ISSN 0027-1314, Moscow University Chemistry Bulletin, 2020, Vol. 75, No. 1, pp. 36–42. © Allerton Press, Inc., 2020.
Russian Text © The Author(s), 2020, published in Vestnik Moskovskogo Universiteta, Seriya 2: Khimiya, 2020, No. 1, pp. 43–51.

Iron-Containing Metalworking Wastes as a Chemosorbent for Wastewater Treatment from Molybdenum Ions

M. A. Chukaeva[a], *, V. G. Povarov[b], and I. P. Sverchkov[a]
[a]*Saint Petersburg Mining University, St. Petersburg, Russia*
[b]*Department of Analytical Studies of Collective Usage Center, Saint Petersburg Mining University, St. Petersburg, Russia*
**e-mail: chukaeva.mariia@gmail.com*

Received May 14, 2019; revised May 18, 2019; accepted June 14, 2019

Abstract—The extraction mechanism of molybdenum(VI) ions from model solutions with iron-containing metalworking wastes is studied. The experimental X-ray phase analysis and energy dispersive microanalysis data indicate that iron(III) molybdate appears in the first chemisorption stages with the subsequent formation of layers enriched in molybdenum(VI) oxide. The kinetics of the chemisorption of molybdenum(VI) ions from model solutions with iron-containing metalworking wastes is studied. We showed that the total exchange capacity of the modified steel chips having a specific surface of more than 15 cm^2/g relative to molybdenum(VI) ions is limited only by the corrosion rate of steel chips and is achieved after its complete dissolution. The effectiveness of the chemisorption process is found. We also showed that iron-containing metalworking waste may be used for the purification of wastewater from molybdenum(VI) ions to the standard values.

Keywords: chemisorption, molybdenum(VI) ions, metalworking waste, kinetics, wastewater treatment

DOI: 10.3103/S0027131420010058

The concentration of molybdenum in unpolluted fresh surface water is usually low. Indeed, it is about 0.5 $\mu g/dm^3$ in river water, whereas it is no more than 10.0 $\mu g/dm^3$ in marine and oceanic water [1–3].

Nevertheless, the problem of natural water pollution with molybdenum is important. The maximum permissible concentrations ($MPC_f = 1\ \mu g/dm^3$) for molybdenum are significantly high in water bodies located near the mining, mineral processing, petrochemical, and metallurgical industries. The concentration of molybdenum in the wastewater of copper smelters, nonferrous metal processing plants, mines, and enrichment plants is 40–50, 50–60, 100–8000, and 2500–4000 $\mu g/dm^3$, respectively.

The mining enterprises located in Kirovsk (Murmansk oblast), for example, have a significant anthropogenic impact on surface water. The main sources of pollution are discharges of mine and quarry water from mines, as well as wastewater from enrichment plants. MPC in wastewater is significantly high for a number of components (Mo, F, and Al); however, one of the main pollutants of natural waters is molybdenum found near the extraction and processing of apatite-nepheline ores in an amount $C_{Mo} = 80–200\ \mu g/dm^3$, which is significantly higher than that both for fishery ponds and the background values.

This deposit of apatite-nepheline ores is assigned to the Khibiny massif, in which there is a molybdenite (MoS_2) having no industrial importance. Natural geological conditions are violated and the redox conditions are changed during its development, which leads to the oxidation of molybdenite and leaching of molybdenum. Sodium water and pH values shifted to the alkaline region facilitate the transition of molybdenum from an insoluble form to a solution.

The main methods for the purification of wastewater from molybdenum ions are reverse osmosis, ultrafiltration, electrodialysis, sorption, and ion exchange [4–6].

The electrodialysis and purification processes with osmotic membranes have some disadvantages despite their high efficiency. Firstly, electrodialyzers and reverse osmosis plants have a high cost and require high-energy consumption. Secondly, they require thorough water treatment, so that they are inappropriate for the purification of large tonnage mine waters with a multicomponent composition.

