EXTRACTION OF Cu$^{2+}$, Zn$^{2+}$ AND Ni$^{2+}$ CATIONS FROM INDUSTRIAL WASTEWATER BY IONITE KU-2-8

Ob`єктом дослідження є модельні розчини стічних вод та промивних вод металооброблювальних підприємств, що містять іони міді, нікелю та цинку. Одним з найбільш проблемних місць є те, що недостатньо вивчені процеси сорбції катіонів міді, нікелю та цинку на сильнокислотному катіоніті КУ-2-8 при високих концентраціях металів.

В роботі було вивчено процеси сорбції та десорбції іонів Cu$^{2+}$, Zn$^{2+}$ та Ni$^{2+}$ на катіоніті КУ-2-8 в H$^+$-формі, використовуючи модельні розчини сульфат металів за високих концентрацій. Досліди проводили в іонообмінній колонці діаметром 2 см$^2$ із завантаженим катіонітом об`ємом 20 см$^3$. У процесі проведення досліджень вимірювали концентрацію металів титромерними, фотометричними і інструментальними методами (концентрація іонів міді, цинку і нікелю, кислотність, лужність, рН). Модельні розчини іонів важких металів Cu$^{2+}$, Zn$^{2+}$ і Ni$^{2+}$ концентрацією 10, 20 та 50 мг-екв/дм$^3$ пропускали через іоніт КУ-2-8 у H$^+$-формі. Ємність іоніту при сорбції 0,01 н модельних розчинів у середньому досягала 2073 мг-екв/дм$^3$, при 0,02 н – 2140 мг-екв/дм$^3$ і при 0,05 н – 2100 мг-екв/дм$^3$. У роботі після вилучення металів з модельних розчинів та повного насичення іоніту було вивчено умови регенерації катіоніту в Cu$^{2+}$, Zn$^{2+}$ та Ni$^{2+}$-формі розчинами 5, 8 та 10 % сірчаної кислоти. Ефективність десорбції іонів двохвалентних металів з іоніту складала майже 100 %.

Наукова новизна роботи полягає в тому, що було проведено сорбцію іонів металів при концентраціях 10, 20 та 50 мг-екв/дм$^3$ в перерахунку на метал та їх десорбцію 5, 8 та 10 % сірчаною кислотою з катіоніту.

Після проведення досліджень було запропоновано схему очищення промивних вод за допомогою іонного обміну та електролізу, що дасть змогу на підприємствах гальванічних виробництв організувати екологічно-безпечні процеси обробки металів.

Ключові слова: важкі метали, іонний обмін, сорбція іонів металів, стічна вода, гальванічне виробництво.

Copyright © 2019, Koliehova A., Trokhymenko H., Magas N.
This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0)
2. The object of research and its technological audit

The object of research is model solutions of metal ions – Cu\(^{2+}\), Zn\(^{2+}\) and Ni\(^{2+}\). For sorption of these metals, KU-2-8 cation exchanger was used in H\(^+\) form with a volume of 20 cm\(^3\). Ionite is placed in an ion-exchange column (Fig. 1), where sorption and desorption of heavy metal ions are performed.

Regeneration is carried out with sulfuric acid at a concentration of about 1000, 1600 and 2000 meq/dm\(^3\).

This cation exchanger is highly selective for doubly charged metal cations, which allows the purification of washings and their regeneration, as well as the creation of complex low-waste technologies for wastewater treatment from metal cations.

There are many methods for extracting heavy metals from wastewater, but they all have both disadvantages and advantages [6–8].

Fig. 2 presents the traditional scheme of treatment of wastewater in Ukraine [9].

The main disadvantage of such a galvanic draining treatment scheme is the use of expensive reagents and a large amount of sludge is formed that must be disposed of, which also requires energy. The untreated wastewater discharges into the environment and has a negative effect on both living organisms and humans.

Therefore, the main task is improvement of the purification schemes of wash water containing heavy metal ions to create low-waste production at galvanic plants.

3. The aim and objectives of research

The aim of research is studying the processes of sorption and desorption of heavy metal cations – Cu\(^{2+}\), Zn\(^{2+}\) and Ni\(^{2+}\) from highly mineralized wastewater using ion exchange under dynamic conditions.

