

35. Environmental and economic assessment methods for waste management decision-support: possibilities and limitations / Finnveden G. et al. // Waste Management & Research. 2007. Vol. 25, No. 3. P. 263–269. doi:10.1177/0734242x07079156
36. Huang G. H., Anderson W. P., Baetz B. W. Environmental Input-Output Analysis and its Application to Regional Solid-waste Management Planning // Journal of Environmental Management. 1994. Vol. 42, No. 1. P. 63–79. doi:10.1006/jema.1994.1061
37. Gurevich I. M., Zelichenko A. Ya., Kulik Yu. G. Tekhnologiya sudostroyeniya i sudoremonta: handbook. Moscow: Transport, 1976. 416 p.
38. Pupan L. I., Kononenko V. I. Perspektivnyye tekhnologii polucheniya i obrabotki materialov: handbook. Kharkiv: NTU «KhPI», 2008. 261 p.
39. Perov V. N. Tekhnologiya utilizatsii sudov: handbook. Nikolayev: UGMTU, 2002. 24 p.
40. Metallicheskie materialy // Flot.com. URL: <https://flot.com/publications/books/shelf/chainikov/25.htm?print=Y> (Last accessed: 11.04.2018).
41. Morozov D. Eksportnaya poshlina na lom spasla ukrainskuyu metallurgiyu v proshlom godu (Part 2). URL: <http://uaprom.info/article/6212-denis-morozov-eksportnaya-poshlina-lom-spasla-ukrainskuyu-metallurgiyu-proshlom-godu-chast.html> (Last accessed: 11.04.2018).
42. PAO «Artemovskiy zavod po obrabotke tsvetnykh metallov». URL: <https://pao-artemovskij-zavod-po-obrabotke-tsvetnyh.uaprom.net> (Last accessed: 13.04.2018).
43. Proizvodstvo tsvetnykh metallov v Ukraine // Biznes-katalog. URL: <https://www.ua-region.info/kved/Ind.27.4> (Last accessed: 14.04.2018).
44. Metallurgicheskoye proizvodstvo // Biznes-katalog. URL: <https://www.ua-region.info/kved/Ind.27> (Last accessed: 14.04.2018).

Pizintsali Ludmila, PhD, Associate Professor, Department of Ships' Repair, Odessa National Maritime University, Ukraine, e-mail: lpizintsali@gmail.com, ORCID: <https://orcid.org/0000-0002-8046-0917>

Alexandrovska Nadiya, PhD, Associate Professor, Department of Ships' Repair, Odessa National Maritime University, Ukraine, e-mail: a.nadegda@gmail.com, ORCID: <https://orcid.org/0000-0001-6591-2068>

UDC 628.1.034.2

DOI: 10.15587/2312-8372.2018.129633

**Gomelya N.,
Trohymenko G.,
Shabliy T.,
Hlushko O.**

EFFICIENCY ESTIMATION OF CATION-EXCHANGE RECOVERY OF HEAVY METALS FROM SOLUTIONS CONTAINING THEIR MIXTURES

Об'єктом дослідження є промивні стічні води гальванічних виробництв, що містять катіони важких металів. Найбільш поширені реагентні методи очистки гальванічних стоків не забезпечують необхідний ступінь очищення води, супроводжуються втратою цінних компонентів і утворенням значних об'ємів токсичних шламів. Іонний обмін є перспективним в створенні технологій очистки стічних вод гальванічних виробництв.

Одною з найбільш головних проблем іонообмінної технології є процеси регенерації іонітів, а, зокрема, утилізації відпрацьованих регенераційних розчинів. Найбільш перспективним при відновленні регенераційних розчинів є електрохімічний метод. Проте, електроекстракція цинку та нікелю практично неможлива з кислих розчинів без розділення електродного простору мембраною. Крім того, стоки гальванічних виробництв містять суміші іонів важких металів. Це ускладнює процес очистки стічних вод та повернення цінних компонентів у виробництво.

В ході дослідження використовували сильнокислотний катіоніт КУ-2-8 в Na^+ -формі для вивчення процесів сумісної сорбції іонів важких металів. Регенерацію катіоніту проводили розчинами сірчаної та соляної кислот. Електроекстракцію цинку та нікелю з кислих регенераційних розчинів здійснювали в двохкамерному електролізері з аніонообмінною мембраною МА-41.

Отримано результати, які свідчать, що в умовах концентрування важких металів на катіоніті КУ-2-8 досягнути ефективного розділення їх неможливо. Встановлено, що іони важких металів сорбовані індивідуально і в сумішах з іншими іонами важких металів ефективно десорбуються розчинами сірчаної та соляної кислот.

Використання двохкамерного електролізера, на відміну від проведення процесів електролізу без розділення електродного простору, дозволило практично повністю вилучити іони цинку та нікелю з кислих регенераційних розчинів. А також отримати розчин сірчаної кислоти в анодній камері в концентрації 239–651 мг-екв/дм³.

Ключові слова: очищення стічних вод, електроекстракція катіонів важких металів, метод іонного обміну.

1. Introduction

The issue of pollution of natural water bodies refers to global environmental problems. It is known that the toxicity of the aquatic environment is formed due to the receipt of harmful substances of anthropogenic origin, the

accumulation of significant amounts of them and their violation by the influence of natural geochemical cycles of the matter cycle.

