Austrian Journal of Technical
and Natural Sciences, 2026 No 7–8
ISSN 2310-5607

PREMIER Publishing
ppublishing.org

DOI:10.29013/AJT-26-7.8-18-24

RECOVERY OF RHENIUM AND MOLYBDENUM FROM INDUSTRIAL WASTEWATER USING THE KAOLIN-CHITOSAN COMPOSITE BIOSORBENT: SORPTION KINETICS AND ELEMENTAL ANALYSIS

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Cite: *Berdikulov B., Ikhtiyarova G. (2026). Recovery of Rhenium and Molybdenum From Industrial Wastewater Using the Kaolin-Chitosan Composite Biosorbent: Sorption Kinetics and Elemental Analysis. Austrian Journal of Technical and Natural Sciences 2026, No 7–8.*
https://doi.org/10.29013/AJT-26-7.8-18-24

Abstract

In this study, the ability of the previously synthesized and characterized AK-Xz (kaolin-chitosan, 5:1) composite biosorbent to take up rhenium (Re) and molybdenum (Mo) from an industrial wastewater sample containing these metals was investigated. The sorption experiment was carried out by keeping 1 g of sorbent in 100 mL of solution for contact times ranging from 10 to 300 minutes, while the process was monitored by UV–Vis spectrophotometry. The results showed that the absorbance of the solution decreased with time and stabilized within the 150–300 minute range, indicating that equilibrium had been reached. The kinetic data fitted the pseudo-first-order model with high accuracy (R^2 = 0.9934), whereas the pseudo-second-order model showed a markedly lower fit (R^2 = 0.7256). XRF elemental analysis confirmed that, after sorption, the Mo content of the solid phase increased from 0.836% to 2.97% (3.55-fold) and the Re content from 0.0410% to 0.0830% (2.02-fold). These findings indicate that the AK-Xz composite is a promising sorbent for recovering strategic metals from industrial wastewater.

Keywords: *AK-Xz, kaolin-chitosan composite, biosorbent, rhenium, molybdenum, sorption kinetics, pseudo-first-order, XRF*

Introduction

Biosorption based on natural and modified biopolymers has emerged as a low-cost, environmentally friendly alternative to conventional metal-recovery technologies (Aksu, Z., 1998; Qasem, N.A.A., Mohammed, R.H., Lawal, D.U., 2021). Rhenium (Re) and molybdenum (Mo) are strategic metals extensively used in the petrochemical industry – for example, in reforming and hydrotreating catalysts – whose natural reserves are limited and whose extraction is costly (Shen, L., Tesfaye, F., Li, X., Lindberg, D., Taskinen, P., 2021). Consequently, recovering such metals from industrial wastewater and catalyst-processing solutions is of considerable environmental and economic importance (Qasem, N.A.A., Mohammed, R.H., Lawal, D.U., 2021; Miyah, Y., El Messaoudi, N., Benjelloun, M., Geor-

gin, J., Franco, D. S. P., Viscusi, G., Messali, M., Knani, S., 2026). In earlier work, an AK-Xz composite biosorbent was synthesized from local Angren kaolin (Dill, H.G., Kus, J., Dohrmann, R., Tsoy, Y., 2008) and chitosan obtained from beekeeping waste (Apis mellifera) by the ionic gelation method (Rahaeng, K., Oraintara, A., Mahakham, W., 2026), and its composition was characterized by SEM-EDX and FTIR. The presence in the FTIR spectrum of the Amide I (1646 cm^{-1}) and Amide II (1557 cm^{-1}) bands characteristic of chitosan (Guibal, E., 2004; Zubir, A., Normaya, E., Danial, W.H., Goh, P. S., Piah, M. B. M., Show, P.-L., Ismail, A. F., Ahmad, M. N., 2026), together with accompanying changes in SEM morphology, confirmed the successful synthesis of the composite, consistent with previously reported kaolin- and clay-based chitosan composites (Gao, Z., Li, X., Wu, H., Zhao, S., Deligeer, W., Asuha, S., 2015; Gu, S., Kang, X., Wang, L., Lichtfouse, E., Wang, C., 2019; Liu, B., Wang, D., Yu, G., Meng, X., 2013). However, the actual practical sorption efficiency of the composite – in particular toward strategic metals – had not yet been tested.The aim of this work was to provide a preliminary evaluation of the ability of the AK-Xz composite biosorbent to take up Re and Mo from an industrial wastewater sample containing these metals. The objectives of the study included: (i) monitoring the sorption process over time by UV–Vis spectrophotometry; (ii) analyzing the obtained kinetic data using the pseudo-first-order and pseudo-second-order models 2, (Simonin, J.-P., 2016); (iii) comparing the elemental composition of the samples before and after sorption by XRF; (iv) drawing preliminary conclusions on the sorption mechanism based on the results obtained.