Reagent purification methods of wastewater from molybdenum implies the conversion of molybdenum to an insoluble form and its subsequent removal from the solution. Their disadvantages include the low degree of extraction of molybdenum from dilute solutions, which does not allow reaching the MPC_f values for water to be purified. In addition, the significant

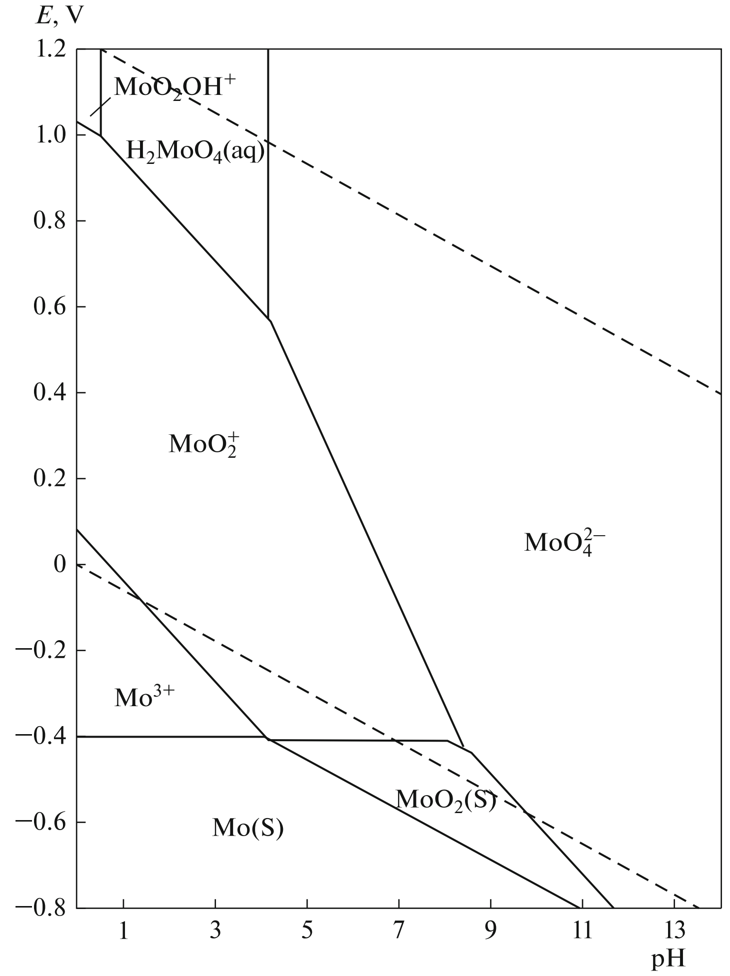

Fig. 1. Diagram of various molybdenum forms depending on *E* and pH.

consumption and high cost of the reagents together with the bulkiness of equipment make it impossible to use them to purify mine water from molybdenum to the standard values.

The published data showed that sorption and ion-exchange purification methods from molybdenum are currently most widely used, because they possess environmental and economic efficiency [7, 8]. Nevertheless, the current purification technological methods based on sorption and ion exchange require substantial refinement, because wastewater from mining enterprises has specific properties (multicomponent, multitonnage, and irregularity of inflow). Currently, the sorbents based on production waste are considered to be promising, because this leads not only to a solution of environmental problem but also to a significant decrease in the cost of the final product [9].

EXPERIMENTAL

The hydrochemistry of Mo depends on its forms in solutions at certain *E* and pH values; Fig. 1 shows the diagram of various molybdenum forms depending on *E* and pH. This diagram allows predicting the occurrence of molybdenum in general terms [10].

Molybdenum migrates in groundwater in a hexavalent form. Molybdenum exists as its acid compounds ($H_2Mo_4^0$, $HMoO_4^-$, and MoO_4^-) in oxygen-containing groundwater at pH > 2. Most part of molybdenum in natural waters is in a dissolved state, because its oxoanions ($HMoO_4^-$ and MoO_4^{2-}) have a weak affinity to the solid surface [2, 11].