Among the most common highly toxic substances in fresh water bodies, one of the leading places is occupied by heavy metals. A characteristic feature of these ions is that

they do not collapse under natural conditions, but only change the form of finding, gradually accumulating in various components of the ecosystem. They are pollutants of reservoirs of increasing importance, which is due to their stability in the external environment and high biological activity. For example, Cd, Pb, Hg are able to accumulate by organisms of hydrobionts and to biomagnify behind trophic chains.

The main source of heavy metals entering the reservoirs is the waste water of electrochemical plants, which are present at virtually every machine-tool and instrument-making enterprise. In addition, to a large extent, the entry of heavy metals into water bodies, along with other industrial enterprises, is affected by nuclear power plants [1, 2]. These industrial facilities are characterized by a high level of thermal pollution and large volumes of sewage discharged into water bodies. Enterprises of ferrous and non-ferrous metallurgy, mining and processing complexes, enterprises for the extraction of solid and liquid fuels are also polluting the environment by heavy metals.

Cations of heavy metals, in particular zinc and nickel, are included in the group of the most dangerous metals-toxicants. Nickel, for example, refers to the most common and dangerous environmental pollutants that affect the normal course of physiological, ecological and biochemical processes, the growth and development of all constituent biota. In high concentrations for animals, nickel is toxic, and for humans, its toxicity level is 20 mg/day. The maximum permissible concentration of nickel compounds in water, air in populated areas and working areas is 0.1 mg/l, 0.00002 mg/m³, 0.005 mg/m³, respectively [3].

It should also be noted that the typical urban water treatment plants do not provide for the stage of extraction of heavy metal ions from sewage. In this regard, a necessary and important issue is the development of technologies for local wastewater treatment from heavy metal ions in the treatment plants of enterprises to prevent the accumulation of hazardous toxicants in surface water bodies. Therefore, it is relevant to study in the field of non-waste technologies for sewage treatment of galvanic plants.

2. The object of research and its technological audit

The object of research is model solutions containing ions of heavy metals – analogues of waste waters of galvanic industries. The extraction of heavy metal ions from aqueous solutions by the ion exchange method is not a difficult problem. Strongly acid cation exchanger KU-2-8, in particular, has a high sorption capacity that is to metal cations. However, the wastewater from the galvanic plants contains mainly mixtures of heavy metal ions in its composition. In addition, ion-exchange technologies are advisable in the case when problems of regeneration of ion exchangers and recycling of regeneration solutions are solved. It is known that the use of solutions of hydrochloric and sulfuric acids makes it possible to achieve fairly high degrees of regeneration KU-2-8. The known methods for recycling of regeneration solutions of ion-exchange heavy metal extraction from washing waters of galvanic industries are neutralization and precipitation of metal hydroxides, solution evaporation, electrodialysis and electrolysis. The latter are the most promising, since they make it possible to remove metals and allow reuse of regeneration

solutions. But since waste waters of galvanic industries contain mixtures of heavy metal cations, the extraction of these ions from galvanic rocks by the ion exchange method and subsequent electrochemical processing of regeneration solutions leads to a mixture of metals. Therefore, it is important to study the processes of joint sorption of heavy metal ions on the strongly acid cation exchanger and processes of their desorption by solutions of sulfuric and hydrochloric acids. Electrochemical extraction of copper and cadmium ions is not a difficult problem and has been considered sufficiently in previous publications [4, 5]. Therefore, it is important to study the conditions of electroextraction of zinc and nickel from acid regeneration solutions to ensure the repeated use of acid in the regeneration of ion exchangers.

3. The aim and objectives of research

The aim of research is development of an efficient ion-exchange technology for the extraction of heavy metal ions from waste water from galvanic plants.

To achieve the aim it is necessary to solve the following tasks:

1. To determine the mutual influence of heavy metal ions on sorption on strong acidity cation exchanger KU-2-8 when extracted from aqueous solutions – analogues of washing waters of galvanic industries.
2. To determine the efficiency of desorption of cations of heavy metals from ion exchangers when treated with solutions of sulfuric acid, depending on the type of sorbed cations.
3. To determine the efficiency of desorption of nickel and zinc ions by the strongly acid cation exchanger KU-2-8 using solutions of hydrochloric acid.
4. To determine the conditions for electroextraction of zinc and nickel from sulfuric acid solutions in a two-cell electrolyzer in order to obtain metals in free form and acid solutions in concentrations suitable for reuse.

4. Research of existing solutions of the problem

When recovering ions of heavy metals, reagent, sorption, baromembrane and ion-exchange methods are used. Each of the methods has advantages and disadvantages. When cleaning wastewater from galvanic plants, it is always important to return valuable components to production. Heavy and non-ferrous metals can be isolated as individual compounds or in metallic form by ion exchange methods, chemical and electrochemical reduction [6, 7]. Of course, the efficiency of reduction of metal ions in wash wastewater at low concentrations is very low. It is more expedient to concentrate the ions by the ion exchange method and then electrochemically isolate them from concentrated regeneration solutions, in comparison with waste water. It is ion exchange [8] that is promising in the creation of closed systems for washing parts in galvanic plants. This makes it possible to use demineralized water for washing parts and effectively removes cations of heavy metals and chromates from water. In addition, in closed systems for washing parts, the concentration of heavy metal ions should not be more than 10 mg/dm³, whereas when discharging water into the sewage system, this figure is reduced to 0.5 mg/dm³.

