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INTERPOLYMER KU-2-8: AV-17-8 SYSTEMS FOR SELECTIVE SORPTION OF RHENIUM, MOLYBDENUM AND TUNGSTEN

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Abstract. In this paper, the processes of sorption and desorption of rhenium ions Re(VII), molybdenum Mo(VI) and tungsten W(VI) from model aqueous solutions are studied using a series of interpolymer systems based on the strongly acidic cationite KU-2-8(H^+) and the strongly basic anionite AV-17-8(OH^-). The aim of the study was to develop and optimize interpolymer systems for the selective extraction of rhenium ions in the presence of molybdate and tungstate ions. The sorption process was studied under static (batch) conditions by varying the contact time between the solution and the interpolymer systems with different component ratios. The study showed that the

determining factors for the sorption process are the composition of the interpolymer system used and the duration of phase contact during which the phases interact. The highest sorption capacity was observed for the KU-2-8(H-): AV-17-8(OH-) system at a molar ratio of 2:4, where the degree of rhenium removal exceeded 85-90%, and the residual concentration decreased from 150 to 13.5 mg/L in 48 hours. Desorption studies using 4 M HCl confirmed the reversible ion-exchange mechanism of rhenium binding; the degree of desorption reached significant values, which indicates the possibility of sorbent regeneration without significant loss of activity. The results obtained demonstrate a pronounced synergistic effect of the KU-2-8(H+): AV-17-8(OH-) interpolymer systems in comparison with individual ionites and confirm the prospects of their use for the selective extraction of rhenium ions from multicomponent industrial and technological solutions containing molybdate and tungstate ions.

Keywords: rhenium; molybdenum; tungsten; sorption; interpolymer systems; ion exchange

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РЕНИЙ, МОЛИБДЕН ЖӘНЕ ВОЛЬФРАМДЫ СЕЛЕКТИВТІ СОРБЦИЯЛАУҒА АРНАЛҒАН KU-2-8: AV-17-8 ИНТЕРПОЛИМЕРЛІ ЖҮЙЕЛЕРІ

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Аннотация: Бұл жұмыста рений иондарының Re(VII), молибден Mo(VI) және вольфрам W(VI) модельдерінің сулы ерітінділерінен сорбциясы мен десорбциясы процестері жоғары қышқыл катионит КУ-2-8(H+) және жоғары негізді анионит АВ-17-8(ОН -) негізіндегі интерполимерлі жүйелер сериясы арқылы зерттеледі.). Зерттеудің мақсаты молибдат және вольфрам иондарының қатысуымен рений иондарын іріктеп алу үшін интерполимерлік жүйелерді әзірлеу және оңтайландыру болды. Сорбция процесі статикалық (пакеттік) жағдайда ерітінді мен интерполимер жүйелері арасындағы байланыс уақытын әр түрлі компоненттік қатынастармен өзгерту арқылы зерттелді. Зерттеу көрсеткендей, сорбция процесінің анықтаушы факторлары қолданылатын интерполимер жүйесінің құрамы және фазалар өзара әрекеттесетін фазалық байланыстың ұзақтығы болып табылады. Ең жоғары сорбциялық сыйымдылық ку-2-8(Н-): АВ-17-8 (ОН -) жүйесі үшін молярлық қатынасы 2:4 кезінде байқалды, мұнда ренийді кетіру дәрежесі 85-90% - дан асты, ал қалдық концентрациясы 48 сағат ішінде 150-ден 13,5 мг/Л-ге дейін төмендеді. 4 М HCl көмегімен десорбциялық зерттеулер рениймен байланысудың қайтымды ион алмасу механизмін растады; десорбция дәрежесі маңызды мәндерге жетті, бұл белсенділіктің айтарлықтай жоғалуынсыз сорбенттердің регенерациялану мүмкіндігін көрсетеді. Алынған нәтижелер ku-2-8(H+): AV-17-8(OH-) интерполимерлі жүйелерінің жекелеген иониттермен салыстырғанда айқын синергетикалық әсерін көрсетеді және оларды молибдат пен вольфрам иондары бар көп компонентті өнеркәсіптік және технологиялық ерітінділерден рений иондарын іріктеп алу үшін қолдану перспективаларын растайды.

Түйін сөздер: рений; молибден; вольфрам; сорбция; интерполимерлік жүйелер

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ИНТЕРПОЛИМЕРНЫЕ СИСТЕМЫ KU-2-8:AV-17-8 ДЛЯ СЕЛЕКТИВНОЙ СОРБЦИИ РЕНИЯ, МОЛИБДЕНА И ВОЛЬФРАМА

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Аннотация: В данной работе изучены процессы сорбции и десорбции ионов рения Re(VII), молибдена Mo(VI) и вольфрама W(VI) из модельных водных растворов с использованием серии интерполимерных систем на основе сильнокислотного катионита KU-2-8(H-) и сильноосновного анионита AV-17-8(OH-). Целью исследования является разработка и оптимизация интерполимерных систем для селективного извлечения ионов рения в присутствии ионов молибдата и вольфрамата. Процесс сорбции изучался в статических (периодических) условиях путём варьирования времени контакта раствора с интерполимерными системами различного состава. Установлено, что определяющими факторами процесса сорбции являются состав интерполимерной системы и продолжительность фазового контакта. Наибольшая сорбционная ёмкость наблюдалась для системы KU-2-8(H^-):AV-17-8(OH^-) при мольном соотношении 2:4, где степень удаления рения превышала 85–90%, а остаточная концентрация снижалась со 150 до 13,5 мг/л в течение 48 часов. Исследования

десорбции с использованием 4 M HCl подтвердили обратимый ионообменный механизм связывания рения; степень десорбции достигала высоких значений, что свидетельствует о возможности регенерации сорбента без существенной потери активности. Полученные результаты демонстрируют выраженный синергетический эффект интерполимерных систем KU-2-8(H-):AV-17-8(OH-) по сравнению с индивидуальными ионитами и подтверждают перспективность их использования для селективного извлечения ионов рения из многокомпонентных технологических растворов, содержащих ионы молибдата и вольфрамата.

