

## NIOBIUM(V) RECOVERY FROM LEACHING SOLUTION OF TITANIUM WASTES: KINETIC STUDIES

Received – Primljeno: 2021-12-30  
Accepted – Prihvaćeno: 2022-03-10  
Preliminary Note – Prethodno priopćenje

This paper deals with the removal of Nb content from chemically leached solutions of titanium wastes using static ion exchange technology. The chemically leached solutions contained 2 g/L of Nb. The investigations involved the optimization of process parameters, such as contact time at different concentrations of niobium at room temperature. Sorption experiments are performed to evaluate the optimum conditions at a concentration of HCl 3,0 M, 1,0 g resin dose for 3,5 h contact time at room temperature. The maximum sorption capacity reaches to 0,089 g/g. Kinetics studies were proposed for the process by pseudo-first-order, pseudo-second-order, and intraparticle diffusion models.

*Key words:* titanium wastes, niobium, leaching, sorption, kinetic studies.

### INTRODUCTION

Niobium is a rare refractory metal. Its content in the earth's crust is  $2 \cdot 10^{-3}$  % of the mass. The main application of niobium is in steel production. Niobium is also used in rocketry, space and aviation technology, nuclear power, radio engineering, electronics, and in the chemical industry [1].

Nowadays more than 150 niobium minerals are known, which are represented mainly by complex oxides. An important feature of niobium is its high affinity for titanium. This leads to the formation of numerous niobium minerals with titanium, as well as the appearance of niobium impurities in titanium minerals. Moreover, according to [2] only two mineral groups (titanoniobates and tantaloniobates) are considered economically feasible options for niobium extraction. As a result, titanium raw materials are the main source of niobium production.

Niobium is extracted by several methods, such as sorption [3], precipitation [4], and solvent extraction [5].

However, methods such as precipitation and solvent extraction are expensive and inefficient for extracting niobium from pregnant leach solutions. Thus, in this regard, any other alternative method capable of selectively removing niobium from an aqueous solution will be of great importance. One of such methods is sorption, which is widely used because of its ease of operation, simplicity, and the limited application of solvents [6,7]. Due to the several advantages of the ion exchange pro-

cess, which include low cost, high selectivity, and high efficiency, it has become a suitable method for niobium extracting. The ion exchange process also does not have issues of phase separation, third phase formation, or solvent loss, and is particularly advantageous for the adsorption of metals present in low concentrations. These benefits of the sorption processes therefore justify further research in this area with an aim of further developing its potential. Ion exchange resins have been developed as a major option for niobium sorption over the past few decades. Selective resins allow the extraction of niobium from pregnant leach solutions, even in the presence of impurities.

The present work is aimed at evaluating the kinetics, equilibrium, and error analysis during the adsorption of niobium onto Purolite-C104 and KU-2-8 H ion exchange resins by the adsorption process.

### EXPERIMENTAL PROCEDURES

#### Materials

The exhausted melt of titanium chlorators (EMTC) used in this experiment is from the plant of JSC "UK TMK" (Kazakhstan). After crushing and screening, the content of the main elements was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The ICP-AES determination results showed that the EMTC mainly contained 19,1 % sodium, 10,7 % potassium, 7,42 % iron, 6,53 % carbon, 5,18 % silicon, and 4,61 % magnesium. The niobium content in the initial sample was 0,009 %.

The cation exchange resin KU-2-8 H and Purolite-C104 was used in this study for the sorption of niobium from pregnant leach solution.

A. Khabiyev, O. Baigenzhenov (o.baigenzhenov@satbayev.university),  
A. Toishybek, T. Chepushtanova, B. Orynbayev, Satbayev university,  
Almaty, Kazakhstan  
Zh. Korganbayeva, Abay university, Almaty, Kazakhstan

Analytical grade HCl was used for dissolutions and dilutions were done using deionized water. All glassware was cleaned with dilute hydrochloric acid and was rinsed with distilled water several times before use.