Simplicity of operation, the possibility of wastewater treatment with specified concentrations, low energy costs, concentration of pollutants of a degree that provides the possibility of further recycling, controllability of the process allow successfully solving the tasks of creating closed cycles of washing parts in galvanic plants. It is possible to use local ion exchange units with replaceable filters. It is known that the strongly acid cation exchanger KU-2-8 is characterized by a high capacity for cations, including cations of heavy metals. This cation exchanger has a high capacity when used in both salt and acid form. This makes it possible to use this cation exchanger to remove heavy metals in weakly alkaline, neutral and acid media [9]. With equal selectivity of ion exchangers for different ions, the main factor affecting the ion-exchange recovery of heavy metals from water is the level of their concentrations and the content of hardness ions in water. At low concentrations of heavy metal ions, withdrawing them from water with a high level of rigidity will be ineffective [10]. An important issue in the application of ion-exchange technologies is the possibility of regeneration of ion exchangers and processing of regeneration solutions. It is known that solutions of sulfuric and hydrochloric acids are better than reagents for the regeneration of cation exchangers from nickel and zinc ions [11, 12]. Recycling of regeneration solutions is possible by electrochemical reduction of heavy metals [13]. It is known that heavy metal ions, such as copper, lead and other metals in the series of activity after hydrogen, as well as cadmium, due to overvoltage of hydrogen evolution from the surface of a given metal, electrochemical, even from acidic solutions, are easily restored. Metals such as zinc and nickel are reduced from acidic solutions only at high concentrations (>90 – 100 g/dm³), and at a concentration of <50 g/dm³, these metals are not reduced from acidic solutions. Usually the concentrations of heavy metals in acid regeneration solutions do not exceed 30 – 35 g/dm³ [14]. Under such conditions, zinc and nickel are almost impossible to remove from these solutions by electrolysis. And at neutralization of a regenerative solution they can't be reused for regeneration of an ion exchanger. Recycling of spent regeneration solutions by other methods is another difficult problem.

Thus, the results of the analysis allow to conclude that the processes of joint sorption of heavy metals from aqueous solutions have not been sufficiently studied. As well as the unresolved issue of electrochemical processing of acid regeneration solutions containing zinc and nickel ions, in order to separate metals in free form and obtain acid solutions suitable for reuse.

5. Methods of research

A strongly acid cation exchanger KU-2-8 in Na⁺-form was used in the work. Sorption was studied under dynamic conditions by passing solutions containing mixtures of heavy metal sulfate ions in various combinations. The concentrations of copper ions in the mixture were maintained at 31 – 35 meq/dm³, cadmium 16 – 20 meq/dm³, zinc 14 – 35 meq/dm³, nickel 22 – 42 meq/dm³. The volume of ion exchanger was 10 – 20 cm³. The flow rate of water under dynamic conditions through an ion exchange column 2 cm in diameter was 10 – 15 cm³/min. Regeneration of the ion exchanger was carried

out with a 3 – 10 % solution of hydrochloric acid and a 5 % solution of sulfuric acid. The rate of regeneration solution is 1 – 3 cm³/min. The concentration of copper, cadmium, zinc and nickel, and the pH of the medium were monitored in samples of purified water or a regeneration solution [15, 16]. To investigate the conditions for electroextraction of metals, a two-cell electrolytic cell with a stainless steel cathode and a titanium anode coated with ruthenium oxide was used. The cathode and anode space were separated by an anion exchange membrane MA 41. The cathode chamber contained a sulfate solution of nickel sulfate or zinc sulphate. In the anode chamber is a solution of sulfuric acid with a concentration of 50 meq/dm³. As model solutions, separately used solutions of nickel sulfate and zinc sulfate in various concentrations of heavy metal ions ($[Ni^{2+}] = 126$ – 134 meq/dm³, $[Zn^{2+}] = 120$ – 128 meq/dm³) and sulfuric acid $[H_2SO_4] = 98$ – 540 meq/dm³).

6. Research results

Since the cation exchanger KU-2-8 is characterized by a large capacity of double-charged metal cations, it was interesting to investigate the joint sorption of heavy metal ions on KU-2-8 in Na⁺-form. As the results of the experiment indicate, this cation exchanger effectively removes heavy metal ions from solutions containing mixtures of metals (Fig. 1, 2). The cation exchanger capacity for cadmium and zinc, cadmium and nickel, zinc and nickel, cadmium and copper cations amounts to ~ 2000 meq/dm³. When controlling the concentration of separately copper ions and ions of other metals, it was shown (Fig. 2), the cation exchanger KU-2-8 has a close efficiency for copper, nickel and zinc ions. However, according to cadmium ions, ionite has a lower selectivity compared to copper ions. As can be seen from Fig. 2 (curve 4), in the first stage of sorption, cadmium and copper ions were absorbed almost completely. This is due to the fact that the capacity of the ion exchanger at this stage was not completely filled. However, in the future, with the passage of 800 – 1000 cm³ of the solution, copper continued to be sorbed, whereas cadmium ions were displaced from the ion exchanger.