The chemical properties of molybdenum (solubility of its oxides, molybdenum acid, and molybdenum compounds with sodium) determine its significant migration ability and accumulation in natural waters within large *E* and pH values in various chemical compositions of groundwater.

A study of the hydrochemistry of molybdenum showed that molybdenum is coadsorbed onto many hypergene neoplasms and especially with iron hydroxides [2, 11].

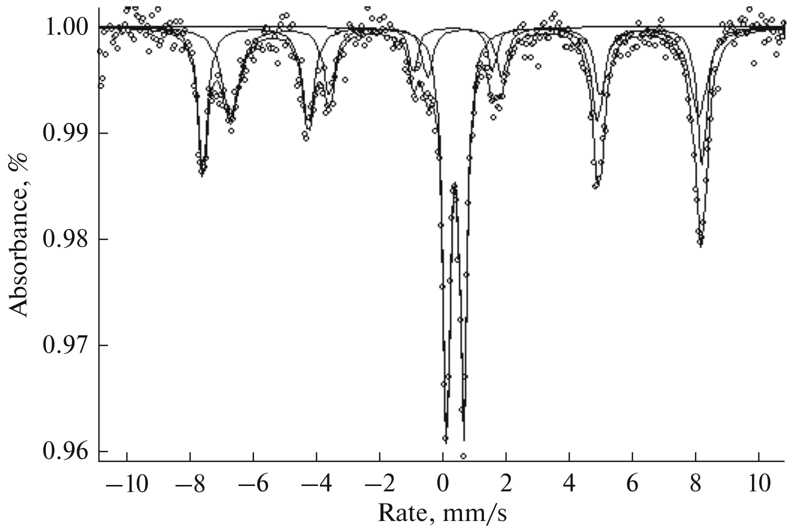

Fig. 2. Mössbauer absorption spectrum of corrosion products of St3sp1 steel chips obtained at pH = 5.

The wastes containing reactive iron are assigned to those from the chemical industry, metallurgical production, and metal processing waste. Metal wastes are considered to be promising as a sorbent, because they are cheap and available iron-containing material, which is obtained at most industrial enterprises.

The St3sp1 unalloyed steel chip sample was used in the laboratory studies. The chips were moistened with distilled water and then kept in air for 24 h to obtain oxidized iron forms with a developed specific surface area and increased reactivity.

The sorption ability of modified sorbent relative to molybdenum was assessed on model solutions under static conditions. Chemically pure ammonium molybdenum acid $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, which gives the molybdate ion MoO_4^{2-} during dissociation, was used to prepare model molybdenum solutions. The model solutions were prepared with a concentration of C_{Mo} = 100 μg/dm^3, corresponding to the average amount of molybdenum in the mine waters of the production facilities.

Steel chips were placed into a model solution in a mass ratio S : L = 1 : 250 while stirring on a KS 260 basic IKA orbital shaker (at a stirring rate of 300 rpm) for 20 h. The studies were performed at 18°C and a pH of 5.2. The concentration of molybdenum was found before and after purification on an AAS-7000 atomic absorption spectrometer with electrothermal atomization. As a result, we found that the efficiency of purification of model solutions from molybdenum on a metal waste sorbent is more than 99%.

RESULTS AND DISCUSSION

An St3sp1 unalloyed steel sample was used to identify the mechanism of purification of model solutions from molybdenum with iron-containing metalworking waste. Iron corrosion products have a different composition depending on the corrosion conditions. $Fe(OH)_3$, $Fe(OH)_2$, FeOOH, FeO, Fe_3O_4, and Fe_2O_3 appear frequently [12]. Iron corrosion products are evenly distributed over the entire metal surface, have a loose structure, and occupy a volume that is 2.5–3 times larger than that of corroded steel.