Materials and Methods

Sorbent

The previously synthesized AK-Xz composite biosorbent was used in this study. Angren kaolin (Dill, H.G., Kus, J., Dohrmann, R., Tsoy, Y., 2008) was acid-activated with 0.1 N HCl and thermally treated at 450 °C for 2 h (AK-450) (Gao, Z., Li, X., Wu, H., Zhao, S., Deligeer, W., Asuha, S., 2015; Chai, J.-B., Au, P.-I., Mubarak, N.M., Khalid, M., Ng, W.P.-Q., Jagadish, P., Walvekar, R., Abdullah, E.C., 2020), and was then mixed with a 1% chitosan–acetic acid solution at a 5:1 (kaolin: chitosan) mass ratio; granules were formed by the ionic gelation method (0.5 N NaOH/30% ethanol bath) (Rahaeng, K., Oraintara, A., Mahakham, W., 2026).

Industrial water sample

An industrial wastewater sample containing Mo, Re and other metals was selected as the object of the study. The full elemental composition of the initial solution was determined by XRF (Rigaku NEX CG, FP method) (Table 1).

Sorption experiment

One gram of AK-Xz sorbent was added to 100 mL of the industrial water and kept in contact for 10, 20, 30, 40, 50, 60, 90, 120, 150 and 300 minutes. The colour intensity of the solution, characteristic of Mo/Re complexes (Basak, A., 1995), was measured at each time point as absorbance (A) using a UV–Vis spectrophotometer. After each contact time, the sorbent was separated from the solution and rinsed with distilled water (to reduce surface residue) and prepared for further analysis.

Solid-phase analysis

The elemental composition of the loaded (post-sorption) solid sample was determined by XRF (“Bulk”, Scatter method) (Table 3).

Kinetic models

Two classical models were applied to describe the sorption kinetics (Sangoremi, A.A., 2025; Simonin, J.-P., 2016):

Pseudo-first-order (Lagergren):

$$\ln(q_e - q_t) = \ln(q_e) - k_1 \cdot t$$

Pseudo-second-order (Ho and McKay):

$$t/q_t = 1/(k_2 \cdot q_e^2) + t/q_e$$

where q_t and q_e are the relative (absorbance-based) uptake at time t and at equilibrium, respectively, and k_1 and k_2 are the rate constants of the corresponding orders. Since a proportionality based on the Beer–Lambert law was assumed between absorbance and concentration, $q_t = A_0 - A_t$ was used as the relative sorption quantity (Fadl, M. G., 2023).

Results

Elemental composition of the initial industrial water

Table 1. *XRF (FP method, assuming an aqueous solution) analysis results of the initial industrial water (major elements; the full spectrum comprises 27 elements)*

