

VARIOUS TECHNOLOGICAL  
PROCESSES

**Mechanism and Equilibrium Modeling of Re and Mo Adsorption  
on a Gel Type Strong Base Anion Resin<sup>1</sup>**

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**Abstract**—A static-batch technique was used to demonstrate the adsorption behavior of Re (VII) and Mo ions onto Dowex 21K at equilibrium in single and binary component systems. The single equilibrium adsorption data were modeled through a linear form of four widely used equilibrium isotherm equations. The results indicated that Freundlich and D-R models for Re, and Temkin and D–R isotherms for Mo fitted the obtained data satisfactorily. Binary adsorptions of Re and Mo ions onto Dowex 21K were also analyzed using Extended Langmuir, Modified Langmuir, Extended Freundlich and Langmuir–Freundlich models. The competitive Extended Freundlich model fitted the binary adsorption equilibrium data adequately. Studies on mutual interference effects of Mo ions on Re adsorption capacity indicated that the adsorption of perrhenate ions is always suppressed. In this perspective, the results from EDX studies confirmed the rhenium atom decrease in the simulated Re–Mo adsorption. However, under the studied conditions the affinity of the Dowex 21K for rhenium ions is marginally greater than that of molybdenum ions.

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INTRODUCTION

Rhenium is one of the rarest and most expensive non-ferrous metals and has found wide applications in high-end technologies including metallurgy, chemical and petrochemical, defense and spaceflight industries [1]. The primary source of rhenium is copper–molybdenite ores where it is recovered as a refining by-product. Rhenium can also be extracted from spent platinum–rhenium catalysts used in petrochemical industries and also as a by-product of uranium leaching[2]. Due to its very close association and similarity in chemical property and ionic radius with molybdenum, effective separation of Re from Mo is difficult and has become an important field of study. Available methods to recover Re from solutions mostly dealt with solutions containing high concentrations of Re. Separation of Re from solutions with low concentrations and with coexisting metal ion complexes, specifically Mo, are too complicated and almost impossible [3]. The continuing

price spike for Re (\$2,300/kg, Metal Bulletin, March 2017) coupled with the increasing volume of pregnant leach solutions being processed suggest that further studies should be conducted to improve existing flow sheets and understand better the recovery of rhenium from Re-bearing solutions of low concentrations.

The main method to separate Re from aqueous solutions is ion exchange. Rhenium is present normally as perrhenate anions ( $\text{ReO}_4^-$ ) in solution at a wide pH range and these ions exhibit high affinity to functionalized resins[4]. Sorption and desorption processes of rhenium depend on basicity of amines or anion exchangers after their synthesis[5]. A variety of resins, including the strongly basic alkyl amine type, have been used or studied for such purpose. Sejda and colleagues (2007) compared 30 strong and weak base ion exchange resins to recover Re from aqueous solution of ammonium perrhenate. The researchers found that regardless of type of conditioning, high sorption yields (mostly above 99.5%) were obtained for all strong base anion exchangers [6]. However, another study [7]

<sup>1</sup> The text was submitted by the authors in English.

reported that in Re-bearing solutions, Mo ions generally are the more dominant species and are preferentially adsorbed by the resins than perrhenate ions affirming the difficulty of their separation process. Hence, the selection of types of functional groups as well as the internal structure of the resin beads plays significant roles in the development of selective adsorption process for Re and Mo [8].

The choice and employment of suitable ion exchangers for low-grade rhenium solutions can only be achieved when accurate data concerning the mechanisms and phenomenon governing the mobility of a substance from the aquatic environment to a solid-phase in such systems are available. In practice, the analysis and optimization of an adsorption system is possible with the aid of equilibrium studies. Adsorption equilibria provide fundamental physicochemical information to assess the applicability of the adsorption process. Moreover, the capacity of the adsorbent can also be calculated by equilibrium studies [9].

The aim of this work was to demonstrate the mechanism and adsorption behavior of rhenium and molybdenum ions using a gel type strong base anion exchange resin (Dowex 21K) in two different systems [single (Re) and joint component (Re–Mo)]. Dowex 21K has been used in previous studies in a variety of precious metals recovery, i.e., uranium, gold, aluminum, iron, indium and separation of gallium from indium, thallium and aluminum [10–13]. The current study is the first attempt to apply Dowex 21K in the separation of Re from Mo. It was envisaged that the experimental results may provide useful information towards the development of more efficient and economical hydrometallurgical process for rhenium purification from molybdenum.