This led to an increase in the concentration on the initial cadmium sorption curve (curve 4) to 31 – 35 meq/dm³. Obviously, this is possible only due to the desorption of previously sorbed cadmium ions, they were displaced from the ion exchanger by copper ions.

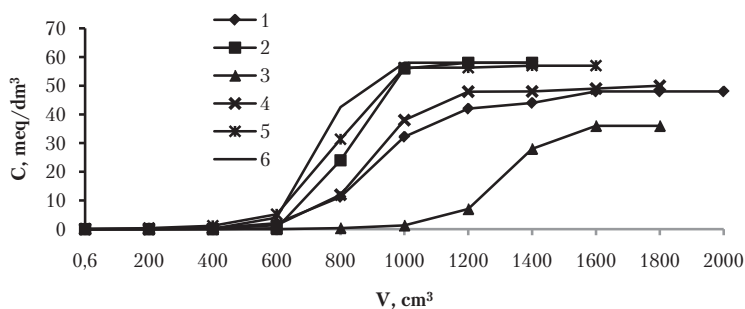


Fig. 1. Dependence of output concentrations:

1 – cadmium and zinc; 2 – cadmium and nickel; 3 – zinc and nickel; 4 – cadmium and copper; 5 – copper and zinc; 6 – copper and nickel from the volume of solutions containing ions in concentrations, meq/dm³: 1 – Cd²⁺ – 18.0, Zn²⁺ – 30.0; 2 – Cd²⁺ – 16.0, Ni²⁺ – 42.0; Zn²⁺ – 14.0; 3 – Ni²⁺ – 22.0; 4 – Cu²⁺ – 32, Cd²⁺ – 18.0; 5 – Zn²⁺ – 14, Cu²⁺ – 33; 6 – Cu²⁺ – 32, Zn²⁺ – 35. (Complete exchange dynamic capacity, meq/dm³: 1 – 2041; 2 – 1997; 3 – 2153; 4 – 2037; 5 – 2099; 6 – 2286) by filtration through the cation exchanger KU-2-8 in Na⁺-form ($V_f = 20$ cm³)

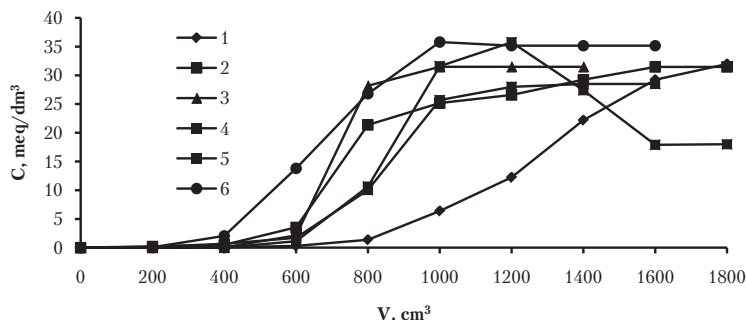


Fig. 2. Dependence of output concentrations:

1–3 – copper; 4 – cadmium; 5 – zinc; 6 – nickel from the volume of solutions containing mixtures of ions: 1, 4 – copper and cadmium; 2, 5 – copper and zinc; 3, 6 – copper and nickel in concentrations, mg/dm³: 1, 4 – Cu²⁺ – 1016, Cd²⁺ – 1012; 2, 5 – Cu²⁺ – 1000, Zn²⁺ – 933; 3, 6 – Cu²⁺ – 1000, Ni²⁺ – 1033 through the cation exchanger KU-2-8 in Na⁺-form (*V* = 20 cm³). (Total exchange dynamic capacity, meq/dm³: 1 – 1841; 2 – 1147; 3 – 955; 4 – 197; 5 – 952; 6 – 1332)

Later, when the bulk of sorbed cadmium ions were displaced, their concentration in the initial solution decreased to an initial level of 18 meq/dm³. The total exchangeable dynamic capacity of copper ion exchanger reached 1841 meq/dm³. However, the difference in the selectivity of cation exchanger KU-2-8 from the cations under study in the range of investigated concentrations was insufficient to effectively separate them during sorption.

The expediency of using ion exchange essentially depends on the regeneration processes of ion exchangers and recycling of regeneration solutions. It is known [17] that solutions of sulfuric acid work quite efficiently when regenerating cation exchanger KU-2-8. Mixtures of ions of heavy metals during acid regeneration are washed out of cation exchanger KU-2-8 no worse than from ion exchangers sorbed by one type of ions.

As the results confirm, are shown in Fig. 3, it is better to remove cadmium, zinc and copper ions, a mixture of copper with zinc and nickel, from the cation exchanger KU-2-8. At the same time, in general, regeneration efficiency was high, and the degree of desorption of metals reached 81–99 %.

It should be noted that the difference in the selectivity of the cation exchanger KU-2-8 in double-charged cations of heavy metals was not so significant that they could be separated during the regeneration of the cation exchanger. This is evident from the desorption curves of copper and cadmium (Fig. 3, curve 1, 4). Copper and cadmium were washed out of the cation exchanger almost simultaneously in quantities equivalent to the amount of sorbed ions.