A steel chip sample (1 g) was placed in 250 cm^3 of deionized water with a pH of 3, 5, 7, and 9 while being stirred for 72 h to obtain corrosion products. The precipitate obtained was separated from the solution, dried, and analyzed on an MS1104Em Mössbauer spectrometer with a 57Co(Cr) source, which makes it possible to study nuclear gamma resonance spectra on iron ions. The composition of the corrosion products at different pH values is almost the same but their mass varies quite strongly, because the rate of the corrosion process is different. The Mössbauer spectroscopy data indicate (Fig. 2) that the doublet is assigned to iron(III) oxide, whereas the sextets are attributable to iron(II) and iron(III) oxides; and in addition, the Fe_2O_3 and Fe_3O_4 is 32.2 and 67.8%, respectively.

Pure iron(II) and chemically pure iron(III) oxides were used as reagents in the experiments to find the efficiency of the molybdenum purification of the model solutions with each of the corrosion products obtained. Samples of 1 g of FeO, Fe_2O_3, and Fe_3O_4 were placed in the model solutions with a molybdenum concentration of 1 mg/dm^3 and a volume of 250 cm^3 under stirring on a KS 260 basic IKA orbital shaker (the stirring rate is 300 rpm) for 20 h. The experiments were performed at 18°C and a pH of 5.2. Moreover, the model solutions were degassed with a water-jet vacuum pump and closed with a plug throughout the entire contact time to avoid the oxidation of FeO and

Table 1. Efficiency of molybdenum purification of model solutions with FeO, Fe_3O_4, and Fe_2O_3

Iron-containing reagent	FeO	Fe_3O_4	Fe_2O_3
Purification efficiency, %	34.8	41.3	99.9

Fe_3O_4 to Fe_2O_3. Then the solutions were sedimented for 30 min and centrifuged.

The concentration of molybdenum was found before and after purification on an AAS-7000 atomic absorption spectrometer. Table 1 shows the results of the analysis obtained after the calculation of the mean arithmetic purification efficiency from two parallel experiments. It indicates that the extraction of molybdenum ions proceeds in the presence of all iron oxides but a higher purification efficiency from molybdenum is achieved with iron(III) oxide.

The model molybdenum solution (C_{Mo} = 1000 mg/dm^3) was mixed with 1 g of a St3sp1 steel chip sample under stirring for 72 h to find the composition of the products after purification. The chips were preliminarily wetted with distilled water and then kept in air for 24 h for the oxidation processes to proceed.

The resulting precipitate was separated from the solution, dried, and analyzed on a Shimadzu XRD-6000 X-ray diffractometer.

The X-ray phase analysis showed that the product obtained after purification of the model solution from molybdenum is partially presented as an X-ray amorphous phase. The identification of a crystalline phase, however, indicates that it corresponds to the reference X-ray spectrum of $Fe_2(MoO_4)_3$ (no. 31-0642 of the PDF ICDD file standard) according to the interplanar distances and line intensities (Fig. 3).

The data obtained make it possible to assume that the mechanism of purification of model solutions from molybdenum on iron-containing metalworking waste is based on the chemisorption process, which proceeds with the formation of insoluble iron molybdates and their subsequent sorption on the developed corroded steel chip surface.