### Preparation of pregnant leach solution

For preparation of the niobium containing solution, two-stage leaching was provided. In the first stage, samples of EMTC (100 g) were ground to a size of  $> 0,5$  mm and were leached with water. The leaching experiments were conducted in 500 mL round-bottom flasks. The temperature, solid-liquid ratio and agitation speed were fixed at 25 °C, 1:4 and 400 r/min respectively. After water leaching, the slurry was filtered to separate the pregnant leach solution from the niobium-enriched residue. The obtained pregnant leach solution was directed to a sequential processes of scandium extraction and carnallite synthesis. The residue was washed with distilled water to remove the remaining acid and was directed to acid leaching. During the subsequent process of acid leaching, the hydrochloric acid concentration was 3,0 M. The leach medium was prepared using reagent-grade hydrochloric acid and deionized water. Leaching tests were carried out in a temperature-controlled three-necked flat bottom glass flask (cap. 250 mL) on a hot-plate cum magnetic stirrer with a reflux condenser in order to avoid any loss due to evaporation. The leaching time was recorded after successive addition of the niobium-enriched residue sample and hydrochloric acid solution to the reaction vessel, and then this vessel was put in an oil bath maintained at 80 °C. The liquid-solid ratio and agitation speed were fixed at 2:1 and 400 r/min respectively. Following the completion of the leaching experiment, the hot slurry was filtered and the solid residue was dried at 70 °C until a constant weight was obtained.

### SORPTION KINETICS STUDIES

Sorption kinetics is described by general equations, such as those ascribed to pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. The kinetic parameters are helpful in the prediction of adsorption rate and provide important information on modeling sorption processes. As a result, the niobium sorption kinetics was studied at three different initial Nb concentrations (1,0, 1,5, and 2,0 g/L), while all other parameters were kept constant ( $T = 25$  °C,  $\tau = 3,5$  h. and at 3,0 M hydrochloric acid concentration).

Pseudo-first-order model of niobium sorption onto the KU-2-8 H and Purolite-C104 cationites were presented in Figures 1a and 1b, respectively.

The linear form of this pseudo-first order model can be represented by Lagergren equation. As Fig. 1 shows, linear plots were obtained. Table 1 lists the parameters

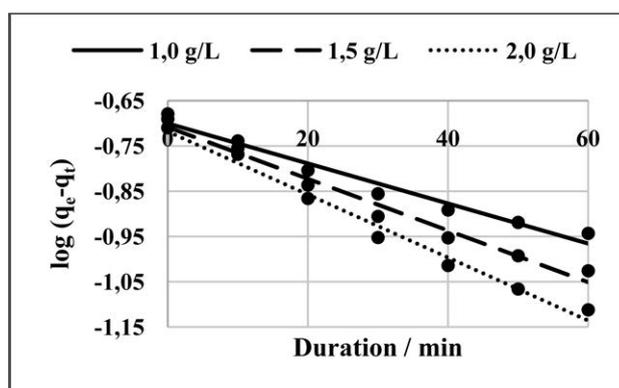


Figure 1a Pseudo-first-order model of niobium sorption onto the KU-2-8 H cationites

for pseudo-first-order, pseudo-second-order, and intraparticle diffusion models

A pseudo-first-order model is widely used in physical chemical engineering and focuses on the assumption that the rate-limiting stage can be a chemical adsorption that involves valence forces, which exhibit sharing or exchange of electrons between adsorbent and adsorbate. The low values of the rate constant suggest that the adsorption rate decreases with the increase of the phase contact time and that the adsorption rate was proportional to the number of unoccupied sites. The  $k_1$  and  $q_e$  were calculated from the slope and intercept of the plot,  $\ln(q_e - q_t)$  versus  $t$  respectively (Figures 1a and b).