## EXPERIMENTAL

### *Materials and Chemicals*

Rhenium and molybdenum standard stock solutions were prepared by dissolving  $\text{NH}_4\text{ReO}_4$  (Aldrich) and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  (Aldrich), respectively, in double-distilled water. The ion exchanger Dowex 21K (from Dow chemical) was used as the sorbent. The physical and chemical properties of the resin are provided in Table 1. The microstructure of the resins was examined by a Philips XL30 model Scanning Electron Microscopy (SEM). The elemental analysis was conducted using energy-dispersive X-ray spectroscopy (EDX) DX-series PV 9462/30 (model: NEW XL30 144-10). The concentration of metal ions in solutions was determined by Inductively Coupled Plasma-

**Table 1.** Physical and chemical properties of Dowex 21K ion exchange resin

Basic information	
Structure	gel type
Matrix	Styrene–DVB
Functional group	Quaternary amine
Ionic form	$\text{Cl}^-$
Physical/chemical	
Bead size	0.707–0.841 mm
Specific gravity	1.08
Moisture retention	50–58% (in $\text{Cl}^-$ form)
Total capacity	1.2 meq/mL

Optical Emission Spectroscopy (ICP-OES, Optima 7300 DV Perkin Elmer). All reagents were of analytical grade and were used without further purification.

### *Method*

**Pretreatment of the anion exchange resin.** Before the resin was added into the aqueous solution for adsorption experiments, desired amounts of the sorbent were introduced into conical flasks (150 mL) containing water and then placed in horizontal shaker overnight for swelling.

**Experimental procedure.** The equilibrium adsorption experiments were carried out under batch/static condition using conical flask (150 mL). The amount of adsorbed metal ions on resin was determined from the difference between its initial and final concentration in the solution. All equilibrium adsorption isotherm experiments were conducted at 290 K. The pH of the investigated solutions was adjusted to 1 by adding sulfuric acid and the value was held constant all throughout the studied temperature range. At this pH, selective separation of Re from Mo can be enhanced by the abundant existence of cationic form of Mo and anionic form of Re [14]. For equilibrium experiments involving single metal ions, the concentrations of the ions were varied from 50 to 250  $\text{mg L}^{-1}$ . For experiments comprising binary solutions, the concentrations of Re and Mo were simulated comparable to real conditions where Mo is higher than Re. The equilibrium experiments in this case utilized Re concentrations of 20 to 100  $\text{mg L}^{-1}$  and Mo concentration ranging from 100 to 500  $\text{mg L}^{-1}$ . For each test, about 0.1 g of the resin was added with 50 mL sample solution. The flasks were kept in a shaker equipped with a thermostat

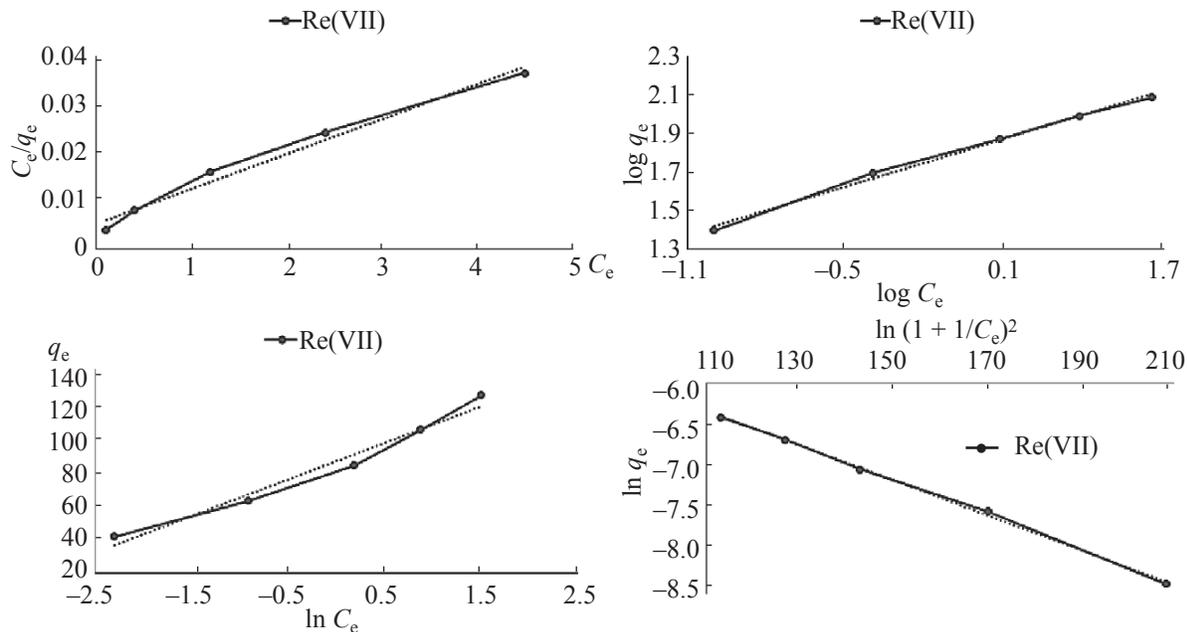


Fig. 1. The adsorption isotherms of single Re ions by Dowex 21K (pH 1, contact time 24 h, temperature: 290 K).

at a speed of 180 rpm for 24 h. The amount of metal ion adsorbed was calculated from the mass balance equation as follows:

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

where  $C_0$  is the initial concentration of ions in solution ( $\text{mg L}^{-1}$ ),  $C_e$  stands for the equilibrium concentration measured after adsorption ( $\text{mg L}^{-1}$ );  $V$  is the total volume of solution (l) and  $W$  is the weight of dry resin (g).