Ключевые слова: рений; молибден; вольфрам; сорбция; интерполимерные системы

Introduction. Rare and dispersed elements such as rhenium, molybdenum, and tungsten play a key role in modern industry due to their unique physico-chemical properties and high thermal and chemical stability (Que et al., 2022). Rhenium, in particular, is used in the production of heat-resistant alloys, catalysts, and electronics, but its natural content is extremely low, and extraction from ore sources involves significant technological difficulties (Xu et al., 2024). Therefore, the development of effective and environmentally friendly methods for extracting rhenium from secondary and industrial aqueous media containing related elements, molybdenum and tungsten, remains an urgent task (Batueva et al., 2022).

In recent decades, there has been a growing interest in polymer and interpolymer sorption systems with controlled properties, chemical resistance, and the possibility of selective interaction with metal ions of various natures (Jumadilov et al., 2021). Among them, acidic and basic ionites, such as KU-2-8(H^+) and AV-17-8(OH-), which are capable of forming interpolymer complexes with improved characteristics compared to individual resins, attract special attention (Dyussembayeva et al., 2024). The synergistic effect resulting from the combination of cation- and anion-exchange components provides an increase in the degree of sorption due to the combined action of electrostatic and interphase interactions in the macromolecular matrix (Jumadilov et al., 2025).

Separate data on acid-base type interpolymer systems are presented in the literature, however, complex studies devoted to the joint sorption and the process of releasing Re(VII), Mo(VI) and W(VI) in an interpolymer system consisting of KU-2-8(H+) together with AV-17-8(OH^-) and with varying molar ratios of components, are practically absent. It has been shown that the rate and degree of sorption significantly depend on the content of the anion-exchange component AV-17-8(OH) and the interaction time (Yu et al., 2019). This necessitates a systematic study of the effect of the composition of the interpolymer system and the contact time on the kinetics of the process, selectivity and regenerative ability of the sorbent (Baishibekov et al., 2025).

The aim of the work is to develop and evaluate interpolymer systems KU-2-8(H^+):AV-17-8(OH^-) for selective sorption and partial desorption of rhenium ions from model aqueous solutions in the presence of molybdenum and tungsten, to identify the optimal molar ratio of components and to establish the basic patterns of sorption and desorption.

Methods and materials.

Reagents and preparation of model solutions. Salts containing rhenium, molybdenum, and tungsten ions were used to study sorption properties. Ammonium perrenate (NH-ReO-) was used as a source of rhenium, sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) as a source of molybdenum, and tungstic acid (H_2WO_4) as a source of tungsten. Model solutions were prepared by dissolving samples of the corresponding salts in distilled water to a concentration of 150 mg/L for each of the studied ions. The solutions were prepared fresh before the experiments. The initial pH of the model solutions was adjusted to pH = 5.5 ± 0.1 by adding dilute NaOH or HCl solutions. The pH was controlled using a pH meter and maintained constant throughout the sorption experiments. The ionic strength of the solution was stabilized by introducing a neutral electrolyte background. The temperature regime during the measurements was stabilized at 25 °C with a tolerance of ± 1 °C.

Interpolymer sorption Systems. The study materials were KU-2-8(H_2) cationite with pronounced acidic properties and AV-17-8(OH-) anionite, which belongs to the strongly basic ones. A series of interpolymer systems with different molar ratios of components was prepared from these ionites.: 6:0, 5:1, 4:2, 3:3, 2:4, 1:5 and 0:6 (KU-2-8: AV-17-8). Each composition was formed by co-swelling the resins in distilled water and then evenly mixing until a homogeneous phase distribution was achieved. Before use, the ionites were washed with distilled water to a neutral reaction medium and dried to a constant weight at room temperature. The mass ratio of the solid phase to the liquid was 0.06 g per 100 ml of solution. All sorption experiments were carried out in closed reaction cells with constant stirring on a magnetic stirrer until equilibrium was established. All sorption experiments were carried out under static (batch) conditions, where the interaction between the solid sorbent and the solution was studied as a function of contact time at different component ratios.

Sorption procedure. Sorption kinetics was determined at different contact times: 0.5, 2.5, 6, 24, and 48 hours. After a predetermined period of time, aliquots of 5 ml were taken from the reaction mixture to analyze the residual concentration of metals. The concentrations of Re(VII), Mo(VI), and W(VI) in solution were determined spectrophotometrically. All experiments were carried out in three repetitions; the results were averaged; the discrepancy did not exceed 5%.

Desorption technique. After the completion of the 48-hour sorption process, desorption experiments were performed to evaluate the reversibility of ion binding. 4 M HCl was used as the eluent. The amount of desorption was expressed as a percentage relative to the amount of metal sorbed in the previous step.

Processing of experimental data. Sorption efficiency (η, %) was calculated by the expression:

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \qquad (1)$$

where C_0 - is the initial concentration, C_e – is the equilibrium concentration (mg/L)
The degree of desorption (R, %) was determined as:

$$R = \frac{m_{desorbed}}{m_{sorbed}} \times 100\% \quad (2)$$

The degree of binding (θ, %) was calculated as the ratio of the number of metal ions bound at time t (q_t) to the maximum sorption capacity (qm_{ax}):

$$\theta = \frac{q_t}{q_{max}} \times 100\% \quad (3)$$

The effective dynamic exchange capacity (Q, mmol/g) was determined by the expression:

$$Q = \frac{v_{sorb}}{m_{sorbent}} \times 100\% \quad (4)$$

v_{orb} - the amount of the substance of the sorbed metal, mmol;
$m_{sorbent}$ - weight of dry sorbent, g.