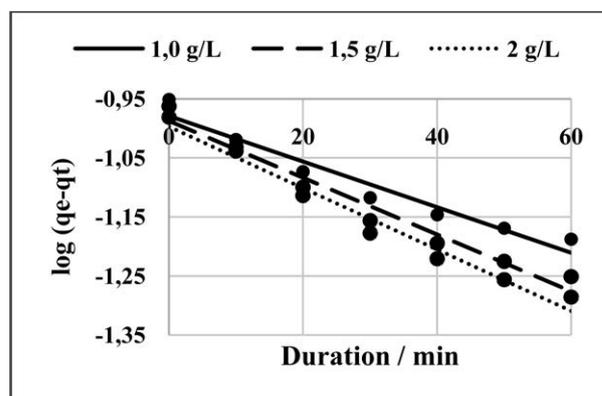
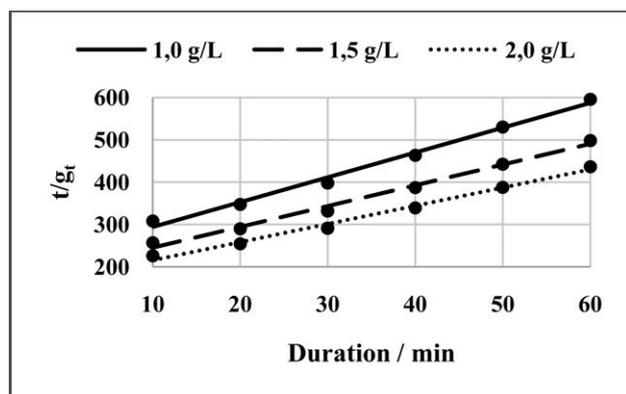


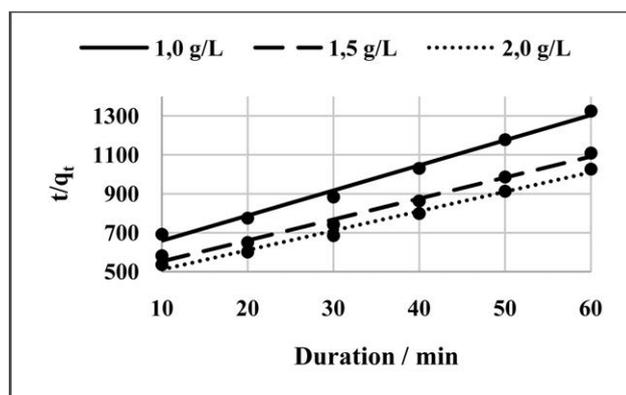
Figure 1b Pseudo-first-order model of niobium sorption onto the Purolite-C104.

The calculated  $q_e$  shown in (Table 1) were higher than the experimental values. In addition, the  $R^2$  of the pseudo-first-order model was lower than the intraparticle diffusion and pseudo-second-order models. As Table 1 shows, the sorption capacities were determined from the intercept of the plots and were found to be 0,209 mg/g, 0,203 mg/g, and 0,217 mg/g for KU-2-8 H and 0,111, 0,108 mg/g and 0,109 mg/g for Purolite-C104 at 1,0, 1,5 and 2,0 mg/L concentrations respectively. Besides that, the  $R^2$  values for these models were 0,972, 0,978 and 0,977 for KU-2-8 H and 0,948, 0,965 and 0,975 for Purolite-C104 at 1,0, 1,5 and 2,0 mg/L concentrations respectively. The pseudo-first-order model does not accurately describe the kinetics of Nb, as indicated by the poor model fit.

Pseudo-second-order model of niobium sorption onto the KU-2-8 H and Purolite-C104 cationites are shown in Figures 2a and b, respectively. The pseudo-second-order model assumes that the driving force for sorption process is the difference between the adsorbate concentration and the equilibrium concentration. Studies have revealed that the pseudo-second-order model is also based on the assumption that the rate-limiting step may be chemisorption, which involves valence forces that exhibit sharing or electron exchange between the adsorbent and the adsorbate. Hussaini [5]



**Figure 2a** Pseudo-second-order model of niobium sorption onto the KU-2-8 H cationites.



**Figure 2b** Pseudo-second-order model of niobium sorption onto the Purolite-C104 cationites

have previously reported that, if the initial metal concentration of solution is low, the adsorption process is carried out by the pseudo-second-order model. On the contrary, pseudo-first-order models can be applied to higher initial concentrations. The obtained data confirmed that this model was suitable for the characterization of sorption kinetics.

Kinetic data of Nb sorption could be more appropriately defined by the pseudo-second-order model, as compared to the intra-particle diffusion and pseudo-first-order model. The correlation coefficients ( $R^2$ ) from the intra-particle diffusion model did not reach 99 %, which were lower than pseudo-second-order models.