## RESULTS AND DISCUSSION

**Perrhenate ion adsorption in a single component system.** Equilibrium isotherms play important roles in predicting models to explain the possibility of adsorbate interactions with sorbent surface sites. Generally, isotherm models are characterized by certain parameters the values of which define the surface properties and affinity of the adsorbent. At a fixed temperature at equilibrium, adsorption isotherms describe the equilibrium relationships between adsorbent and adsorbate, and the ratio between the amount adsorbed and that remaining in the solution. In the current study, the adsorption equilibrium data were analyzed using the most frequently applied isotherm models, namely, Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich [Eqs. (2)–(5)].

The obtained experimental data were fitted via linear regression techniques to evaluate the phenomena involved in the adsorption process [15].

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

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

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

Dubinin–Radushkevich (D–R):

$$\ln q_e = \ln q_m - \beta \left[ RT \ln \left( 1 + \frac{1}{C_e} \right) \right]^2, E = \frac{1}{\sqrt{2\beta}}, \quad (5)$$

where  $q_e$  is the amount of metal adsorbed on resins ( $\text{mg g}^{-1}$ ) in equilibrium state,  $C_e$  is the concentration of metal remained in the solution ( $\text{mg L}^{-1}$ ),  $q_{\max}$  is the maximum loading capacity of the resin,  $K_L$  is the Langmuir constant related to the energy of adsorption ( $\text{L mg}^{-1}$ ),  $K_F$  is the Freundlich constant related to the adsorption capacity ( $\text{L mg}^{-1}$ ),  $1/n$  is the heterogeneity factor,  $A$  and  $b$  are the Temkin constants,  $q_m$  is the Dubinin–Radushkevich monolayer capacity ( $\text{mg g}^{-1}$ ) and  $\beta$  ( $\text{mol}^2 \text{kJ}^{-2}$ ) is a constant with dimensions of energy,

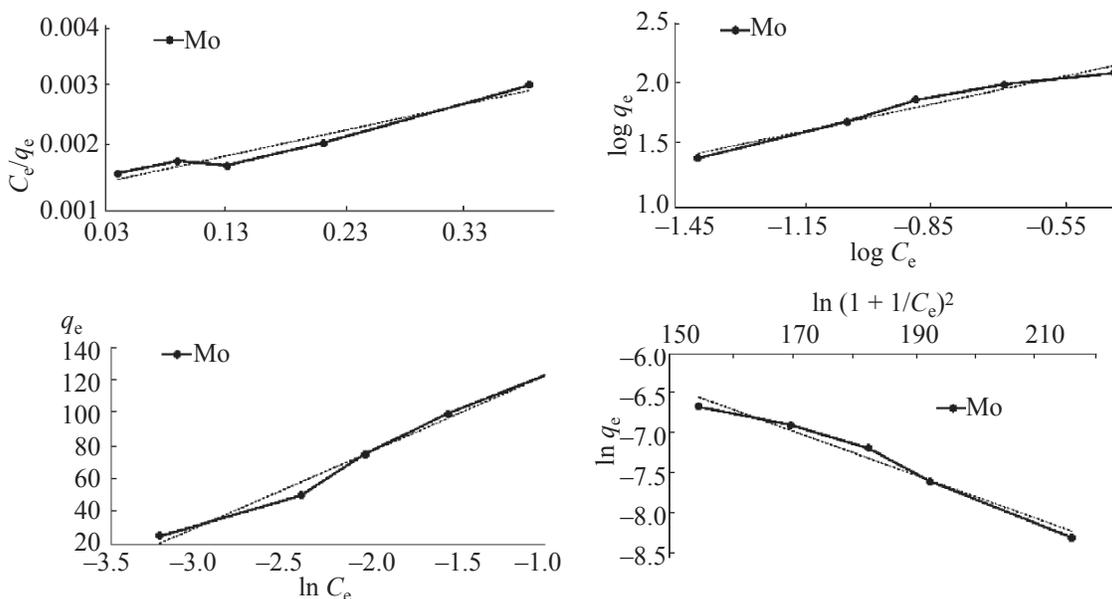


Fig. 2. The adsorption isotherms of single Mo ions by Dowex 21K (pH 1, contact time 24 h, temperature: 290 K).