Results. Sorption kinetics and the effect of the composition of the interpolymer system

The sorption of rhenium, molybdenum, and tungsten ions was studied in model solutions at constant pH, ionic strength, and temperature. The ratio of solid to liquid was maintained at 0.06 g per 100 ml, and the initial concentration of each ion was 150 mg/L. To evaluate the sorption properties, a series of KU-2-8(H^+):AV-17-8(OH^-) interpolymer systems with molar ratios from 6:0 to 0:6 were tested. The residual concentration of rhenium, molybdenum, and tungsten ions (C_e, mg/L), depending on the contact time, at various ratios of KU-2-8:AV-17-8 are shown in Figure 1.

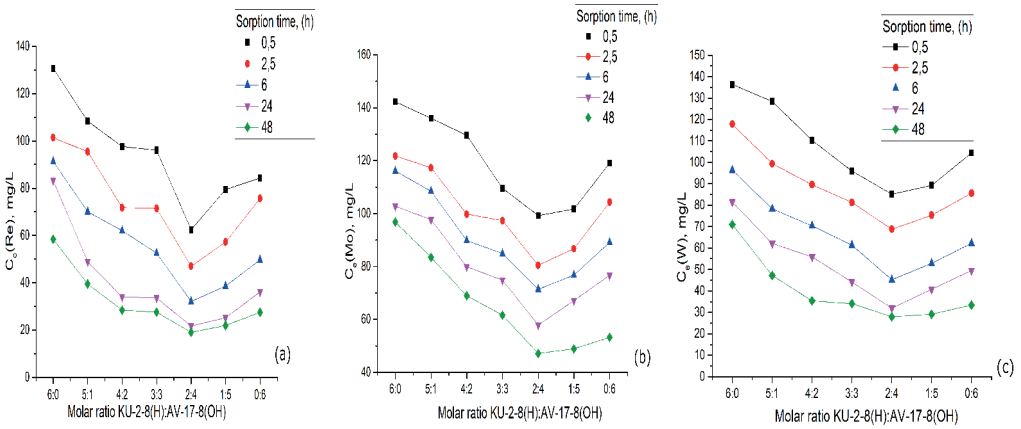

Figure 1. Residual concentrations of Re(VII)(a), Mo(VI)(b), and W(VI)(c) ions on KU-2-8(H):AV-17-8(OH) interpolymer systems at different molar component ratios.

Figure (a) shows the dependence of the residual concentration of rhenium ions in the model solution on the molar ratio of the components of the interpolymer system KU-2-8(H+):AV-17-8(OH-) at different sorption times. As can be seen from the figure,

in all the studied systems, with increasing sorption time, a decrease in the residual rhenium concentration is observed, which indicates the gradual extraction of ions from the solution and the sorption process. The highest residual concentration is recorded for individual KU-2-8(H+) cationite (ratio 6:0), whereas the introduction of AV-17-8(OH-) anionite leads to a noticeable increase in rhenium extraction efficiency.

For individual KU-2-8(H+) (6:0) cationite, the residual rhenium concentration decreases sequentially with increasing contact time: from about ~130 mg/L after 0.5 hours to ~100 mg/L after 2.5 hours (a decrease of ~23%), ~92 mg/L after 6 h (-29%), ~85 mg/L after 24 h (-35%) and ~60 mg/L after 48 h (-54% relative to 0.5 h).

When switching to the 5:1 interpolymer system, an additional decrease in C_e is observed. So, after 0.5 hours, the concentration decreases from ~110 to ~96 mg/L, and after 48 hours — from ~60 to ~40 mg/L (-33% compared to 6:0).

For the 4:2 composition, the residual concentration continues to decrease: after 0.5 hours — about ~100 mg/L, after 24 hours — ~35 mg/L, and after 48 hours — ~28 mg/L.

In the 3:3 system, the decrease persists, but becomes less pronounced: C_e after 0.5 hours is ~96 mg/L, and after 48 hours — ~27 mg/L.

The most noticeable decrease in the residual concentration is observed at a ratio of 2:4 and 1:5. In these molar ratios of sorbents to each other, the minimum values for all sorption times are fixed. For example, for a ratio of 2:4 from the initial 64 mg/L after half an hour of sorption, 20 mg/L remains near the end of equilibrium, while for a ratio of 1:5 from the initial 82 mg/L, 23 mg/L remains by the end of the experiment.

For the individual anionite AV-17-8(OH+) (0:6), the residual concentration increases: after 48 hours, the residual concentration reaches ~26 mg/L.

Thus, quantitative analysis shows that:

• an increase in sorption time from 0.5 to 48 hours leads to a 2-3-fold decrease in the residual rhenium concentration for all the systems studied;

• the transition from monocomponent ion exchangers to binary interpolymer systems provides an additional reduction in C_e by 30-70%;

• Optimal sorption characteristics are achieved at intermediate ratios of KU-2-8(H+):AV-17-8(OH-) ≈ 2:4-1:5, where the residual concentration is minimal (about 20 mg/L after 48 hours).

The results obtained indicate a pronounced synergistic effect of interpolymer systems in the extraction of perrenate ions from multicomponent solutions.

The results of the study also showed that the determining factors of the sorption process are the composition of the interpolymer system and the duration of the phase contact. In the initial period (0.5–2.5 hours), mainly rapid extraction of Re(VII) is observed, while sorption of Mo(VI) and W(VI) proceeds more slowly and reaches equilibrium only after 24-48 hours.

Figure (b) shows the effect of the composition of the interpolymer system KU-2-8(H+):AV-17-8(OH-) and the duration of phase contact on the residual molybdenum content in the model solution. A pronounced time dependence can be traced over the entire range of conditions studied: as the duration of the interaction of the solid and liquid phases increases, the concentration of Mo(VI) in solution decreases sequentially.

For the individual cation exchange resin KU-2-8(H-) (6:0), the values of C_e remain the highest among all samples. At the initial moment (0.5 h), the molybdenum content is about ~142 mg/L and gradually decreases to ~95 mg/L after 48 hours, which corresponds to a decrease of about 33%. This indicates the limited ability of cationite to extract molybdate ions.