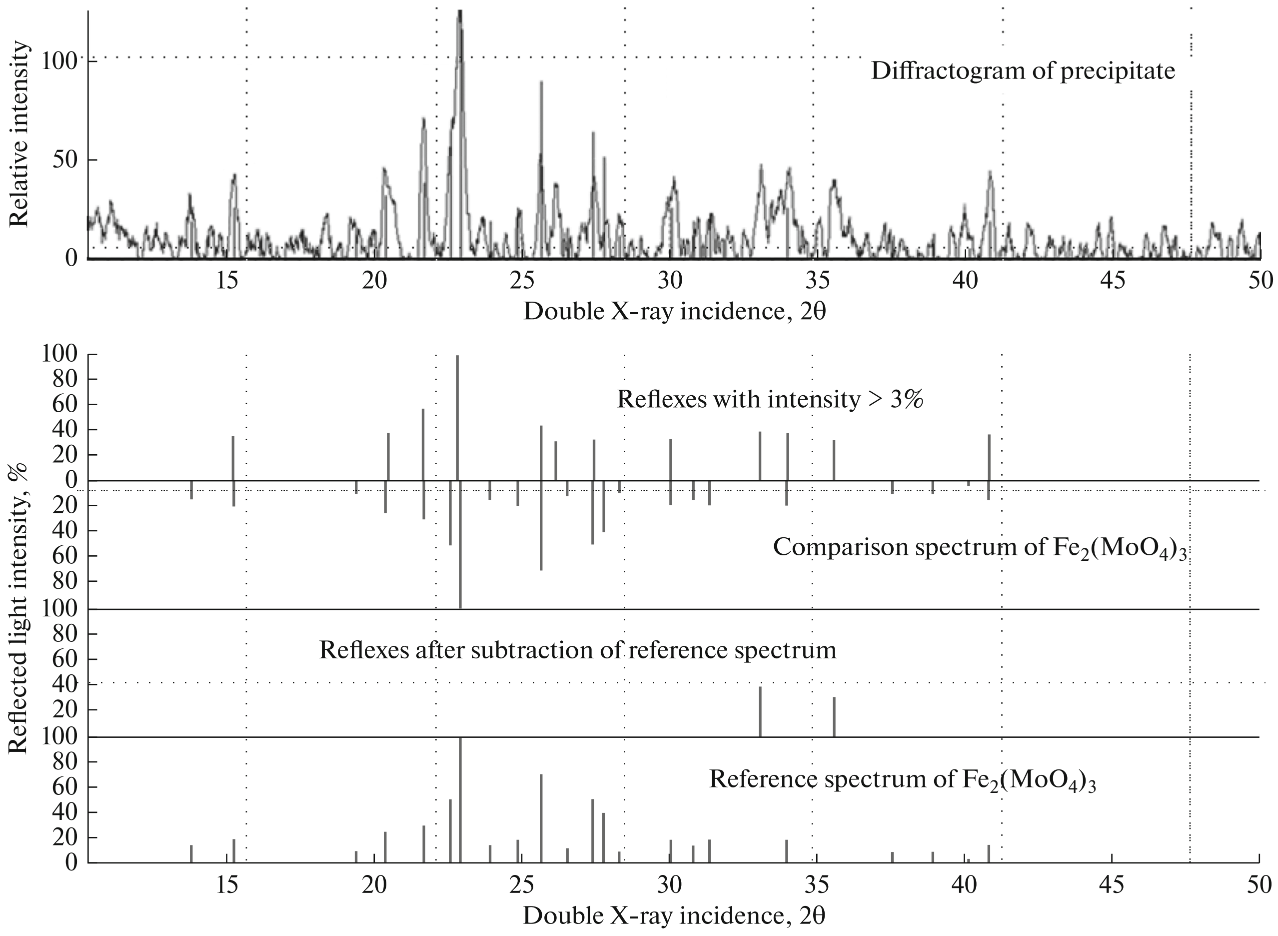

Fig. 3. Diffractogram of product obtained after purification of model solution from molybdenum and the library reference spectrum of $Fe_2(MoO_4)_3$.

The gross analysis of the products obtained after the interaction between the molybdenum-containing solution and the corrosion products of steel chips, however, does not allow the identification of the structural features of the precipitate formed. As a result, electron microscopy was used to confirm the hypothesis and to describe the structure of the compounds formed. For this purpose, an St3sp1 unalloyed steel plate, previously treated with distilled water in air, was placed in the model solution with a molybdenum concentration of 1000 mg/dm^3. The solution was stirred by shaking to intensify the formation of iron and molybdenum compounds on the surface of the plate. The experiment was performed for 7 days, and the plate was removed from the solution and dried in air. Visual inspection of the product showed that the upper layer of the sediment was presented as a loose ocher X-ray amorphous phase, whereas the layer adjacent to the metal had a denser structure and darker color. Both layers were studied with scanning electron microscopy and energy dispersive analysis on a Tescan Vega TS electron microscope equipped with an Oxford Instruments INCAx-ACT energy dispersive microanalysis system (Fig. 4): region A corresponds to the lower sediment layer, whereas region B is assigned to the upper one.