To achieve this aim, the following objectives are set:

1. To investigate the efficiency of sorption of copper, zinc and nickel ions on KU-2-8 cation exchanger in the H\(^+\) form by the ion-exchange method with highly mineralized wastewater and wash water.
2. To study the processes of cation exchange regeneration from ions of copper, zinc and nickel with the help of sulfuric acid.
3. To determine the efficiency of ion exchange for highly saline wastewater containing heavy metal ions.

4. Research of existing solutions of the problem

The most promising methods for the extraction of heavy metal ions from wastewater of various origins are ion exchange [10] and electrolysis, which make it possible to organize closed (drainless) water use cycles and ensure the creation of low-waste processes for processing waste regeneration solutions [11].

The efficiency of extraction of heavy metal cations by various methods from wastewater from electroplating plants decreases at low concentrations of these ions. Therefore, the use of ion exchange methods is more promising for ion concentration [12] for the further reduction of metals by electrochemical methods.

Organic and inorganic (mineral) ion exchangers are most often used for ion exchange [13]. The most practical value for the desalination of wastewater was found to be artificial organic ion exchangers with a large sorption surface. KU-2-8 cation exchanger is one of such ion exchangers; it has a large exchange capacity, mechanical and chemical resistance to media [14]. KU-2-8 brand ionite is widely used for desalination of water in various ranges of cation concentrations, including the extraction of heavy metals [15, 16]. In these works, the high absorption capacity of this cation exchanger to divalent cations is shown. This is due to the presence of one type of fixed ions – the sulfo group. At the same time, working both in salt and acid forms, cation exchanger is easily regenerated by both acids and salt solutions, and it allows creating a wide range of complex technologies for the purification of waters contaminated with ions of heavy metals.

In [17], the sorption of copper ions on KU-2-8 cation exchanger is studied under static and dynamic conditions at a concentration of 1 to 30 mg/dm\(^3\). The research results show that under dynamic conditions, sorption occurs more efficiently than under static conditions, while the capacity of the ion exchanger increases.

In [18], a series of experiments are carried out to study the kinetics of sorption of copper, zinc, and cadmium on synthesized cation exchangers of the KU-2-8 grade. These works show its high selectivity to the ions of these metals.
The authors of [19] develop a method for purifying acidic wash water from pickling shops from metal ions Cu, Zn, Ni, and Cr at concentrations in the range from 3 to 250 mg/ml. The components contained in the wastewater are concentrated on selective sorbents and then separated by chromatographic methods.

The ion exchange capacity of ion exchangers decreases with an increase in the rate of passage of the solution in the ion exchange column, as well as with a decrease in the concentration of heavy metal ions, which is explained by the formation of stable aquocomplexes [20].

Thus, the results of literature analysis allow to conclude that KU-2-8 cation exchanger can be used for wastewater treatment of metal processing enterprises in various concentration ranges. Ionite is also easily regenerated by acids and can be used repeatedly.

5. Methods of research

A cation exchanger with a volume of 20 cm$^3$ was placed in an ion-exchange column (Fig. 1) with a diameter of 2 cm. The flow rate of the model solution during sorption was 10–15 cm$^3$/min, and the flow rate of the solution during desorption of metal ions was 2–5 cm$^3$/min.

As model solutions, copper sulfate, zinc sulfate and nickel sulfate dissolved in distilled water were used. Sorption and regeneration were carried out one at a time in a model solution on cation exchanger at concentrations: Cu$^{2+}$ – 10, 20, 50 meq/dm$^3$; Zn$^{2+}$ – 10, 20, 50 meq/dm$^3$ and Ni$^{2+}$ – 10, 20, 50 meq/dm$^3$. During sorption, samples with a volume of 100–500 cm$^3$ were taken and analyzed for copper content by spectrophotometry [21], zinc and nickel by trilonometry taking into account copper concentration [21]. Acidity and pH were also monitored in the samples.

The KU-2-8 cation exchanger was regenerated with 5, 8, and 10 % sulfuric acid in the ion-exchange column (Fig. 1). The volume of samples taken was 20–50 cm$^3$. The samples also controlled the concentration of cations, acidity, alkalinity and pH.