The introduction of an anion-exchange component leads to a noticeable improvement in performance. At a ratio of 5:1, after 0.5 hours, about ~137 mg/L is fixed, while by 48 hours the value decreases to ~83 mg/L. For the 4:2 system, a further downward shift of the curves is observed: the final values reach ~65 mg/L.

With an equimolar composition (3:3), the decrease becomes more pronounced. At this point, by the end of the experiment, the concentration of molybdenum is approximately ~60 mg/L, which is significantly lower than in cationite-enriched systems.

The deepest extraction of Mo(VI) is realized in the area of increased anionite content. So, at a ratio of 2:4, after 0.5 hours, about ~ 100 mg/L is fixed, and by 48 hours the indicator decreases to ~ 43 mg/L. For the 1:5 composition, the final value increases slightly to ~47 mg/L, but remains significantly lower than for mixtures with a predominance of KU-2-8(H+).

For the individual AV-17-8(OH-) (0:6) anionite, a partial loss of efficiency is observed compared to optimal binary compositions: after 48 hours, the residual concentration increases to ~53 mg/L, which indicates the presence of a pronounced cooperative effect in the interpolymer systems of intermediate composition.

Comparison of kinetic curves shows that the most intense binding of molybdenum occurs in the first hours of contact, after which the process rate decreases markedly and the system gradually reaches a steady level in the range of 24-48 hours.

In general, the obtained dependences demonstrate that:

— an increase in the proportion of the anion-exchange component contributes to a more efficient removal of molybdate ions from the solution;

— the maximum effect is achieved in binary compositions with a predominance of AV-17-8(OH-);

— individual ion exchangers are inferior in efficiency to interpolymer combinations;

— the equilibrium state for Mo(VI) is established more slowly than for Re(VII), which indicates differences in the mechanisms of mass transfer and ion exchange interaction.

The presented data confirm the important role of the composition of the interpolymer system in controlling the selectivity of component extraction from multicomponent solutions.

Figure (c) shows the change in the residual tungsten content in the solution depending on the composition of the interpolymer composition KU-2-8(H+):AV-17-8(OH-) and the duration of phase contact. The obtained curves demonstrate a systematic decrease in the concentration of W(VI) with an increase in the interaction time, which indicates the gradual involvement of tungstate ions in the ion exchange process.

For KU-2-8(H+) cationite without the addition of anionite (6:0), the highest values of C_e are recorded in the entire time interval. After 0.5 hours, the W(VI) content is about

~137 mg/L and decreases only to ~70 mg/L after 48 hours, which indicates the limited ability of this resin to bind anionic forms of tungsten.

The addition of AV-17-8(OH-) leads to a consistent downward shift in dependencies. At a ratio of 5:1, the final concentration decreases to about ~47 mg/L, and for a 4:2 system — to ~36 mg/L. This indicates the increasing contribution of the anion exchange centers to the fixation process of W(VI).

In the 3:3 composition, a further deepening of the solution purification is observed: by 48 hours, the residual tungsten content is about ~34 mg/L. However, the most pronounced effect is seen with an increase in the proportion of AV-17-8(OH-).

The minimum values are achieved with a ratio of 2:4. At this point, after 0.5 hours, the concentration is about ~ 86 mg/L, and by the end of the experiment it decreases to ~ 28 mg/L. When switching to the 1:5 composition, there is a slight increase in the final value (up to ~30 mg/L), which may indicate a deviation from the optimal ratio of active centers.

For the individual AV-17-8(OH-) (0:6) anionite, the efficiency remains high, but is somewhat inferior to the best binary system: after 48 hours, about ~34 mg/L is fixed. This result confirms the existence of a cooperative interaction between the components of the interpolymer pair.

Kinetic analysis shows that the main decrease in the concentration of W(VI) occurs in the first 6 hours, after which the rate of the process slows down noticeably and by 24-48 hours the system approaches the equilibrium state.

In general, it is established that:

— an increase in the content of the anion exchange component significantly improves the extraction of tungstate ions;

— mixed interpolymer compositions show higher performance compared to individual resins;

— the optimal composition region is located near the ratio of KU-2-8(H+):AV-17-8(OH-)≈2:4;

— achieving steady-state values for W(VI) requires a longer contact time compared to Re(VII) or Mo(VI), which is due to the peculiarities of the transfer and exchange of tungsten oxoanions.

The data obtained confirm the prospects of selecting the composition of interpolymer systems for directional control of the extraction of components from multicomponent solutions.

The effect of the molar ratio on sorption efficiency. A comparative analysis showed that an increase in the proportion of the anion-exchange component AV-17-8(OH^-) contributes to an increase in sorption activity with respect to rhenium. The maximum recovery of Re(VII) (> 85-87%) was achieved at a molar ratio of 2:4, where the residual ion concentration in solution decreased from 150 mg/L to 13.5 mg/L after 48 hours. For molybdenum and tungsten, the equilibrium concentrations were about 53 mg/L and 23 mg/L, respectively, which indicates a lower affinity of these ions to the active centers of the system. The effect of the molar ratio of KU-2-8:AV-17-8 on the sorption efficiency of Re(VII), Mo(VI) and W(VI) ions (t = 48 h) is shown in Figure 2.

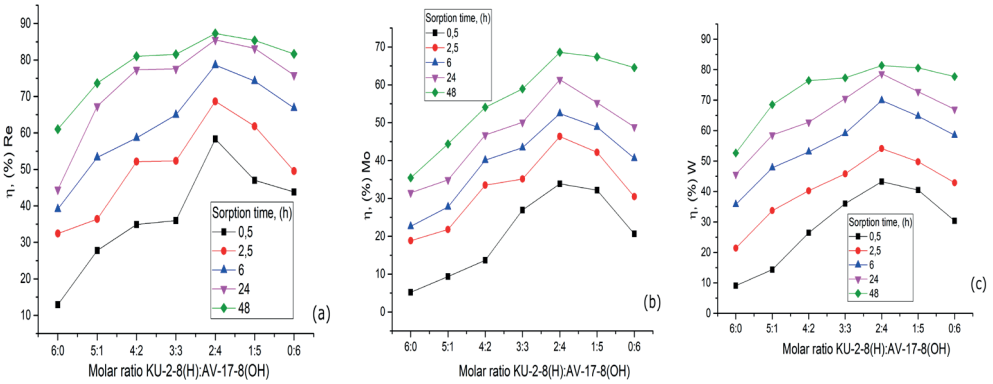

Figure 2 – Dependence of the sorption degree h(Re)(a), h(Mo)(b), h(W)(c) on the molar ratio of the components KU-2-8:AV-17-8 at a contact time of 48 hours.