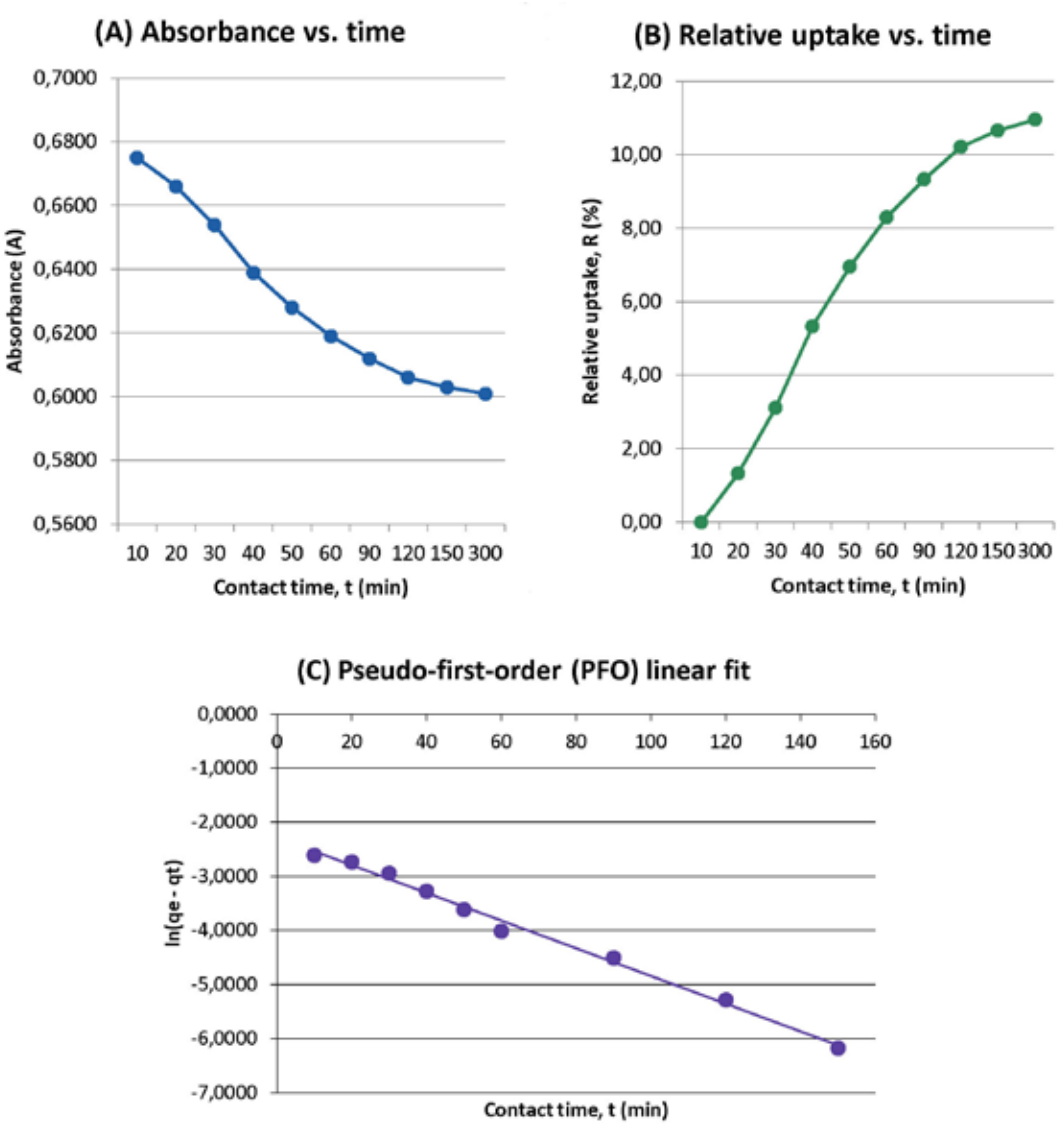
No.	Element	Result (mass%)	Unit
1	Mg	0.102	mass%
2	Al	0.0931	mass%
3	Si	0.0262	mass%
4	S	3.71	mass%
5	K	0.0257	mass%
6	Ca	0.0093	mass%
7	Ti	(0.0004) – below LLD	mass%
8	Cr	(0.0001) – below LLD	mass%
9	Mn	0.0332	mass%
10	Fe	0.117	mass%
11	Co	(0.0004) – below LLD	mass%
12	Cu	0.0470	mass%
13	Zn	0.0014	mass%
14	As	0.0007	mass%
15	Se	0.0009	mass%
16	Rb	0.0001	mass%
17	Mo	0.836	mass%
18	Ag	0.0005	mass%
19	Sn	0.0018	mass%
20	Pb	0.0004	mass%
21	Zr	0.0450	mass%
22	Re	0.0410	mass%