6. Research results

The results of sorption of copper, zinc and nickel ions on the cation exchanger under dynamic conditions are presented in Fig. 3–5.

As studies have shown (Fig. 3), the total exchange dynamic capacity (TEDC) of the ion exchanger reaches an average of 2073 meq/dm$^3$ when passing 0.01 n model solutions. 2.5–3 dm$^3$ of model solutions were passed to the breakthrough of heavy metal ions in the analyzed solution, and 5–5.5 dm$^3$ had to be skipped before the ion exchanger was completely saturated, as can be seen from the graphs in Fig. 3.

When passing model solutions with a concentration of 0.02 n, the total exchange dynamic capacity of the ion exchanger reached an average of 2140 meq/dm$^3$. The volume...
of missed model solutions before the breakthrough of heavy metals was approximately 1.5 dm³. For complete saturation of the cation exchanger, it was necessary to skip about 3.25 dm³ of heavy metal solutions (Fig. 4).

When transmitting 0.05 n model solutions, the exchange capacity of cation exchanger was an average of 2100 meq/dm³. The complete saturation of the cation exchanger occurred when 1.2 dm³ of the solution was passed through; 0.6 dm³ of the solution was passed into the metal breakthrough, as can be seen from Fig. 5.

From the presented graphs (Fig. 3–5) it is seen that the pH of the samples increased with decreasing acidity, while the KU-2-8 ion exchanger was saturated with Cu²⁺, Zn²⁺ and Ni²⁺ cations. In general, the sorption of metal ions occurred quite efficiently, as expected.

In order to evaluate the effectiveness of ion-exchange water purification from heavy metals, it is necessary to take into account not only the sorption capacity, but also the degree of regeneration of cation exchanger. Therefore, after studying the sorption of heavy metals on cation exchanger, sulfuric acid was regenerated.

The results of ion exchanger regeneration in Cu²⁺, Zn²⁺ and Ni²⁺ forms are shown in Fig. 6–8.

During the desorption of metal ions with 5 % sulfuric acid (Fig. 6), the concentration of Cu²⁺, Zn²⁺ and Ni²⁺ cations in the first sample averaged 583 meq/dm³, and in the last sample reached 0 meq/dm³. In this case, the acidity increased on average from 298.3 meq/dm³ to 998.3 meq/dm³, and the pH of the solutions decreased.

The regeneration of KU-2-8 ion exchanger under dynamic conditions of 8 % H₂SO₄ is shown in Fig. 7.

The graphs show that the efficiency of metal desorption reaches 100 %. The concentration of metals in the first sample was, on average, 808 meq/dm³; in the last sample, on average, 0 meq/dm³. Acidity also increased, and the pH of the solutions decreased.

The desorption of heavy metal ions by 10 % acid shows greater efficiency than the regeneration of 5 or 8 % sulfuric acid, as can be seen from the graphs in Fig. 8. The concentration of cations in the first samples averaged 836.4 meq/dm³, and in the last – 0 meq/dm³, while the acidity increased with each breakdown.

The experiments show a rather effective regeneration of the ion exchanger with 5, 8 and 10 % sulfuric acid. At 10 % H₂SO₄, the desorption of metal ions was more effective than with 5 and 8 % acid regeneration.

After obtaining regeneration solutions of metal mixtures, it is advisable to carry out their electrolysis, which is the next step in the treatment of wastewater contaminated with heavy metals [5].

After carrying out the studies, a flow chart was proposed for purifying wash water from heavy metal ions, including copper, zinc and nickel (Fig. 9).
Waste rinse water containing metal cations enters the cation exchanger, where ion-exchange on the KU-2-8 ion exchanger takes place. After that, regeneration solutions containing a high concentration of metal and sulfuric acid enter the electrolyzer, where the electrochemical separation of metal and acid takes place. The pure acid from the electrolyzer returns again to the regeneration of cation exchangers. Thus, it is possible to organize waste-free processes for the extraction of metals from the washing water of galvanic plants, which are environmentally friendly and economically viable.