Fig. 4, 5 presents the results of desorption of zinc and nickel ions by solutions of hydrochloric acid. The

concentration of hydrochloric acid was changed from 3 to 10 %. In all cases, the efficiency of regeneration increased with increasing concentration and consumption of the acid solution. With a specific consumption of an acid solution (*q_p*) of 5 volumes per 1 volume of ion exchanger, a complete reduction of the ion exchanger capacity was achieved using a 10 % solution of hydrochloric acid. The degree of desorption was 100 %. For 3 % acid, *Z* = 82 % for nickel and 84 % for zinc. For 5 and 8 % solutions of HCl, the desorption degree of both metals exceeded 92 %.

It has already been mentioned earlier that removal of metals from waste regenerative solutions of electrical extraction is a promising method. The efficiency of the process depends on the conditions of electrolysis. It is known that the nickel is recovered with high current output only in a weakly acid medium (pH = 3–4) [18]. Thus, the authors [19] largely solved the problem of removing nickel from acidic regeneration solutions containing nickel sulfate. But the problem was that the composition of regeneration solutions changed with the use of borax and boric acid, which negatively affected the processes of regeneration of cation exchangers, with the reuse of these solutions. The use of quaternary salts in regeneration solutions is inadmissible, since they will be efficiently sorbed on the cation exchanger, reducing its capacity by metal cations. The authors [4] investigate the processing of hydrochloric and sulfuric acid solutions of heavy metal ions in single-chamber and two-chamber electrolytes, and it was shown that the energy consumption of electrical extraction increases with increasing acidity of solutions.

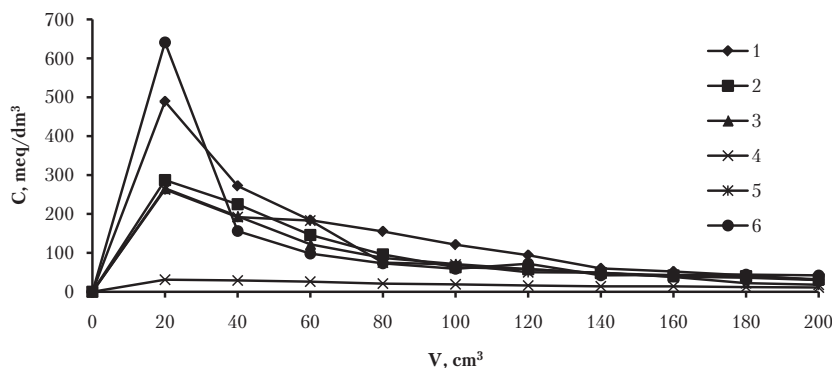


Fig. 3. Change in the initial concentration of ions:

1–3 – copper; 4 – cadmium; 5 – zinc; 6 – nickel from the volume of the 5 % solution of sulfuric acid passed through the cation exchanger KU-2-8 in: 1, 4 – Cd²⁺, Cu²⁺; 2, 5 – Cu²⁺, Zn²⁺; 6 – Cu²⁺, Ni²⁺-form (*V* = 20 cm³)

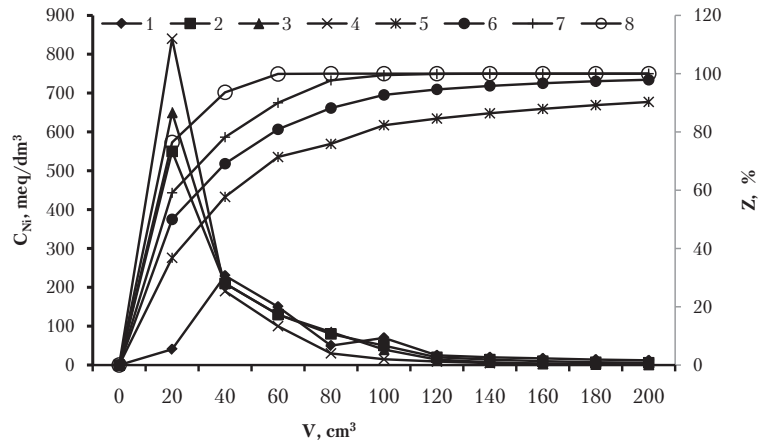


Fig. 4. Dependence: 1–4 – the initial concentration of nickel ions and 5–8 – the degree of their desorption from the cation exchanger KU-2-8 in the Ni^{2+} -form ($V=20$ cm^3) from the consumption of the hydrochloric acid solution by concentration, %: 1, 5 – 3; 2, 6 – 5; 3, 7 – 8; 4, 8 – 10