$\varepsilon$  is the Polanyi sorption potential which is the amount of energy required to pull a adsorbed molecule from its sorption site and  $E$  is the mean free energy of adsorption per mole of the adsorbate ( $\text{kJ mol}^{-1}$ ).

Single adsorption equilibrium tests were carried out at varying levels of concentrations of Re and Mo and the obtained data were plotted based on the parameters of the different models considered (Figs. 1 and 2). The calculated relative constants are listed in Table 2. It is clear from the results that the experimental data fit well within the isotherm models in terms of the determination of coefficients ( $R^2$ ) as the values are higher than 0.95. This strongly suggests that all the models considered can generate a satisfactory fit for the experimental data for both Re and Mo. It can be deduced that amongst the studied models, Freundlich and D–R isotherm models best describe Re ion adsorption, while Temkin and D–R isotherms show better fit for Mo adsorption.

As shown in Table 2, the maximum monolayer coverage capacities ( $Q_m$ ) from Langmuir Isotherm for Re and Mo are  $142.86 \text{ mg g}^{-1}$  and  $250 \text{ mg g}^{-1}$ , respectively. The  $K_1$  values for Mo (4) are also higher than Re (1.4). These results suggest that in non-competitive equilibrium state, molybdenum ions have higher affinity to bind to the Dowex 21K functional groups rather than perrhenate ions.

Researchers have tried to link the Freundlich parameters ( $K_F$  and  $1/n$ ) to mechanisms of adsorption.

Generally,  $K_F$  and  $n$  are constants incorporating all factors affecting the adsorption capacity and an indication of the favorability of metal ion adsorption onto adsorbent, respectively [16]. To be classified as a favorable adsorption, the value of  $n$  should fall in the range of 1 to 10. Smaller  $1/n$  values can be attributed to the greater adsorption surface heterogeneity[17]. As seen from the

Table 2. Isotherm constants for different models for Re and Mo adsorption on Dowex21K

Models	Constants	Re	Mo
Langmuir	$q_{\max}$ , $\text{mg g}^{-1}$	142.86	250
	$K_1$ , $\text{L mg}^{-1}$	1.4	4
	$R^2$	0.981	0.952
Freundlich	$K_F$ , $(\text{mg g}^{-1})/(\text{mg L}^{-1})^{1/n}$	68.08	289.73
	$n$	2.41	1.36
	$R^2$	0.994	0.967
Temkin	$A$ , $\text{L mg}^{-1}$	21.46	39.19
	$b$ , $\text{J mg}^{-1}$	96.44	53.91
	$R^2$	0.972	0.985
Dubinin–Radushkevich (D–R)	$q_m$ , $\text{mg g}^{-1}$	0.004	0.097
	$\beta$ , $\text{mol}^2 \text{kJ}^{-2}$	$2.7 \times 10^{-9}$	$4.4 \times 10^{-9}$
	$E$ , $\text{kJ mol}^{-1}$	13.62	10.66
	$R^2$	0.998	0.975

data in Table 2, the  $n$  value of both metals are more than one, indicating a favorable and easy adsorption of Re and Mo from aqueous medium by the resin while values of  $n$  for Re and Mo are 2.41 and 1.36, respectively. The value of  $1/n$  for Re demonstrates that the Dowex 21K resin shows greater heterogeneity for Re than Mo ions. Meanwhile, the  $K_F$  values indicate the higher uptake of Mo by Dowex 21K compared to Re ions.

The D–R model is another data-adapted model with best correlation coefficients for both metals. This model is generally used to describe adsorption mechanisms [18]. The approach is usually applied to distinguish the physical and chemical adsorption of metal ions by a constant  $E$ . The value of  $E$  represents the amount of mean free energy that is needed for removing a molecule of adsorbate from its location in the sorption space to the infinity [19]. When the value of  $E$  is below  $8 \text{ kJ mol}^{-1}$ , the adsorption process can be considered as the physical adsorption while if it be in the range of  $8\text{--}16 \text{ kJ mol}^{-1}$ , it is the chemical adsorption [20]. As summarized in Table 2, both sorbents have mean free energy,  $E$ , values above  $8 \text{ kJ mol}^{-1}$  signifying that the effect of chemical adsorption plays a dominating role in the adsorption process of Re and Mo on Dowex 21K.

**Multi-component adsorption models.** Established multicomponent adsorption theories and models and their improvements have attracted much attention in the past. Because of the presence of other metal ions which may either interact with adsorbate of interest or compete for same binding sites of adsorbent, no single component isotherms can demonstrate the nature of interaction between adsorbate and adsorbent at the time of equilibrium [9]. Several methodologies have been developed to evaluate the multicomponent adsorption systems. In the present work, developed forms of the Langmuir and Freundlich isotherm models for multicomponent adsorption isotherms namely Extended Langmuir, Modified Langmuir, Extended Freundlich and Langmuir–Freundlich models [Eqs. (6)–(9)] were used to describe the nature of the process.