For single-component systems (6:0 and 0:6), the sorption degree was significantly lower, which confirms the synergistic effect when using cation- and anion-exchange resins together. The most efficient ion extraction is due to the formation of interfacial zones and enhanced electrostatic interactions between oppositely charged groups.

Selectivity of sorption. A comparison of the extraction efficiency of the three elements showed a pronounced selectivity of the system with respect to Re(VII). Under the same conditions and initial concentrations, rhenium was preferentially sorbed compared to Mo(VI) and W(VI), which is explained by differences in charge, hydration radius, and the nature of the anionic complexes. Due to its smaller size and high mobility, the perrenate ion penetrates more easily into the micropores of the interpolymer matrix and interacts with cationic centers.

Desorption behavior. To assess the reversibility of the process, desorption experiments were performed after 48 hours of sorption. The degree of desorption increased with an increase in the content of the anion-exchange component and reached maximum values in the 2:4 system, amounting to 34.12% for rhenium, 9.34% for molybdenum and 22.74% for tungsten. The dependence of the degree of desorption of R(Re), R(Mo), R(W) on the molar ratio of KU-2-8:AV-17-8 is shown in Figure 3.

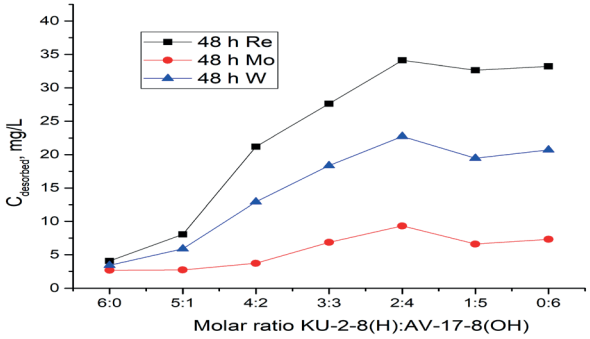

Figure 3. The degree of desorption of Re(VII), Mo(VI), and W(VI) ions from the KU-2-8(H):AV-17-8(OH) interpolymer systems, depending on the molar ratio of the components.

The results obtained confirm that the binding of rhenium is predominantly ion-exchange and reversible, whereas Mo(VI) and W(VI) are retained more weakly due to coordination and Van der Waals interactions. These results are in agreement with previously reported data, which confirm the reversible ion-exchange mechanism of rhenium binding in strongly basic anion exchangers (Liu et al., 2018).

Parameter analysis of Q and θ. The dependence of the sorption efficiency (η, %) on the contact time and the composition of the system corresponds to an increase in the values of Q and θ with an increase in the proportion of AV-17-8. In the optimal 2:4 system, the values of h for Re(VII), Mo(VI), and W(VI) were 87.28%, 68.6%, and 81.4%, respectively. For the same composition, the maximum values of $Q_{Re} \approx 0.0117$ mmol/g, $Q_{Mo} \approx 0.0179$ mmol/g, $Q_{W} \approx 0.0111$ mmol/g and $\theta_{Re} \approx 21.6$, $\theta_{Mo} \approx 33.0$, $\theta_{W} \approx 20.4$ were obtained. The calculated values of the effective dynamic exchange capacity of Q for Re, Mo, and W ions at various ratios KU-2-8(H^+):AV-17-8(OH^-) are shown in Figure 4.

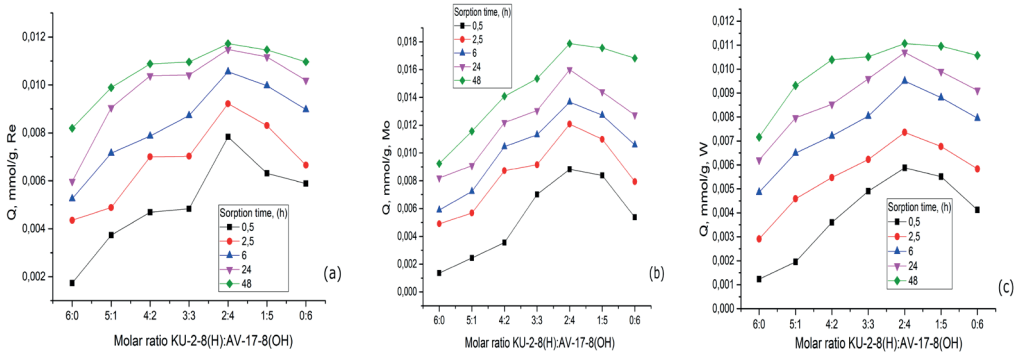

Figure 4. Effective dynamic exchange capacity Q for Re(VII)(a), Mo(VI)(b) and W(VI)(c) on interpolymer systems KU-2-8(H):AV-17-8(OH).

The calculated values of the degree of binding θ for Re(VII), Mo(VI), and W(VI) ions at various ratios of KU-2-8(H):AV-17-8(OH) are shown in Figure 5.