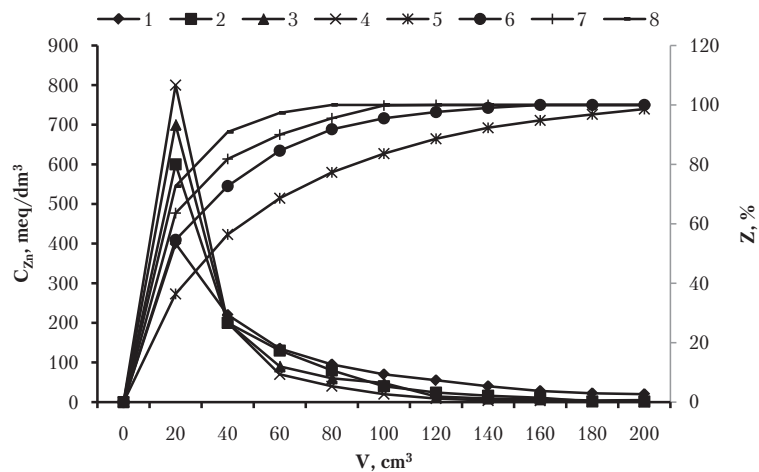


Fig. 5. Dependence: 1–4 – the initial concentration of zinc ions and 5–8 – the degree of their desorption from the volume of the solution of hydrochloric acid in the concentration, %: 1, 5 – 3; 2, 6 – 5; 3, 7 – 8; 4, 8 – 10 from cation exchanger KU-2-8 in Zn^{2+} -form ($V=20$ cm^3)

When switching from single- or double-cell electrolyzers, energy costs increase 2–3 times. However, the efficiency of extraction of metals from eluates in two-chamber electrolyzers is more than one-chamber. Therefore, the choice of the design of the electrolyzer is connected with the prospects of using the products of electrical extraction.

As hydrochloric acid provides high efficiency of desorption of nickel and zinc ions with strongly acidic cation exchangers KU-2-8, it is expedient to study the electrolysis processes of hydrochloric solutions containing nickel and zinc ions. However, it is known that in the presence of chlorides, electrodes are rapidly degraded during the process of electrochemical reduction of heavy metals. In addition, on the anode, the release of active chlorine occurs. Removal of zinc, nickel and other metals displaces hydrogen from aqueous solutions of acids in two- and three-chamber electrolytes [5] from hydrochloric acid regeneration solutions, is accompanied by the use of expensive membranes, low reliability of the latter and significant energy costs.

Therefore, the processes of electrolysis of acid solutions of nickel sulfate and zinc in a two-chamber cell are carried out. The results are presented in Tables 1, 2.

It should be noted that, in contrast to the processing of acidic solutions containing zinc ions, in single-cell electrolyzers, in a two-cell electrolyzer, zinc is restored quite

efficiently (Table 1). At the first stage of the process, the acidity in cation exchanger decreased to 30–60 meq/dm^3 from 100–560 meq/dm^3 , and then zinc reduction takes place. The maximum yield of zinc is reached only on the 2nd–4th hours of electrolysis. This is due to the competing process of hydrogen evolution at the cathode, which is accompanied by the diffusion of sulfates into the anode region. Only after the decrease in acidity in the cathode area did the intensity of zinc reduction increase. It should be noted that during electrolysis, as the zinc is reduced and the sulfates are diffused into the anodic region, the acidity of the anion exchanger increases and reaches 239–641 meq/dm^3 . The extraction rate of zinc by the 8:00 am electrolysis is 91–99 %.

A similar dependence is noted in the electrolysis of acidic solutions of nickel sulfate in a two-compartment electrolyzer (Table 2). In this case, nickel begins to be efficiently reduced at acidity to catholyte at a level of 50–90 meq/dm^3 . Extraction rate is 99 %.

This approach is important only when analyzing mixtures of metals. In addition, it is inapplicable in the purification of water from heavy metal ions, when the problems of concentrating metals and completely removing the latter from the eluates in the form of a metal powder are highlighted [16].

Table 1

Dependence of efficiency of zinc extraction in a two-cell electrolyzer (Membrane MA-41) from the time of electrolysis at a voltage of 25 V at the acidity of the solutions (H₂SO₄), meq/dm³: 100 (I), 250 (II), 540 (III)

t, h	C _{Zn²⁺} , meq/dm ³			I, A			K, meq/dm ³						B, %		
	I	II	III	I	II	III	Cation exchanger			Anion exchanger			I	II	III
							I	II	III	I	II	III			
0.0	128	127	120	0.315	0.685	0.690	100	250	560	50	50	50	–	–	–
1.0	75	83	85	0.185	0.190	0.210	32.2	60.0	60.1	171	284	585	42.5	17.3	14.0
2.0	25	29	32	0.050	0.040	0.060	32.7	45.1	50.2	221	327	628	72.7	76.4	67.9
3.0	16	20	16	0.030	0.030	0.060	32.4	35.4	40.3	226	339	640	80.4	61.6	72.7
4.0	14	14	6	0.010	0.030	0.040	28.8	35.2	40.1	231	343	641	53.7	52.4	45.5
5.0	13	10	4	0.010	0.030	0.030	28.9	30.1	35.4	234	342	643	26.9	35.7	13.4
6.0	12.0	8	3	0.010	0.030	0.030	28.0	30.0	30.1	238	343	642	26.9	17.9	8.6
7.0	11.7	6	2	0.005	0.030	0.030	26.0	30.0	30.0	239	344	642	16.1	16.9	8.4
8.0	11.5	4	1	0.005	0.030	0.030	24.0	29.9	30.0	239	343	641	10.8	16.5	8.2