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

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

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

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

where,  $q_{e,i}$  is the equilibrium amount of component  $i$  adsorbed in the multicomponent system,  $C_{e,i}$  is the equilibrium concentration of component  $i$ ,  $C_{e,j}$  ( $j = 1, 2, \dots, N$ ;  $N$  is the number of the components) is the equilibrium concentration of each component in the system,  $K_{L(i,j)}$  and  $(K_{F(i,j)}, n_i)$  are the Langmuir and Freundlich constants for component  $i$  and  $j$ , respectively and  $q_{\max,i}$  is the maximum adsorption capacity of component  $i$ . The parameters  $q_{\max,i}$ ,  $n_i$  and  $K_{L,F(i,j)}$  are obtained from the single adsorption isotherm. The other parameters ( $\eta_{i,j}$ ,  $x_i$ ,  $y_i$ ,  $z_i$ ,  $a_i$ ,  $b_j$ ,  $m_{i,j}$ ) can be obtained from the optimized fitting of relevant equation with the experimental data for the equilibrium adsorption of components in the multi-component system [21, 22].

The isotherm parameters of multi-component models were calculated using the MATLAB program. RMSE (root of mean square errors) was used to test the adequacy and accuracy of the fit of various isotherm models with the experimental data. RMSE is given as:

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (X_{\text{obs},i} - X_{\text{model},i})^2}{n}}, \quad (10)$$

where  $X_{\text{obs},i}$  are the observed values and  $X_{\text{model},i}$  are the modeled values [23]. The corresponding constants of the fitting isotherms are presented in Table 3 along with correlation coefficients ( $R^2$ ) and (RMSE).

Comparing the different models considered, it can be deduced from the results shown in Table 3 that the Extended Freundlich obtained the highest coefficients of determination  $R^2$  and the lowest RMSE value, signifying that this isotherm provides the best fit for the experimental data. This was expected as Dowex 21K has heterogeneous surface and the adsorption of the single metal ions has also been well represented by the Freundlich isotherm. In addition, since the extended form of Freundlich model (Eq. 8) considers reasonably the interactive effects of individual metal adsorbate ions between and among themselves and the adsorbent, the binary adsorption

**Table 3.** Multi-component isotherm parameter values for the simultaneous adsorption of Re and Mo adsorption on Dowex 21K

Adsorbate	Extended Langmuir		Modified Langmuir				
	RMSE	$R^2$	$\eta_i$	$\eta_j$	RMSE	$R^2$	
Re	15.34	0.1234	242.8	4265	2.339	0.9336	
Mo	43.37	0.1856	832	44.01	28.58	0.0892	
Adsorbate	Extended Freundlich						
	$x_i$	$y_i$	$z_i$	RMSE	$R^2$		
Re	-2.33	78.62	-0.54	1.714	0.9643		
Mo	-3.98	0.28	-3.15	2.54	0.9732		
Adsorbate	Langmuir–Freundlich						
	$a_i$	$m_i$	$m_j$	$b_i$	$b_j$	RMSE	$R^2$
Re	68	3.048	1.263E+04	2.553	17.8	4.097	0.7962
Mo	289	4.24	3.465	-42.9	38.13	22.25	0.4483

of Re and Mo ions by Dowex 21K can be represented satisfactorily and adequately by this isotherm.

#### Ions mutual interferences and adsorbent selectivity.

In natural systems, single metallic species rarely exist and in all cases, numerous metal ions with different specifications are present and they compete for available adsorption sites. Hence, it is important to study the selective or successive adsorption and also to explore the interactive effect of one metal ion on the sorption of other metal ions, since the presence of other metal ions can lead to synergism, antagonism or non-interaction mechanism [24]. The study on the effects of the presence of metal ions on adsorption capacity of target species can be done using the formula,  $q_{e,mix}/q_e$ , where  $q_{e,mix}$  and  $q_e$  are the sorption capacity for one metal ion in binary and single systems, respectively. In general, a mixture of different adsorbates may exhibit three possible types of behaviour:  $q_{e,mix}/q_e > 1$ , synergism (sorption of target species will be promoted by the presence of other metal ions);  $q_{e,mix}/q_e = 1$ , no net interaction effect is observed and  $q_{e,mix}/q_e < 1$ , antagonism (the effect of the mixture is less than that of each of the individual adsorbates in the mixture) [25]. In the current study, the  $q_{e,mix}/q_e$  values of Re in Re–Mo binary system were calculated to be  $\approx 0.67$ , implying the inhibitory effect of molybdenum ions on the binding of the perrhenate ions due to competition for vacant sites on adsorbent, which consequently suppressed the adsorption of perrhenate ions.