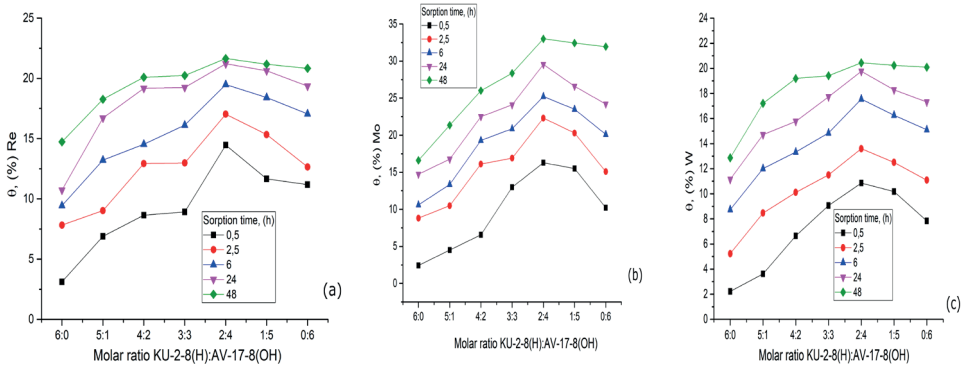

Figure 5. Degree of binding θ for Re(VII)(a), Mo(VI)(b), and W(VI)(c) ions on the KU-2-8(H):AV-17-8(OH) interpolymer systems.

The binding rates for rhenium, molybdenum, and tungsten ions were calculated for each composition within 48 hours. The molar ratio of 2:4 had the best performance in all three systems, which corresponds to the data on the residual concentration after sorption and the degree of sorption η(Re), η(Mo), η(W).

IR spectroscopic analysis of KU-2-8(H^+) cationite and AV-17-8(OH^-) anionite before and after sorption.

Literature review. *IR spectrum of KU-2-8 cationite after sorption.* Figure 6 shows the IR spectra of KU-2-8(H+) cationite before (a) and after sorption (b). The IR spectrum of KU-2-8(H^+) cationite after sorption is characterized by a wide intense band in the region of 3468 and 3437 cm^{-1}, corresponding to the superposition of valence vibrations of OH groups of sulfonic acid centers and adsorbed water (Semushin et al., 1980). The band at 3064 cm^{-1} refers to valence vibrations of the C–H aromatic ring of the polystyrene matrix (Kazitsyna et al., 1980). Asymmetric and symmetrical fluctuations of the methylene groups are recorded at 2925 and 2853 cm^{-1}, which is a characteristic feature of the polystyrene-divinylbenzene framework (Semushin et al., 1980). Deformation vibrations of water molecules are observed in the region of 1638 cm^{-1} (Semushin et al., 1980; Laskorin 1983). The set of bands 1602, 1496, 1451, and 1413 cm-^{1} corresponds to valence vibrations C=C of the aromatic core, partially overlapping with deformation vibrations of the CH_2 groups (Semushin et al., 1980; Laskorin 1983; Uglyanskaya et al., 1989). The most informative region of 1200-1000 cm^{-1} is represented by bands 1184, 1128, 1039, and 1010 cm^{-1}, which uniquely relate to valence vibrations of the SO_3H group associated with the benzene ring (Semushin et al., 1980). Extraplanar deformation vibrations of the C–H disubstituted aromatic ring are recorded at 834 and 776 cm^{-1} (Semushin et al., 1980). The long–wavelength region contains diagnostic bands of the C–S bond: the range 705-570 cm^{-1} is the C–S oscillation region in sulfur containing organic compounds (Kazitsyna et al., 1980) bands at 625 and 570 cm^{-1} are characteristic of the sulfogroup associated with the benzene ring in sulfocationites (Semushin et al., 1980; Kazitsyna et al., 1980) the band 580 cm^{-1} is fluctuations of the C–S sulfogroup (Semushin et al., 1980; Laskorin, 1983) bands 677 and 621 cm^{-1} are additional manifestations of C–S bonds (Laskorin, 1983). Bands in the 380 and 353 cm^{-1} regions are particularly significant, related to the valence vibrations of Me–O (Nakamoto, 1991), which indicates the presence of metal oxoanions (Re, Mo, W) sorbed on KU-2-8(H^+).

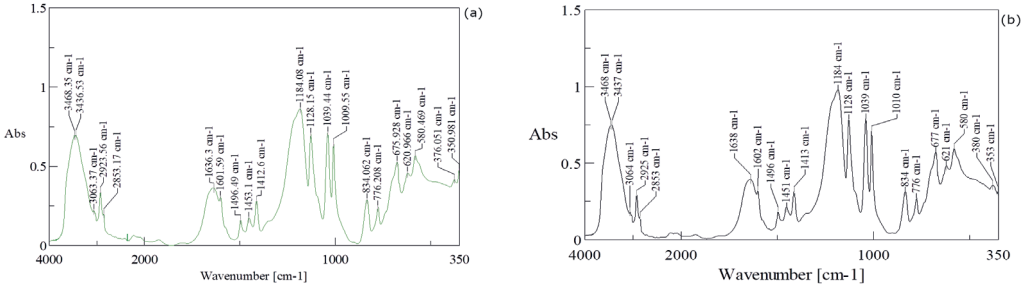

Figure 6. IR spectrum of KU-2-8(H^+) cationite before (a) and after (b) sorption.

The structure of sulfocationite is preserved, but the appearance of Me–O bands indicates the formation of coordination or electrostatic interactions between oxoanions and functional groups $–SO_3H$, confirming the sorption mechanism established by kinetics and desorption.