Table 2

Dependence of efficiency of nickel extraction in a two-cell electrolyzer (Membrane MA-41) from the time of electrolysis at a voltage of 25 V at the acidity of the solutions (H₂SO₄), meq/dm³: 100 (I), 250 (II), 540 (III)

t, h	C _{Ni²⁺} , meq/dm ³			I, A			K, meq/dm ³						B, %		
	I	II	III	I	II	III	Cation exchanger			Anion exchanger			I	II	III
							I	II	III	I	II	III			
0.0	126	132	134	–	–	–	100	280	540	50	50	50	–	–	–
1.0	94	77.0	71	0.395	0.508	0.810	50	80	90	132	305	563	22.1	14.8	21.0
2.0	58	42.0	31	0.155	0.185	0.135	30	65	65	193	355	619	62.1	50.9	80.2
3.0	27	16.0	14	0.105	0.080	0.065	32	60	50	221	386	639	79.5	86.7	70.8
4.0	7	6.0	4	0.085	0.060	0.060	30	60	50	243	395	651	64.5	45.5	44.8
5.0	2	1.0	1.3	0.030	0.050	0.040	28	55	50	250	398	657	44.6	26.9	33.3
6.0	1	0.5	1.0	0.010	0.010	0.010	29	50	40	250	397	658	26.9	13.4	8.1
7.0	0	0.4	0.6	0.010	0.004	0.005	28	50	40	251	398	657	26.5	9.1	8.0
8.0	–	–	0.4	–	–	0.003	–	–	40	–	–	657	–	–	4.2

7. SWOT analysis of research results

Strengths. It is almost impossible to completely eliminate zinc and nickel ions from acid regeneration solutions. The degree of extraction is more than 90 %. This makes it possible to return valuable components to production. In addition, the acid concentration in the anion exchanger increases to values that allow it to be used repeatedly in regeneration processes. Thus, the results of the research create the basis for the creation of low-waste ion exchange technologies for the neutralization of waste waters from galvanic industries.

Weaknesses. By carrying out the process of recovery of acid regeneration solutions containing zinc and nickel ions in two-cell electrolyzers, this leads to an increase in energy costs when implementing such scheme for the utilization of eluates. Since the processes of metal reduction and hydrogen reduction proceed in parallel.

Opportunities. Scraps of sewage waste from galvanic plants often contain mixtures of heavy metal ions, it would be advisable to investigate the electrochemical processing of regeneration solutions after ion-exchange treatment of such wastewater. This would allow the return of valuable

components to production and prevent the entry of harmful toxicants into natural water bodies.

Threats. The use of electrochemical processing of regeneration solutions at existing water treatment plants will lead to an increase in production costs. As compared to reagent methods, electrochemical processing has significant energy costs.

This method is advisable to use for cleaning of sewage effluents of galvanic industries, because it is unsuitable for concentrating metals and completely removing the latter from the eluates in the form of a metal powder.

8. Conclusions

1. Sorption of cations of heavy metals from solutions containing their mixtures is carried out on the strongly acidic cation exchanger KU-2-8. It is established that the cation exchanger KU-2-8 has the highest selectivity for Zn²⁺, Ni²⁺, Cu²⁺ ions in comparison with the Cd²⁺. However, under the conditions of concentrating heavy metals on cation exchangers, when cleaning galvanic rocks, it is impossible to achieve an effective separation of these cations. At 1800 meq of sorbed Cu²⁺, about 190 meq of

the sorbed Cd²⁺ ions). The selectivity of ion exchanger according to Zn²⁺, Ni²⁺, Cu²⁺ is approximately the same.

2. The desorption of cations of heavy metals by solution of sulfuric acid is investigated. It has been established that heavy metal ions are sorbed individually and in mixtures with other heavy metal ions are efficiently desorbed by sulfuric acid, regardless of the ratio in the sorption volume. Using a 5 % solution of sulfuric acid, the degree of desorption of metals reaches 81–99 %.

3. The efficiency of desorption of zinc and nickel ions with strongly acidic cation exchanger is studied using solutions of hydrochloric acid. It is shown that at a specific consumption of 5 volumes of acid per 1 volume of ion exchanger, the degree of desorption of 100 % for cations of nickel and zinc is achieved in the case of using a 10 % solution of hydrochloric acid.

4. The process of electrochemical reduction of zinc and nickel from acidic solutions containing sulfates of these metals is studied in a two-cell electrolyzer. It is established that the maximum yield of metals is reached for 2–4 hours of electrolysis. The degree of metal recovery in 8:00 of electrolysis is 91–99 %. The acidity of the anion exchanger grows from 50 meq/dm³ to 239–641 meq/dm³.