Table 1 also indicated that the initial adsorption rate values ( $h$ ), g/mg min were: 0,004, 0,005, and 0,006 for KU-2-8 H at 1,0, 1,5, and 2,0 mg/L concentrations respectively and 0,002 at all studied concentrations for Purolite-C104. These showed that the initial rate of niobium ions adsorbed on Purolite-C104 cationites increased at higher concentration. It is important to identify the step with the lowest rate, which will determine the overall removal rate of niobium ions. Cheira, et al. [8] have proposed that the ion exchange process is a multistep process, in which the first step encompasses transport of ions from the solution to the surface of ionite particles (bulk diffusion). The second step is accompanied by the movement of niobium ions through the liquid film that surrounds the sorbent surface (film diffusion). Finally, the third stage involves transport of metal ions from the surface to the internal sites (surface diffusion or pore diffusion). In our view, the bulk diffusion step can be ignored, because the sorption studies are carried out with intensive shaking. Consequently, the film diffusion and pore diffusion steps should be considered in order to identify which of them determines the overall rate of niobium removal.

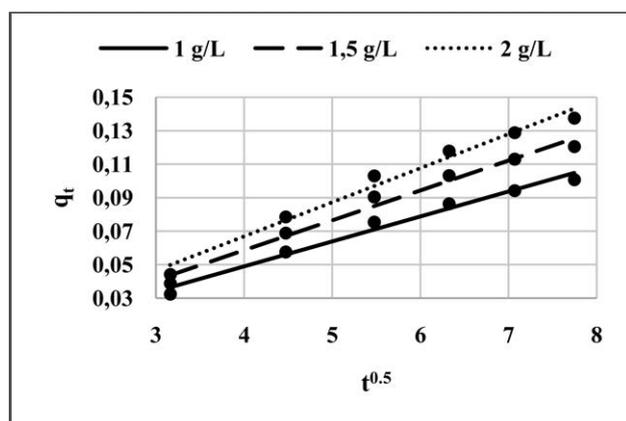
Intraparticle diffusion is the rate-limiting step in the adsorption process, if a plot of metal ions adsorbed against the square root of the contact time yields a straight line. This model implies that the effect of the diffusion of niobium is the rate-controlling step for the

**Table 1 Kinetic parameters for niobium sorption onto the KU-2-8 H and Purolite-C104 cationites.**

Kinetic models	Parameters	1,0 g/L		1,5 g/L		2,0 g/L	
		KU-2-8 H	Purolite-C104	KU-2-8 H	Purolite-C104	KU-2-8 H	Purolite-C104
Pseudo-first-order	$q_e$ / mg/g	0,209	0,111	0,203	0,108	0,217	0,109
	$k_1$ / min	-0,004	-0,004	-0,007	-0,005	-0,006	-0,005
	$R^2$	0,972	0,948	0,978	0,965	0,977	0,975
Pseudo-second-order	$q_e$ / mg/g	0,171	0,078	0,077	0,093	0,233	0,099
	$k_2$ / g/mg-min	0,141	0,314	0,123	0,260	0,106	0,243
	$h$ / g/mg-min	0,004	0,002	0,005	0,002	0,006	0,002
	$R^2$	0,991	0,989	0,991	0,989	0,991	0,989
Intraparticle diffusion	$k_d$ / mg/g-min <sup>1/2</sup>	14,909	6,740	17,827	8,067	20,361	8,695
	$C$ / mg/g	0,010	0,005	0,015	0,006	0,013	0,007
	$R^2$	0,979	0,980	0,989	0,980	0,989	0,981
Practical Capacity	$q_{exp}$ / mg/g	0,197	0,101	0,202	0,108	0,213	0,105

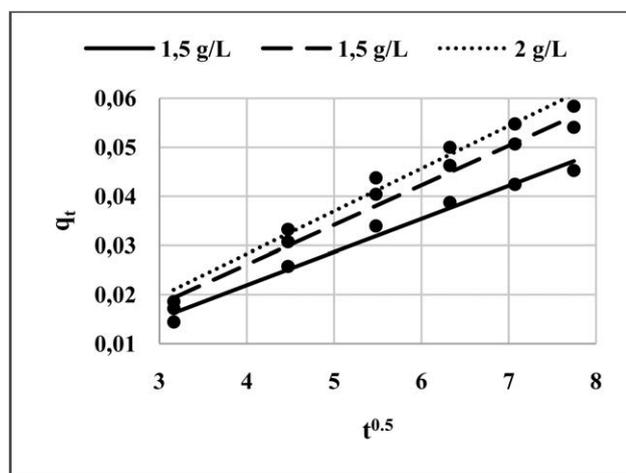
sorption process, that the intraparticle diffusivity is constant, and that the direction of the diffusion is radial. It was used to calculate the intraparticle diffusion rate constant and the intercept of the linear plots, as shown in Figures 6a and b for the KU-2-8 H and Purolite-C104 cationites, respectively.