We found that the mass ratio of Mo and Fe in the upper layer is 6.5 : 1.0, whereas it is 1.5 : 1.0 in the lower layer, which corresponds to iron(III) molybdate. The data indicate that iron(III) molybdate is formed only in the immediate vicinity of the surface of the steel plate, whereas the upper layers are enriched in molybdenum and contain iron only as a minor impurity.

The chemisorption isotherms were constructed to study the kinetics of the purification process of model solutions from molybdenum. St3sp1 steel chip samples with various specific surface areas (30, 25, 15, and 8 cm^2/g) were used in the chemisorption. The specific surface area of the steel chip samples prior to the corrosion processes was found with a BET method on a Quantachrome NOVA 1000e high-speed specific surface and pore size analyzer.

Model solutions with the molybdenum concentration ranging from 0.1 to 1000 mg/dm^3 were prepared to construct chemisorption isotherms. The steel chip samples with various specific surface area values (30, 25, 15, and 8 cm^2/g) with a weight of 0.4 g were added to the model solutions (V = 100 cm^3) under stirring on a KS 260 basic IKA orbital shaker at a stirring rate of 300 rpm for the equilibrium contact time to ensure the ratio S : L = 1 : 250.

The static exchange capacity (SEC) of the chemisorbent was calculated according to the standard method developed at the Scientific Research Institute of Mineral Raw Materials (STO RosGeo 08-002-98. Technological methods for studying mineral raw materials" [13]). The following balance equation can be used if a single injection of a sorbent g (g) and a certain amount of the treated water are known:

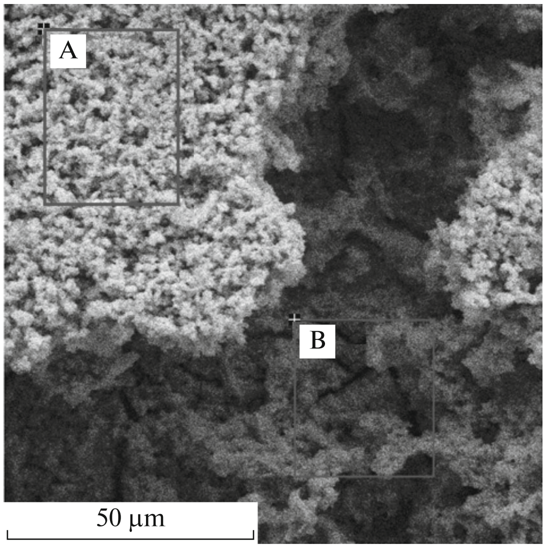

Fig. 4. Electron microscopic image of the product obtained after interaction between iron and molybdenum-containing solution.

$$\mathrm{SEC}\, g + V C_{\mathrm{eq}} = V C_{\mathrm{init}}, \qquad (1)$$

where SEC is the static exchange capacity (mg/g), g is the mass of a dry sorbent (g), V is the volume of the solution added to a sorbent (dm^3), C_{init} is the concentration of the extracted component in the initial solution (mg/dm^3), and C_{eq} is the residual (equilibrium) concentration of the extracted component after interaction with the sorbent for equilibrium time (mg/dm^3).

The SEC under the given operation conditions of the experiment was found from the following balance equation:

$$\left[\mathrm{SEC} = (C_{\mathrm{init}} - C_{\mathrm{eq}})V\right]/g. \qquad (2)$$

The chemisorption isotherms were constructed from the data obtained (Fig. 5).