7. SWOT analysis of research results

Strengths. KU-2-8 brand ionite in acid form is highly selective for divalent metal cations (Cu²⁺, Zn²⁺, Ni²⁺) and the degree of desorption by ion exchangers reached almost 100% on average. Therefore, its use for the concentration of metals in the treatment of washing wastewater is quite effective.

Weaknesses. It is known that in the washing, regeneration and waste waters of metalworking industries are mixtures of heavy metal ions. Therefore, for an objective study and creation of integrated technologies for the purification of these waters, it is necessary to conduct experiments with a mixture of heavy metals.

Opportunities. After the desorption of metals on the formation of KU-2-8 ion exchanger, the formation of regeneration solutions is advisable to be processed by the electrochemical method in a single-chamber electrolyzer, which allows returning valuable components to production.

Threats. Sorption methods for concentration of heavy metal ions on cation exchanger take a lot of time, and the rate of sorption of ions is proportionally dependent on the transmission rate of wastewater.

8. Conclusions

1. Sorption of heavy metal ions (copper, zinc, nickel) on the strongly acidic cation exchanger KU-2-8 in the H⁺ form is carried out. It is determined that the sorption of metals on the cation exchanger occurs efficiently and the selectivity of this cation exchanger is almost the same for these metals. Also, the exchange capacity of ion exchanger varied from metal concentrations in model solutions.

2. The results of the regeneration of a mixture of metals on the KU-2-8 ion exchanger in the Cu²⁺, Zn²⁺ and Ni²⁺ forms at 5, 8 and 10% sulfuric acid showed that regeneration occurs almost 100%.

3. It has been established that after sorption and desorption of heavy metals on cation exchanger it is advisable to conduct electrolysis of these metals.

A flowchart of the treatment of washing water from galvanic plants using ion exchange and electrolysis is proposed, which will allow the creation of closed systems for the treatment of wastewater contaminated with heavy metal ions.

