0.982	0.989	R^2
Temkin	38.29	23.16	$A(L mg^{-1})$
	62.91	86.32	$b(J mg^{-1})$
	0.973	0.962	R^2
D-R	0.096	0.003	$q_m(mg g^{-1})$
	4.2	2.9	$\beta(mol^2 kJ^{-2}) (*10^{-9})$
	10.89	12.97	$E(kJ mol^{-1})$
	0.961	0.995	R^2

Table 2. Two-component isotherm constants for simulating simultaneous adsorption of rhenium and molybdenum on Dowexk21 resin

Model/ element	Extended Langmuir		Modified Langmuir				
	RMSE	R^2	η_i	RMSE	R^2		
Re	17.34	0.125	233.8	2.449	0.9453		
Mo	45.17	0.198	821	27.73	0.782		
Extended Freundlich							
	x_i	y_i	z_i	RMSE	R^2		
Re	-2.13	78.56	-0.39	1.62	0.9841		
Mo	-3.78	0.24	-3.32	2.31	0.9765		
Langmuir-Freundlich							
	a_i	m_i	m_j	b_i	b_j	RMSE	R^2
Re	67	3.013	1.163e+4	2.651	16.7	4.064	0.6964
Mo	276	4.16	3.566	-44.8	37.23	26.15	0.4373

Table 3. The results of simultaneous desorption of rhenium and molybdenum adsorbed from Dowex resin using 0.5 M ammonium acetate

Time (minute)	Re(mg/l)	Desorption (%)	Mo(mg/l)	Desorption (%)
0	0	0	0	0
20	3.2	4.38	130	81.25
50	3.7	5.07	125	78.125
120	4.2	5.75	112	70
210	4.4	6.03	121	75.625
450	9.5	13.01	148	92.15
1140	8.7	11.92	138	86.25
1800	9.5	13.01	125	78.125

**Fig. 1. The changes in the simultaneous washing of rhenium and molybdenum from Dowex resin using 0.5 M ammonium acetate**

The absorption results are given in Table 3 and Figure 1. As the results show, it can be concluded that after about 7 hours, more than 92% of molybdenum adsorbed releases, and in this condition, only about 12% of rhenium is washed and released. By comparing the values of E in the D-R model for each metal, it can be understood that the desired parameter value for rhenium is higher than for molybdenum.

4- Conclusions

Examining the adsorption isotherm of rhenium and molybdenum ions from very similar real solutions produced in the industry, especially the copper industry ($Mo/Re=5$), on a strong non-porous ion exchange resin showed that in both single-component and binary-systems, the presence of ions,

the exchange behavior of the process follows the Freundlich model, which can be used in the first step to evaluate and describe the process, as well as to analyze and optimize an absorption system and determine its capacity. The analysis of the data obtained from the investigated models showed that in single-component conditions, Dowex 21K resin has a great affinity to bind with molybdenum polyanions, due to the presence of quaternary amine function in its structure, so that according to the maximum absorption capacity (q_m) calculated from the Langmuir model, this value was obtained for molybdenum ions more than rhenium ions ($Mo:235$, $Re:147$ mg/gr^{-1}). This phenomenon caused that in competitive adsorption conditions, the presence of molybdenum ions decreased by 47% the capacity of the resin to absorb rhenium.

Also, the investigation of the separation of absorbed ions from 7 samples of charged resins by ammonium acetate with strong basicity and concentration of 0.5 M showed that this compound can effectively release more than 92% of molybdenum ions. This high volume of separation of molybdenum ions can be explained by comparing the value of E calculated from the D-R model for the studied ions, which value is higher for rhenium ions than molybdenum, and this indicates the high amount of energy required to break the bond between rhenium ions and the existing agents.

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HOW TO CITE THIS ARTICLE

M. B. Fathi, B. Rezai, A. R. Azadmehr, *Investigation of rhenium adsorption isotherm from two-component solutions by Dowex 21K and desorption tests using alkaline solutions*, *Amirkabir J. Civil Eng.*, 54(11) (2023) 849-854.

DOI: 10.22060/ceej.2022.20269.7384