Sorption kinetics: absorbance and relative uptake

Table 2. *Time-dependent absorbance and relative uptake (the value at t = 10 min was taken as the initial point Ao, since no measurement prior to contact was available)*

t (min)	Absorbance (A)	**Relative uptake, R (%)**
10	0.675	0.00
20	0.666	1.33
30	0.654	3.11
40	0.639	5.33
50	0.628	6.96
60	0.619	8.30
90	0.612	9.33
120	0.606	10.22
150	0.603	10.67
300	0.601	10.96

Figure 1. *Sorption kinetics analysis of the AK-Xz sorbent: (A) absorbance vs. time; (B) relative uptake vs. time; (C) linear fit of the pseudo-first-order model*



As seen in panels (A) and (B) of Figure 1, the absorbance – and hence the Mo/Re concentration in solution – decreased monotonically over time and remained practically unchanged within the 150–300 minute range, indicating that equilibrium had been reached. The equilibrium relative uptake was approximately 11.0%.

The kinetic modelling results (Figure 1, panel C) showed that the pseudo-first-order model fitted the data with high accuracy: R^2 = 0.9934, rate constant $k_1 \approx 0.0259$ min^{-1}. For comparison, the pseudo-second-order model showed a markedly lower fit (R^2 = 0.7256), confirming the superiority of the pseudo-first-order model under the conditions studied (Simonin, J.-P., 2016; Fadl, M.G., 2023).

Elemental composition of the solid phase after sorption

Table 3. *XRF ("Bulk", Scatter method) analysis results of the loaded solid sample (major elements; the full spectrum comprises 32 elements, including trace elements below the LLD and chemically unreliable ones, discussed in the Discussion section)*

No.	Element	Result (mass%)	Unit
1	Mg	0.585	mass%

No.	Element	Result (mass%)	Unit
2	Al	6.02	mass%
3	Si	15.7	mass%
4	S	5.55	mass%
5	K	2.71	mass%
6	Ca	0.202	mass%
7	Ti	0.306	mass%
8	Fe	1.31	mass%
9	Cu	0.0693	mass%
10	Zn	0.0109	mass%
11	As	0.0062	mass%
12	Rb	0.0143	mass%
13	Zr	0.108	mass%
14	Mo	2.97	mass%
15	Ba	0.0220	mass%
16	Re	0.0830	mass%
17	Hg	0.0093	mass%

Change in Mo and Re content and estimated equilibrium capacity

Table 4. *Comparative summary of Mo and Re content in the two phases*

Parameter	Initial solution	Loaded solid sample	Change
Mo, mass%	0.836	2.97	↑ 3.55-fold
Re, mass%	0.0410	0.0830	↑ 2.02-fold
Re/Mo ratio	0.049	0.028	↓ decreased

Using the solid-phase data, the approximate equilibrium sorption capacity (q_e = element mass% × sorbent mass) was calculated: q_e(Mo) ≈ 29.7 mg/g, q_e(Re) ≈ 0.83 mg/g (Peng, M., Xi, C., Shen, K., Tan, Y., Li, F., 2024; Upadhyay, U., Sreedhar, I., Singh, S.A., Patel, C.M., Anitha, K.L., 2021). In this calculation, the final dry mass of the sorbent was assumed to be approximately equal to the initial 1 g.