Figure 5 indicates that the chemisorption is much higher for chips with a larger specific surface area than those with a lower specific surface area at the same equilibrium concentration. In addition, the isotherm curves of molybdenum chemisorption from a solution on steel chips with various specific surface areas are different. When the specific surface area is 25 and 30 cm^2/g, the SEC increases sharply with an increase in the concentration of molybdenum in the initial solution. There is only a slight increase in the SEC for steel chips with a specific surface area of 15 cm^2/g with an increase in the concentration of molybdenum in the initial solution (SEC = 18 mg/g). When the specific surface area is lower (8 cm^2/g), the SEC takes the form of a saturation curve with the maximum value (SEC = 8.8 mg/g). This is due to the fact that a thin layer of

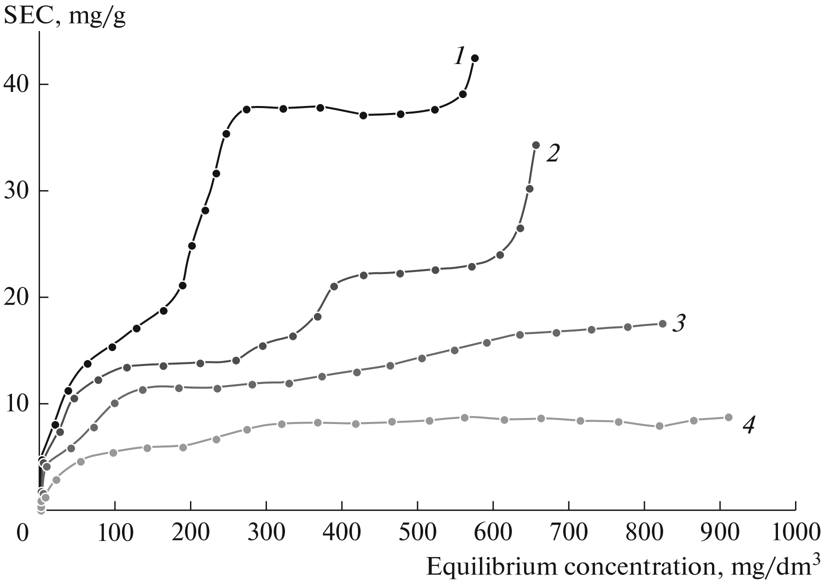

Fig. 5. Isotherms of chemisorption process of molybdenum from model solutions on steel chips (T = 18°C) at a specific surface area: (*1*) 30, (*2*) 25, (*3*) 15, and (*4*) 8 cm^2/g.

iron molybdates is formed on the surface of steel chips with a small specific area at high concentrations of molybdenum in the initial solution, and the passivation proceeds, which prevents the formation of new oxidized iron forms and, as a consequence, the further purification process. In the case of preliminarily treated chips, the surface is initially more developed and the passivation process is slower, so that the SEC is higher. When the specific surface area of the chips is larger the corrosion process is faster than the formation of iron molybdates.

The studies showed that the rate of chemisorption of molybdenum on steel chips from solutions depends on the intensity of the formation of iron oxides to form insoluble molybdenum compounds. The total exchange capacity of the modified steel chips with a specific surface of more than 15 cm^2/g is therefore limited only by its corrosion rate and can theoretically be achieved after its complete dissolution.

In addition, the desorption of molybdenum from chemisorption products was studied. For this purpose, the treated steel chips together with the precipitate obtained after the purification of the model solution from molybdenum were placed into an ultrasonic bath for 120 min at 45°C and 1 dm^3 of deionized water. The resulting solution was removed from the ultrasonic bath and centrifuged; then the concentration of molybdenum was measured on an AAS-7000 atomic absorption spectrometer with electrothermal atomization, which appeared to be lower than the detection limit (less than 0.1 μg/dm^3). These results indicate that there is no desorption of molybdenum from the chemisorption products.

As noted above, the precipitate obtained during the purification process is presented as a mixture of insoluble iron molybdates, oxides, and hydroxides, which can be considered as a commercial intermediate for the production of ferromolybdenum according to the known technologies [14–16]. Such use of the spent chemisorbent is environmentally effective, cost-effective, and allows us to get a valuable industrial product from production waste.

CONCLUSIONS

(1) We found that the mechanism of purification of model solutions from molybdenum with iron-containing metalworking waste implies the formation of iron(III) molybdate as a surface layer with strong adhesion to the steel surface in the first stages and the formation of amorphous layers enriched in molybdenum oxide on the surface of this molybdate(VI) in the following chemisorption stages.