IR spectrum of AV-17-8(OH^-) anionite before sorption. Figure 7 shows the IR spectra of AV-17-8(OH^-) before (a) and after sorption (b). The IR spectrum of the initial AV-17-8(OH^-) corresponds to the structure of a strongly basic anionite in OH form. The wide bands 3430 and 3401 cm^{-1} relate to valence vibrations of OH^- groups of adsorbed water (Semushin et al., 1980; Kazitsyna et al., 1980). The band at 3022 cm^{-1} corresponds to the C–H of the aromatic ring (Semushin et al., 1980; Kazitsyna et al., 1980). Asymmetric and symmetrical oscillations of CH_2 groups are manifested at 2924 and 2852 cm^{-1} (Semushin et al., 1980). Deformation fluctuations of bound hydroxyl groups are recorded at 1632 cm^{-1} (Semushin et al., 1980). The valence vibrations C=C of the aromatic ring are expressed by bands 1614, 1511, and 1488 cm^{-1} (Semushin et al., 1980; Kazitsyna et al., 1980; Laskorin 1983). Fluctuations of CH_2- (1453, 1426 cm^{-1}) and CH_2-groups (1383 cm^{-1}) confirm the presence of alkyl fragments (Semushin et al., 1980). The 1222 cm^{-1} band belongs to C–N aliphatic amines (Semushin et al., 1980), a key structural fragment of the anion exchanger. Planar deformation vibrations of the C–H disubstituted ring are recorded at 976 cm^{-1}, and characteristic vibrations of the quaternary ammonium group $N+(CH_3)_3$ are recorded at 890 cm^{-1} (Semushin et al., 1980). Out–of-plane C-H deformation vibrations are observed at 829, 765, and 706 cm^{-1}. The spectrum fully confirms the structure of polystyrene divinylbenzene anionite with quaternary ammonium centers.

The IR spectrum of AV-17-8(OH^-) anionite after sorption. After sorption, the AV-17-8(OH^-) spectrum retains the main bands, but new and shifted ones appear — evidence of interaction with ReO_4-, $MoO_4$2- and $WO_4$2-. A wide maximum of OH groups is observed at 3412 cm^{-1} (Semushin et al., 1980; Laskorin 1983). An important sign of a change in the chemical structure is the appearance of a 1693 cm^{-1} band related to C=O, which indicates partial degradation of the polymer matrix (Semushin et al., 1980). The diagnostic band 2629 cm^{-1} also appears, corresponding to the OH group associated with the quaternary nitrogen atom (the characteristic range is 2600-2580 cm^{-1} (Semushin et al., 1980)).

Deformation fluctuations of water are manifested at 1659 and 1652 cm^{-1} (Laskorin, 1983), and associated OH groups are in the range of 1627, 1400-1300 cm^{-1} (Semushin et al., 1980). The bands of the aromatic ring are fixed at 1512, 1488 and 1451 cm^{-1}. Fluctuations of CH_2 appear at 1451 cm^{-1}. The 1222 cm^{-1} band remains characteristic of the C–N bond of aliphatic amines (Semushin et al., 1980). Planar deformation vibrations of the C–H disubstituted benzene ring are manifested at 977 cm^{-1}, the $N^+(CH_3)_3$ group at 890 cm^{-1} (Semushin et al., 1980).

Bands at 833 and 765 cm^{-1} are observed, related to out-of-plane deformation vibrations of the benzene ring, as well as 705 cm^{-1} vibrations of the monosubstituted ring (Semushin et al., 1980; Laskorin 1983). Of particular interest is the appearance of bands 1374 and 833 cm^{-1} corresponding to fluctuations of the NO_3 group (Semushin et

al., 1980), which indicates a possible oxidative transformation of functional groups or the presence of nitrates in the solution. Changes in the intensity and displacement of bands of OH^-, C–N-, and $N^+(CH_3)_3$ fragments indicate the participation of anionite in ion exchange. The presence of C=O and NO_3 bands reflects a partial chemical modification of the resin during sorption.

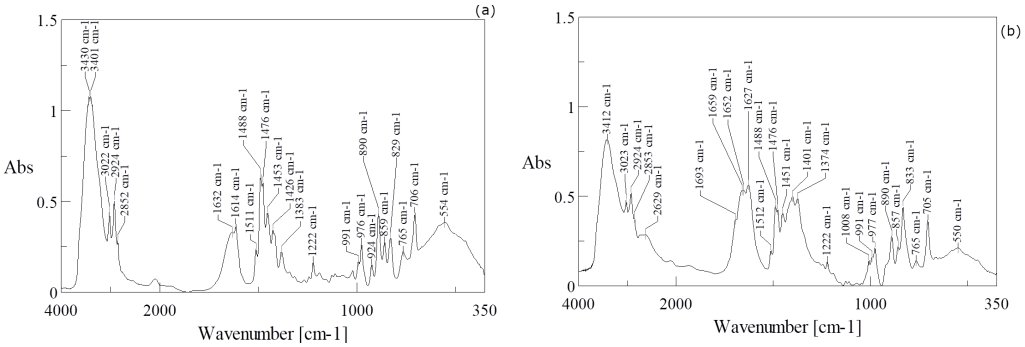

Figure 7. IR spectrum of AV-17-8(OH) anionite before (a) and after (b) sorption.

KU-2-8: sorption of Re, Mo, and W is accompanied by the appearance of Me–O bands and a change in the C–S region, indicating the interaction of oxoanions with $–SO_3H$ groups. AV-17-8: changes in the spectrum (C=O, NO_3-, C–N and N+ shifts $(CH_3)_3$) indicate the participation of quaternary ammonium centers in the exchange of oxoanions and partial degradation of the structure. Both resins show changes confirming the sorption mechanism consistent with the kinetics, Q/θ values, and desorption data.

Discussion. The obtained results demonstrate that the sorption behavior of Re(VII), Mo(VI), and W(VI) ions in KU-2-8(H+):AV-17-8(OH-) interpolymer systems is governed by a complex interplay of structural, kinetic, and compositional factors. The data clearly indicate that both the phase contact duration and the molar ratio of the cation- and anion-exchange components determine the efficiency, selectivity, and reversibility of the extraction process. The synergistic nature of the combined ion exchangers is particularly evident when comparing the interpolymer systems with single-component resins (Han et al., 2023)

Influence of Contact Time and Kinetic Features

One of the most pronounced observations is the difference in sorption kinetics between Re(VII) and the structurally similar oxoanions Mo(VI) and W(VI). During the initial 0.5–2.5 h period, rhenium sorption proceeds rapidly, whereas molybdenum and tungsten demonstrate slower uptake and require 24–48 h to approach equilibrium. This kinetic distinction can be attributed to differences in ionic size, hydration energy, and diffusion mobility in the polymer matrix. The perrenate ion (ReO_4-), characterized by relatively small effective size and high mobility, diffuses more readily into the microporous structure of the interpolymer system. In contrast, molybdate (MoO_4^{2}-) and tungstate (WO_4^{2}-) ions possess higher charge density and stronger hydration shells, which hinder their penetration into active sites. The double negative charge also results

in stronger electrostatic repulsion within confined regions of the matrix, especially when multiple anions compete for nearby functional groups (Candeago et al., 2024; Cyganowski et al., 2025).