References

1. Stanko O. M. Vazhki metaly u vodi: zabrudnennia richky Dnister za ostanni 10 rokov (terytorii Lvivskoi oblasti) // Suchasni problemy toksykologii. 2012. No. 3–4. P. 58–63.
2. Progress in Chemical-Looping Combustion and Reforming technologies / Adanez J. et al. // Progress in Energy and Combustion Science. 2012. Vol. 38, No. 2. P. 215–282. doi:10.1016/j.pecc.2011.09.001
3. Ivanter E. V., Medvedev N. V. Ekologicheskaya toksikologiya prirodnnykh populyatsiy: handbook. Moscow: Nauka, 2007. 229 p.
4. Electroextraction of heavy metals from wastewater for the protection of natural water bodies from pollution / Gomelya M. et al. // Eastern-European Journal of Enterprise Technologies. 2018. Vol. 1, No. 10 (91). P. 55–61. doi:10.15587/1729-4061.2018.123929
5. Elektroliticheskoe izvlechenie ionov tyazhelykh metallov iz solyanokislykh rastvorov / Gomelya N. D. et al. // Energeticheskoye resursoberezhenie. 2017. No. 1. P. 60–67.
6. Sub M., Rub L. Abrennung von Kupfer, Nickel, Chrom, Zink und Silber aus galvanischen Spulwasserh an Jonenansta – uscherharzen und Kohlenstoffsorbenzien // Nachp. Aussenhand. 1998. Vol. 51, No. 244. P. 61–87.
7. Erusalimskaya E. M. Primenenie katodov s razvitoi poverkhnost'yu dlya intensivatsii protsessa elektrokhimicheskoy ochildki promyshlennykh stichnykh vod ot nikelya // Fiziko-khimicheskaya ochildka i metody analiza promyshlennykh stichnykh vod. Moscow, 1988. P. 40–42.
8. Fu F., Wang Q. Removal of heavy metal ions from wastewaters: A review // Journal of Environmental Management. 2011. Vol. 92, No. 3. P. 407–418. doi:10.1016/j.jenvman.2010.11.011
9. Gomelya M. D., Radovenchuk V. M., Hlushko O. V. Ochystka halvanostokov ot yonov kadmyia yonoobmennim metodom // Ekologhiia i resursy. 2007. No. 16. P. 57–62.
10. Removal of Cu(II) and Pb(II) ions from aqueous solutions by adsorption on sawdust of Meranti wood / Ahmad A. et al. // Desalination. 2009. Vol. 247, No. 1–3. P. 636–646. doi:10.1016/j.desal.2009.01.007
11. Izvlechenie ionov nikelya iz otrabotannykh rastvorov khimicheskogo nikelirovaniya // Izv A.N. GSSR. Ser. Khim. 1986. Vol. 12, No. 4. P. 301–303.
12. Gomelya N. D., Sagaydak I. S. Razrabotka ekologicheskoi chistoy tekhnologii izvlecheniya tsinka iz gal'vanostokov // Perspektivnye napravleniya razvitiya ekologii, ekonomiki, energetiki. Odessa, 1999. P. 81–85.
13. Makarenko I. M. Electrochemical desalination of solutions, containing hardness ions // Eastern-European Journal of Enterprise Technologies. 2014. Vol. 4, No. 6 (70). P. 48–53. doi:10.15587/1729-4061.2014.26243
14. Electrochemical removal of nickel ions from neutral and acid regeneration solutions / Omelchuk Y. A. et al. // Eastern-European Journal of Enterprise Technologies. 2011. Vol. 6, No. 6 (54). P. 26–29. URL: <http://journals.urau.ua/eejet/article/view/2291>
15. Fiziko-khimicheskie metody analiza. Prakticheskoe rukovodstvo: handbook / ed. by Aleskovskiy V. B. Leningrad: Khimiya, 1988. 376 p.
16. Lurie Yu. Yu. Analiticheskaya khimiya promyshlennykh stichnykh vod. Moscow: Khimiya, 1984. 448 p.
17. Sahaidak I. S. Lokalizatsiia ta zneshkodzhennia stichnykh vod, zabrudnennykh spolukamy khromu, kadmiu ta tsynku: Abstract's PhD thesis. Kyiv, 2000. P. 11–12.
18. Pikkering U. F. Sovremennaya analiticheskaya khimiya. Moscow: Khimiya, 1977. 560 p.
19. Donchenko M. I., Redko R. M., Kovalenko S. Yu. Elektrokhimichne osadzhennia nikeliu iz sirchanokislykh eliuativ, utvorenykh pry reneratsii kationitiv // Suchasni problemy okhorony dovkillia, ratsionalnoho vykorystannia vodnykh resursiv ta ochystky pryrodnykh i stichnykh vod: 2007 rik. Kyiv: Tovarystvo «Znannia Ukrainy», 2007. P. 69–72.

Gomelya Nikolai, Doctor of Technical Sciences, Professor, Head of the Department of Ecology and Technology of Plant Polymers, National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Ukraine, e-mail: m.gomelya@kpi.ua, ORCID: <http://orcid.org/0000-0003-1165-7545>

Trokhymenko Ganna, PhD, Associate Professor, Head of the Department of Environmental Safety and Occupational Safety, Admiral Makarov National University of Shipbuilding, Mykolaiv, Ukraine, e-mail: antr@ukr.net, ORCID: <https://orcid.org/0000-0002-0835-3551>

Shablii Tatiana, Doctor of Technical Sciences, Associate Professor, Department of Ecology and Technology of Plant Polymers, National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Ukraine, e-mail: dsts1@ukr.net, ORCID: <http://orcid.org/0000-0002-6710-9874>

Hlushko Olena, PhD, Associate Professor, Department of Ecology and Technology of Plant Polymers, National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Ukraine, e-mail: alyona_glushko@ukr.net, ORCID: <http://orcid.org/0000-0002-8243-5707>