References

1. Danylyan, O. H., Taranenko, V. M. (2003). Osnovy filosofii. Kharkiv: Pravo, 332.
2. Earth Overshoot Day 2019 is July 29th, the earliest ever (2019). Global Footprint Network. Available at: https://www.footprintnetwork.org/2019/06/26/press-release-june-2019-earth-overshoot-day/.
3. Khilchevskyi, V. K., Obodovskyi, O. H., Hrebin, V. V. et al. (2008). Zakutse hukrolohiia. Kyiv: Vydavnychopolitikrahichni tsentr «Kyivskyi universytes», 399.
4. Carstea, E. M., Bridgeman, J., Baker, A., Reynolds, D. M. (2016). Fluorescence spectroscopy for wastewater monitoring: A review. Water Research, 95, 205–219. doi: http://doi.org/10.1016/j.watres.2016.03.021
5. Koliehova, A. S., Trokhymenko, H. H., Homelia, M. D. (2018). Vyvchenia ionoobminnykh protsesiv ylyuchenii ioniv midi ta tsynku na kationiti KU-2-8 ta elektrokhimichne rozdilennia reheratsiinykh rozhchyniv u systemi Cu-Zn. Vcheni zapysky Tarasivoho nacionalnoho universytetu imeni V. I. Vernadskoho. Seriya: Tekhnichni nauky, 29 (68 (1 (2))), 142–147.
6. Carolin, C. F., Kumar, P. S., Saravanan, A., Joshiba, G. J., Naushad, M. (2017). Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. Journal of Environmental Chemical Engineering, 5 (3), 2782–2799. doi: http://doi.org/10.1016/j.jece.2017.05.029
7. Gunatilake, S. K. (2015). Methods of Removing Heavy Metals from Industrial Wastewater. Journal of Multidisciplinary Engineering Science Studies, 1 (1), 12–18.
8. Azimi, A., Arazi, A., Rezaakazemi, M., Assampour, M. (2017). Removal of Heavy Metals from Industrial Wastewaters: A Review. ChemBioEng Reviews, 4 (1), 37–59. doi: http://doi.org/10.1002/cben.201600010
9. Pliatsuk, L. D., Melnyk, O. S. (2008) Analiz tekhnolohii ochystky halvamchynkh stokiv v Ukraini. Vnyrk Samaivoho derzhavnoho universytetu. Seriya Tekhnichni nauky, 2, 116–121.
10. Calmon, C.; Calmon, C., Gold, H., Prober, R. (Eds.) (1979). Ion exchange pollution control (Vol. 2). CRC Press, Pub. locationBoca Raton. doi: http://doi.org/10.1201/9781351073868
11. Chaplin, B. P. (2019). The Prospect of Electrochemical Technologies Advancing Worldwide Water Treatment. Accounts of Chemical Research, 52 (3), 596–604. doi: http://doi.org/10.1021/acs.accounts.8b00611
12. Nachod, F. C., Schubert, J. (1956). Ion Exchange Technology. Imprint Academic Press. doi: http://doi.org/10.1016/c2013-0-12449-x
13. Bolshina, S. B., Hurets, H. M., Balabukha, D. S., Miliaeva, D. V. (2014). Ochyschennia stichnykh vod halvanichnykh vyrobnytstv sorbtsiinymi metodamy. Ekologichna bezpeka, 1, 114–118.
14. Minaieva, V. O. (2013). Ionnyi obmin ta ionsoolimina khromotokrafia. Cherkasy: ChNU imeni Bohdana Khmelnytskoho, 128.
15. Gomelya, N., Ivanova, V., Trus, I. (2017). Efficiency of extraction heavy metal ions from diluted solutions by ion-exchange methods. Technical sciences and technologies, 4 (10), 154–162. doi: http://doi.org/10.25140/2411-5363-2017-4(10)-154-162
16. Verbych, S., Hilal, N., Sorokin, G., Leaper, M. (2005). Ion Exchange Extraction of Heavy Metal Ions from Wastewater. Separation Science and Technology, 39 (9), 2031–2040. doi: http://doi.org/10.1081/ss-120039317
17. Homelia, M. D., Ivanova, V. P., Kamaev, V. S., Marushchak, Yu. A. (2017). Kontsentruvannia kationiv vazhkykh metaliv na prykladi ioniv mith pri zastosuvanni kationitu KU-2-8. Ixetkhozvolhnoy i enverbozvezhenia, 4, 70–75.
18. Bohylev, A. E., Ikamina, E. V., Markov, V. F., Maskeva, L. N. (2015). Kompozicionnye sorbenty na osnove kationita KU-2-8 s nanostrukturizovannoi gilroksoiidi ili sulfidnoi aktivnoi komponentnoi. Kondensirovanye sredy i mezhfaznye granicy, 15 (3), 238–246.
19. Sokolova, L. P., Skornyakov, V. V., Kargman, V. B., Saldadse, K. M. (1986). Selective separation of components [copper, nickel, zinc, chromium(VI)] in the process of ion-exchange purification of waste waters. Journal of Chromatography A, 364, 135–142. doi: http://doi.org/10.1016/s0021-9673(00)96203-4
20. Galinova, A. R., Tunakova, Iu. A., Kulakov, A. A. (2013). Issledovanie sorbeionnykh xarakteristik polimernykh ionitov, ispolzuyemykh v vodopodgotovke. Vestnik Kazanskogo tekhnologicheskogo universiteta, 16 (10), 141–145.
21. Lure, Iu. Iu. (1989). Spravochnik po analiticheskoi khimii. Moscow: Khimiia, 448.

Koliehova Anastasiia, Postgraduate Student, Department of Ecology and Environmental Technology, Admiral Makarov National University of Shipbuilding in Mykolayiv, Ukraine, ORCID: http://orcid.org/0000-0002-5119-6942, e-mail: nastya.sukhareva92@gmail.com

Trekhymenko Ganna, Doctor of Technical Sciences, Professor, Head of Department of Ecology and Environmental Technology, Admiral Makarov National University of Shipbuilding in Mykolayiv, Ukraine, ORCID: http://orcid.org/0000-0002-0835-3551, e-mail: antr@ukr.net

Magas Nataliya, PhD, Department of Ecology and Environmental Technology, Admiral Makarov National University of Shipbuilding in Mykolayiv, Ukraine, ORCID: http://orcid.org/0000-0002-2579-1465, e-mail: nataly.magas@gmail.com