**Investigation on resin structure effects on the metal affinity.** In the selection of an ion exchanger, aside from

the type of resin, the internal structure of the resin beads is also an important factor. The beads can either have a porous, multi-channelled structure (macroporous or macroreticular resins) or a dense internal structure with no discrete pores (gel resins, also called microporous resins). Generally, the macroporous resins have high effective surface area such that the ion exchange process is facilitated by providing simple access to the exchange sites for larger ions. On the other hand, in microporous resins, solute ions diffuse through the surface of resin particles to interact with the exchanger's inner sites. These resins offer several advantages despite diffusional limitations on reaction rates, i.e., less fragile, simple handling requirement, faster reaction in functionalization and application reactions, and possess higher loading capacities [26].

The magnitude of Dowex 21K affinity for the studied metal ions was determined by separation percentage ( $r_t$ ) (Eq. 11.), where  $C_0$  and  $C_t$  are the concentrations of the metal ions at  $t = 0$  and time  $t$ , respectively [27].

$$r_t = \frac{C_0 - C_t}{C_0} \times 100, \quad (11)$$

Comparing the  $r_t$  values for Re and Mo ions in binary system shows that for all studied conditions, the rhenium separation percentage values are always higher ( $\approx 9\%$ ) than that of molybdenum. This supported the choice of strongly anionic resin types for the recovery of rhenium from low-grade solutions. This phenomenon can be attributed most likely to the resin structure. Gel

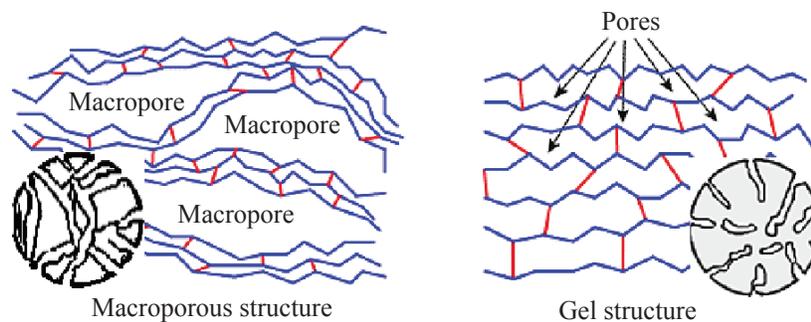


Fig. 3. The structure of macroporous and gel ion exchangers.

structure plays an important role in minimizing the adsorption of molybdenum ions in Re-Mo systems. It is known that in aqueous solutions and at pH range of 1–10, perrhenate ions do not change their structure and have a stable monomeric anion form but the structure of molybdenum ions is dependent on pH of the contacting solution tending to form iso ( $\text{MoO}_4^{2-}$ ,  $5 < \text{pH} < 9$ ) and/or heteropoly ( $\text{Mo}_8\text{O}_{26}^{4-}$ ,  $1 < \text{pH} < 5$ ) anions, which are substantially larger in comparison to perrhenate ions. Moreover, the cationic forms of molybdenum ( $\text{MoO}_2^{2+}$ ,

$\text{Mo}_2\text{O}_5^{2+}$  and  $\text{Mo}_3\text{O}_8^{2+}$ ) can be present at pH values below 2 [28]. The tight structure of the gel type resins, typically pore volumes up to 10 or 15 Å, rejects the larger molybdenum molecules while the perrhenate anions ( $\text{ReO}_4^-$ ) can still penetrate freely into the matrix [reaction (1)]. Inner functional groups of this type of resins are not accessible for molybdenum ions and they allow the Re and Mo separation to take place. The polyanions of molybdenum are partially adsorbed only by surface functional groups [8].