Discussion

The results obtained warrant discussion from several perspectives. First, the significant increase in the Mo and Re content of the solid sorbent (3.55-fold and 2.02-fold, respectively) confirms that the AK-Xz composite is indeed capable of taking up these metals (Peng, M., Xi, C., Shen, K., Tan, Y., Li, F., 2024; Upadhyay, U., Sreedhar, I., Singh, S.A., Patel, C.M., Anitha, K.L., 2021). The decrease in the Re/Mo ratio (0.049 → 0.028) suggests that the sorbent may have a somewhat higher selectivity toward the Mo ion (Miyah, Y., El Messaoudi, N., Benjelloun, M., Georgin, J., Franco, D.S.P., Viscusi, G., Messali, M., Knani, S., 2026; Yefremova, S., Kablanbekov, A., 2026); however, since this conclusion is based on a single experimental data point, it is preliminary in character and requires further confirmation.Second, the kinetic analysis showed the superiority of the pseudo-first-order model (R^2 = 0.9934). In the literature, the pseudo-second-order model is generally associated with chemisorption-type processes (electron exchange or complex formation), while the pseudo-first-order model more often describes processes limited by physical diffusion (Sangoremi, A.A., 2025; Simonin, J.-P., 2016; Fadl, M.G., 2023). From this perspective, the observed result suggests that a physical diffusion stage

may play an important role in the sorption process occurring on the AK-Xz surface. However, drawing a definitive conclusion about the sorption mechanism based solely on the degree of fit of a kinetic model is not scientifically sufficient – additional evidence (e.g., activation energy, thermodynamic parameters, XPS analysis of the loaded sorbent) is required for that.Third, the composition of the AK-Xz composite confirmed by FTIR in the earlier study (free amine groups of chitosan and the porous structure of kaolin) (Guibal, E., 2004; Zubir, A., Normaya, E., Danial, W.H., Goh, P.S., Piah, M.B.M., Show, P.-L., Ismail, A.F., Ahmad, M.N., 2026) suggests two possible mechanisms of Mo/Re uptake: (i) electrostatic attraction/complex formation via protonated amine groups (Guibal, E., 2004; Musarurwa, H., Tavengwa, N.T., 2022) and (ii) physical adsorption within the pores of the kaolin (Gao, Z., Li, X., Wu, H., Zhao, S., Deligeer, W., Asuha, S., 2015; Gu, S., Kang, X., Wang, L., Lichtfouse, E., Wang, C., 2019; Chai, J.-B., Au, P.-I., Mubarak, N.M., Khalid, M., Ng, W.P.-Q., Jagadish, P., Walvekar, R., Abdullah, E.C., 2020). The relatively moderate observed uptake level (~11%) and the pseudo-first-order kinetics can be explained by both mechanisms operating together but being limited by diffusion.

Conclusion

In this study, the ability of the AK-Xz kaolin-chitosan composite biosorbent to take up Re and Mo metals from industrial wastewater was preliminarily evaluated. The results showed that: (1) the sorption process reaches equilibrium within 150–300 minutes; (2) the kinetics fit the pseudo-first-order model with high accuracy ($R^2 = 0.9934$); (3) the Mo and Re content of the solid phase increased 3.55-fold and 2.02-fold, respectively, confirming that sorption occurred; (4) the decrease in the Re/Mo ratio provides a preliminary indication of higher sorbent selectivity toward the Mo ion. The results obtained indicate that the AK-Xz composite is a promising material for recovering strategic metals from industrial wastewater (Qasem, N.A.A., Mohammed, R.H., Lawal, D.U., 2021; Shen, L., Tesfaye, F., Li, X., Lindberg, D., Taskinen, P., 2021; Miyah, Y., El Messaoudi, N., Benjelloun, M., Georgin, J., Franco, D.S.P., Viscusi, G., Messali, M., Knani, S., 2026), consistent with the growing interest in low-cost biosorbents as sustainable alternatives to conventional metal-recovery technologies (Liu, B., Wang, D., Yu, G., Meng, X., 2013; Upadhyay, U., Sreedhar, I., Singh, S.A., Patel, C.M., Anitha, K.L., 2021). At the same time, further studies addressing the methodological limitations described above are needed to establish the absolute sorption capacity, the full isotherm, and the precise sorption mechanism.

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submitted 16.08.2026;
accepted for publication 30.08.2026;
published 31.08.2026

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