(2) The study of chemisorption kinetics showed that the SEC of steel chips relative to molybdenum is limited by the passivation process of iron, which proceeds, when iron molybdates are formed on the surface of steel chips with a specific surface of less than 15 cm^2/g. In addition, the total exchange capacity of the modified steel chips with a specific surface of more than 15 cm^2/g is limited only by the corrosion rate and can theoretically be achieved after its complete dissolution.

(3) The precipitate formed during the purification process, existing as insoluble iron molybdates, oxides, and hydroxides, can be used as a raw material to produce ferromolybdenum.

(4) The laboratory studies indicate that chemisorbent based on iron-containing metalworking waste may be used for the purification of wastewater from molybdenum(VI) ions to the standard values, which will allows us to solve the problem in an environmentally efficient and economical way.

FUNDING

This work was performed within the state contract (no. 5.12850.2018/8.9) "Assessment and reduction of impact of technological environmental disasters at the production facilities of the mineral resource complex."

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

REFERENCES

1. Barceloux, D.G., *Clin. Toxicol.*, 1999, vol. 37, no. 2, p. 231.
2. Linnik, P.N. and Ignatenko, I.I., *Gidrobiol. Zh.*, 2015, vol. 51, no. 2, p. 89.
3. Medley, P.L., Cooper, D.M., Ander, E.L., et al., *Appl. Geochem.*, 2014, vol. 40, p. 144.
4. Tryakina, A.S., *Zap. Gorn. Inst.*, 2017, vol. 227, p. 608.
5. Voronov, Yu.V. and Yakovlev, S.V., *Vodootvedenie i ochistka stochnykh vod* (Sewage and Wastewater Treatment), Moscow: Mosk. Gos. Stroit. Univ., 2006.
6. Proskuryakov, V.A. and Shmidt, L.I., *Ochistka stochnykh vod v khimicheskoi promyshlennosti* (Wastewater Treatment in Chemical Industry), Leningrad: Khimiya, 1977.
7. Kaplan, G.E., in *Ionoobmennye sorbenty v promyshlennosti* (Ion Exchange Adsorbents in Industry), Moscow: Akad. Nauk SSSR, 1963, p. 183.
8. Voropanova, L.A., RF Patent 2229530, 2004.
9. Matveeva, V., Lytaeva, T., and Danilov, A., *J. Ecol. Eng.*, 2018, vol. 19, p. 97.
10. Takeno, N., *Atlas of Eh-pH Diagrams: Intercomparison of Thermodynamic Databases*, Tokyo: Natl. Inst. Adv. Ind. Sci. Technol., Res. Center Deep Geol. Environ., 2005.
11. Krainov, S.R., Ryzhenko, B.N., and Shvets, V.M., *Geokhimiya podzemnykh vod. Teoreticheskie, prikladnye i ekologicheskie aspekty* (Groundwater Geochemistry: Theoretical, Applied, and Environmental Aspects), Moscow: TsentrLitNefteGaz, 2004.
12. Semenova, I.V., Florianovich, G.M., and Khoroshilov, A.V., *Korroziya i zashchita ot korrozii* (Corrosion and Corrosion Protection), Moscow: Fizmatlit, 2002.
13. *STO* (Industry Standard) *RosGeo 08-002-98: Solid Noncombustible Minerals. Technological Methods for the Study of Mineral Raw Materials. Hydrometallurgical Methods for Assessing Mineral Raw Materials. Ion Exchange Processes.*
14. Gedevanishvili, Sh.V., Gorshkov, V.A., Oniashvili, G.Sh., et al., USSR Patent 1605560, 1989.
15. Serebrovskii, V.I., Serebrovskaya, L.N., Serebrovskii, V.V., et al., RF Patent 2174163, 2001.
16. Gasparyan, Yu.B., Chunin, S.N., and Gaspatyan, A.Yu., RF Patent Application no. 2008151017, 2010.

Translated by A. Tulyabaev