Effect of Molar Ratio and Synergistic Interactions

A key finding of the study is the decisive role of the KU-2-8:AV-17-8 molar ratio. The increase in the fraction of the anion exchanger AV-17-8(OH-) enhances sorption activity, particularly toward rhenium. This effect is accompanied by a noticeable increase in the sorption rate, especially at the initial stages of the process. The higher content of AV-17-8(OH-) leads to an increase in the number of available quaternary ammonium functional groups, which act as active centers for the binding of anionic species. As a result, electrostatic attraction between the sorbent and oxoanions is intensified, facilitating faster diffusion of ions into the interpolymer matrix. However, when the content of the anion exchanger becomes excessive (e.g., 0:6), the absence of the cation-exchange component reduces the cooperative interactions between the polymer phases, which limits the overall efficiency and diminishes the kinetic advantage. Therefore, the optimal balance between sorption rate and efficiency is achieved at intermediate compositions, particularly at ratios close to 2:4–1:5.

The improved performance at intermediate compositions demonstrates a synergistic effect. In single-component systems (6:0 or 0:6), sorption efficiency is markedly lower. This confirms that cooperative interactions between oppositely charged polymer networks create favorable conditions for oxoanion uptake.

Selectivity Toward Rhenium

The pronounced selectivity toward Re(VII) represents one of the most technologically significant outcomes of the study. Under identical conditions, rhenium extraction exceeds that of molybdenum and tungsten.

This selectivity can be rationalized by several factors:

Ionic Size and Hydration Radius: Perrenate ions (ReO_4-), where rhenium is in the +7 oxidation state, have lower hydration energy and a smaller effective hydrated radius compared to molybdate and tungstate oxoanions (MoO_4^{2-} and WO_4^{2-}), in which the metals are in the +6 oxidation state. This behavior is consistent with literature data, where the lower sorption activity of molybdate and tungstate ions is attributed to differences in their structure, charge, and hydration characteristics (Yang et al., 2025).

Charge Differences: The single negative charge of ReO_4- facilitates ion exchange at quaternary ammonium sites without requiring compensation of two charges per binding event.

Mobility: Higher mobility enhances diffusion through microporous regions.

Complex Stability: Molybdate and tungstate may form polymeric species in solution, particularly at certain pH ranges, reducing their effective diffusivity.

The preferential sorption of Re(VII) is consistent with the kinetic data and desorption behavior. Importantly, such selectivity has practical implications for hydrometallurgical processes, especially in the recovery of rhenium from multi-component leach solutions containing molybdenum and tungsten impurities(Fathi et al.).

Mechanistic Interpretation

Overall, the sorption mechanism in the KU-2-8:AV-17-8 system can be tentatively described as a multi-stage process based on the experimental data obtained under static (batch) conditions.:

Diffusion of oxoanions to the interpolymer interface.

Electrostatic attraction to quaternary ammonium centers.

Ion exchange replacing OH- groups.

Stabilization via hydrogen bonding or weak coordination.

The synergistic effect arises from the spatial organization of oppositely charged functional groups, which enhances local electric fields and facilitates ion transfer.

Practical Implications

The demonstrated selectivity toward rhenium and optimal performance at 2:4 ratio suggest potential application of this system in selective recovery technologies. The relatively high desorption rate of Re indicates feasibility of regeneration and reuse.

However, the observed partial degradation of AV-17-8 under prolonged contact suggests that operational conditions must be optimized to maintain long-term stability. Further studies on cyclic sorption–desorption performance would be valuable.

It should be noted that the mechanistic interpretation proposed in this study is based on data obtained under static conditions and therefore has a qualitative character. A more rigorous confirmation would require additional experiments under dynamic flow conditions.

From a chemical standpoint, the behavior of the studied ions in solution should also be considered. Rhenium(VII) in aqueous media is predominantly present as a stable perrenate anion (ReO_4-), regardless of pH, and therefore is mainly sorbed via anion-exchange interactions with the functional groups of AV-17-8(OH-).

In contrast, molybdenum(VI) and tungsten(VI) may exist in solution in various forms depending on pH and concentration, including monomeric oxoanions (MoO_4^{2}-, WO_4^{2}-), polymeric species, and partially protonated forms. This speciation may affect their interaction with both anion- and cation-exchange components of the interpolymer system, which could explain the differences in sorption behavior observed at different KU-2-8:AV-17-8 ratios.

Conclusion. A comprehensive study of the sorption and desorption of Re(VII), Mo(VI), and W(VI) ions from model aqueous solutions was performed using interpolymer systems based on KU-2-8(H^+) and AV-17-8(OH^-) with a molar component ratio varying from 6:0 to 0:6. It is shown that the sorption efficiency and selectivity for rhenium significantly depend on the content of the anion-exchange component and the contact time of the phases. It was found that the optimal composition of the interpolymer system is KU-2-8(H^+)/AV-17-8(OH^-) with a molar ratio of 2:4, providing a degree of rhenium removal of more than 85-90% at a residual concentration of about 13.5 mg/L. At the same time, high values of Q and θ are achieved, reflecting the effective involvement of active centers in the sorption process. Desorption experiments have shown that rhenium can be partially eluted (R ≈ 34-39%) using 4 M HCl, which confirms the possibility of sorbent regeneration and cyclic use of the system. Comparison with individual ionites demonstrated the presence of a pronounced synergistic effect for the interpolymer

systems KU-2-8– AV-17-8, which makes it possible to consider them as promising sorption materials for the selective extraction of rhenium from multicomponent industrial and man-made solutions jointly containing molybdenum and tungsten.

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