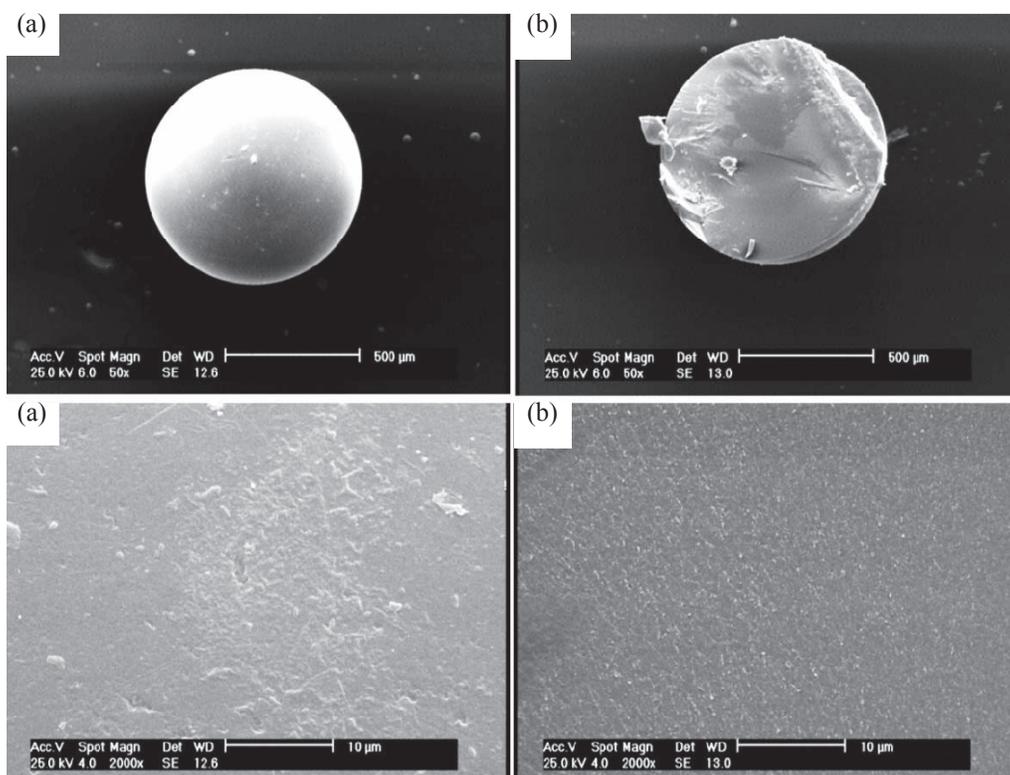
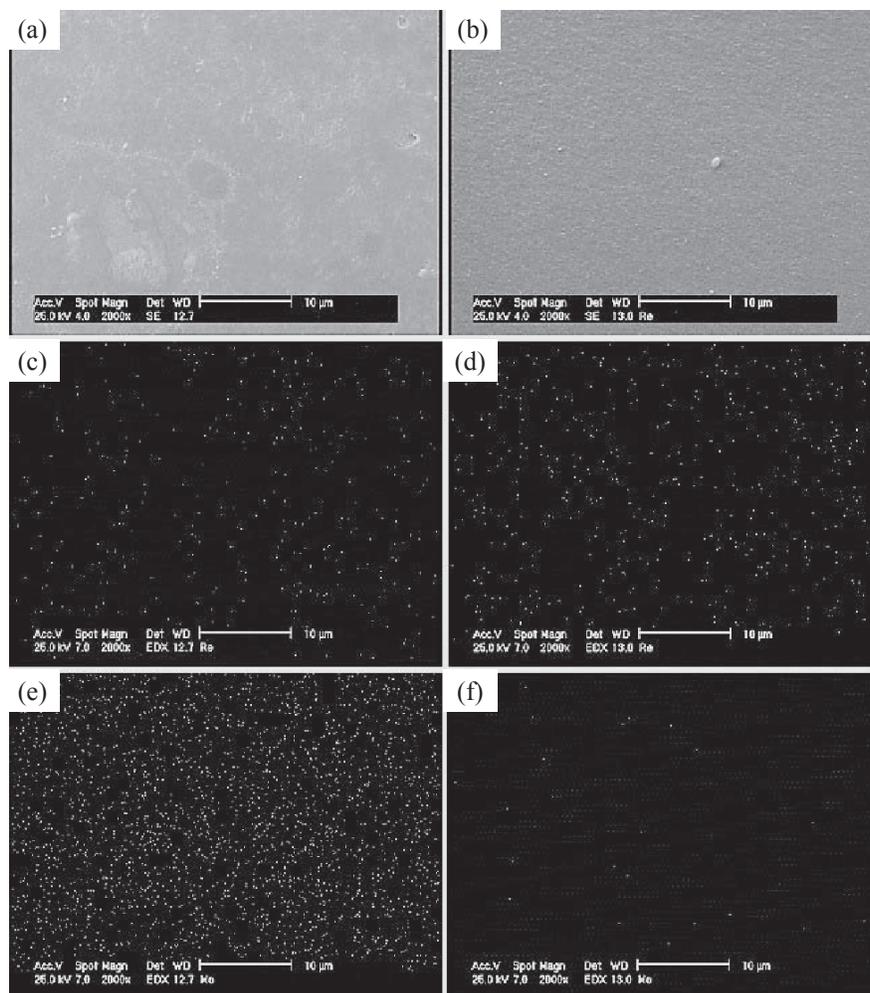
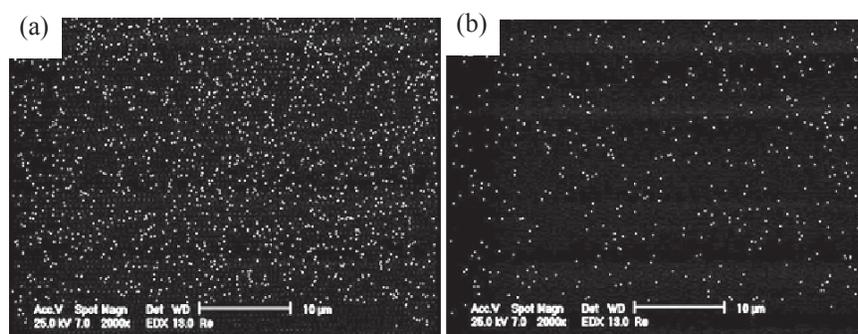


Fig. 4. SEM images of surfaces of Dowex 21K gel resin, (a) top-view, (b) cross-section.