Intraparticle diffusion models of niobium sorption onto the KU-2-8 H and Purolite-C104 cationites are shown in Figures 3a and b, respectively.



**Figure 3a** Intraparticle diffusion model of niobium sorption onto the KU-2-8 H cationites.

The plots of  $q_t$  vs.  $t^{0.5}$  showed that the obtained straight lines passed through the origin relatively well ( $C > 0$ ) (Figs. 3 a,b).



**Figure 3b** Intraparticle diffusion model of niobium sorption onto the Purolite-C104 cationites.

The obtained data in Table 1 indicated that the values of correlation coefficient  $R^2$  were 0,979, 0,989, and 0,989 for KU-2-8 H and 0,980, 0,980, and 0,981 for Purolite-C104, while the intraparticle diffusion rate constants  $K_{id}$  were,  $\text{mg/g}\cdot\text{min}^{1/2}$ : 14,909, 17,827, and 20,361 for KU-2-8 H and 6,740, 8,067, and 8,695 for

Purolite-C104 at 1,0, 1,5, and 2,0  $\text{mg/L}$  concentrations respectively. Finally, from the kinetic parameters of the three kinetic models seen in Table 1, the adsorption kinetics were estimated and fitted well in the intraparticle diffusion model.

## CONCLUSION

A strong acid cationite, KU-2-8 H, and a weak acid cationite, Purolite-C104, were used for niobium recovery from chemically leached solutions of titanium wastes. The results of the investigation indicated that maximum efficiencies were achieved in a duration of 3,5 hours for both KU-2-8 H and Purolite-C104 cationites. Under optimal conditions, the maximum sorption capacity of KU-2-8 H and Purolite-C104 cationites attained at room temperature were 0,089 and 0,071  $\text{g/g}$  respectively. Moreover, the obtained kinetic data were found to fit well with a pseudo-second order model ( $R^2 \geq 0,989$ ), which has been found to be the most appropriate model for explaining the adsorption mechanism.

## Acknowledgements

The research was funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan Grant № AP13067763

## REFERENCES

- [1] Sarsembekov T.K., Yanko T.B., Sidorenko S.A., Pylypenko M.M. Problems of atomic science and technology, 1 (2020) (125), 173-177.
- [2] Shikika A., Sethurajan M., Muvundja F., Mugumaoderha M., Gaydardzhiev S. Hydrometallurgy, 198 (2020) 105496
- [3] Baigenzhenov O., Toishybek A. M., Khabiyev A. T., Aimbetova I.O., Dagubayeva A.T. Complex Use of Mineral Resources, 318 (2021), 97-103.
- [4] Deblonde, G., Chagnes, A., Weigel, V., Cote, G. Hydrometallurgy, 165 (2016), 345-350.
- [5] Hussaini, O.M., Transactions of Nonferrous Metals Society of China, 19 (2009), 474-478
- [6] Patent KZ No. KZ29265-A4. Producing ion-exchange materials, preferably sulfonic cation exchangers, useful for producing ion-exchange materials, preferably sulfonic cation exchangers, which are useful in hydrometallurgy for extraction of heavy metals e.g. lead / Ergozhin E.E., Bektenov N. A., Sadykov K. A. Published on 15.12.2014
- [7] H. Pavolová, S. Khouri, M. Cehlár, L. Domaracká, M. Puzder. Metallurgija, 55 (2016) 4, 712-714
- [8] Cheira M. F., Atia B. M., Kouraim M. N. Journal of Radiation Research and Applied Sciences, 10 (2019), 307-319.

**Note:** The responsible for English language is B. Mishra, USA, Worcester