**Fig. 5.** SEM images of Dowex 21K; (a) top-view, (b) cross-section. EDX mapping images of (c) rhenium top-view, (d) rhenium cross-section, (e) molybdenum top-view and (f) molybdenum cross-section.



**Fig. 6.** Cross-sectional mapping images of rhenium adsorption by Dowex 21K in (a) single component and (b) multi component system (Re-Mo).

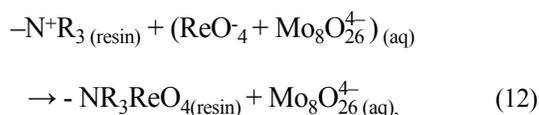


Figure 3 shows the schematic structure of macroporous and gel ion exchangers [29]. The difference between

them lies in their porosity. Macroporous type resins have an additional artificial porosity that are produced by introducing a porogen, for instance homopolystyrene which is soluble in the monomer mixture, and leaching it out later with e.g. toluene, that give the resin other improved characteristics for certain applications like the

access into the beads to the active sites as well as increase in surface area.

The SEM micrographs of used gel resin is presented in Fig. 4. Both the top-surface (Fig. 4a) and cross-section (Fig. 4b) structures are observed to have smooth areas that can decrease the accessibility of functional groups due to core particles formation [30]. In order to investigate in more details the metal distribution, elemental mapping by SEM-EDX, was used for top-view and cross-section of the loaded resin in a Re-Mo system. Fig. 5a, 5c and 5e show the top-view SEM images of the resin and the EDX mapping for rhenium and molybdenum, respectively. The top-view micrographs show that molybdenum (Fig. 5c) is more abundant and has a higher distribution compared to rhenium (Fig. 5e). The cross-sectional images shown in Figure 5b, 5d and 5f, however, show the opposite where high distribution and amount of Re and very minimal presence of Mo is observed. These mapping results indicate that Re was able to pass through the resin surface and are concentrated in the inner structure of the resin. Generally, comparison of Re–Mo distribution in top and cross section surfaces reveals sieving performance of resin gel structure in selective adsorption of perrhenate ions by inner active sites of ionite rather than molybdenum larger ions.

The differences between the average values of  $r_1$  for rhenium in single and multicomponent conditions show a decrease of rhenium ions uptake by Dowex 21K in the presence of the competitive molybdenum ions by a factor of 62.01%. This difference indicates that in spite of the preference of the adsorbent for Re ions, adsorption of perrhenate ions is affected by competitive inhibition and their shield preventing effects due to the presence of molybdenum ions adsorbed by surface functional groups. Figure 6 displays the cross sectional rhenium distribution for both single (Fig. 6a) and binary Re-Mo (Fig. 6b) systems. As shown in Fig. 6b, it is evident that in binary mixture adsorption, rhenium content was dramatically reduced by the presence molybdenum.

## CONCLUSIONS

In summary, the results of sorption experiments for rhenium and molybdenum ionson Dowex 21K from single and binary systems were interpreted by equilibrium modeling. Evaluating the correlation coefficients from the four studied isotherm equations and fitting the obtained data showed that in single systems, Freundlich and D-R models for Re, and Temkin and D-R models for Mo, are

the models that are more applicable and best describe the experimental data. While in the competitive state, adsorptions of both metal ions were described well by Extended Freundlich isotherm. The interactive effect of Mo ions on the adsorption of Re ions by Dowex 21K was found to be antagonistic. In binary Re–Mo system, the study of Dowex 21K affinity showed that under the studied conditions, rhenium separation percentage values are always higher than that of molybdenum due to inner functional groups inaccessibility by molybdenum ions. Scanning electron microscopy coupled with energy-dispersive X-ray microanalysis (SEM-EDX) was also used to provide additional insights into map of metal concentration data within the resin top-view and cross-section. Observed results confirmed the preventive role of Dowex 21K gel structure in adsorption of larger polyanions of molybdenum by inner vacant sites of ionite rather than perrhenate ions.

The results obtained in this study showed that, in general, Dowex 21K is an effective and suitable adsorbent for the recovery of rhenium from aqueous solution, and has a strong potential for applications involving aqueous solutions or wastewater with low concentrations of Re.

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