

Важкі метали потрапляють у водойми в результаті природних та антропогенних процесів, накопичуючись у ґрунті, донних відкладеннях, шламах, можуть далі мігрувати в підземні і поверхневі води. Основними джерелами надходження важких металів у природні водойми є недостатньо очищені стічні води багатьох галузей промисловості. Це робить актуальною проблему видалення важких металів із стічних вод для запобігання надмірного забруднення водойм. Серед існуючих методів очищення води від іонів важких металів при значних обсягах промислових стічних вод досить перспективними є електрохімічні методи. Перевагою методу є можливість переробляти відпрацьовані регенераційні розчини з отриманням металів, які придатні для повторного використання.

Приведені результати досліджень процесів електрохімічного видалення катіонів важких металів в одно- та двокамерних електролізерах із розведених водних розчинів. При проведенні досліджень в двокамерному електролізері катодна і анодна область були розділені аніонообмінною мембраною МА-40. Вивчено залежність впливу жорсткості, рН розчинів, анодної щільності струму та часу електролізу на ефективність видалення іонів важких металів. Показано, що іони цинку, міді та свинцю ефективно вилучаються з водних розчинів з використанням електролізу при початковій концентрації 10 мг/дм³. Встановлено, що при низьких концентраціях іонів вихід за струмом при відновленні металів сягав (4–20) 10–4 % і мало змінювався з концентрацією. Визначено, що ефективність очищення води від іонів важких металів електролізом зростає із підвищенням рН середовища та із зниженням жорсткості води. В двокамерних електролізерах дані фактори практично не впливають на ефективність очищення. Встановлено перспективу використання електролізу для селективного видалення важких металів із водопровідної, пом'якшеної та природної води. Даний метод очистки дозволяє не тільки доочищувати стічні води до гранично допустимих концентрацій, але й дає можливість очищати воду з природних джерел до якості питної води

Ключові слова: стічні води, важкі метали, очистка води, жорсткість води, вихід за струмом, аніонообмінна мембрана, електролізер, електроекстракція

UDC 628.161.2: 628.31: 621.359.7

DOI: 10.15587/1729-4061.2018.148896

PURIFICATION OF WASTEWATER FROM THE IONS OF COPPER, ZINC, AND LEAD USING AN ELECTROLYSIS METHOD

N. Gomelya

Doctor of Technical Sciences,

Professor*

E-mail: m.gomelya@kpi.ua

Ye. Melnychenko

Postgraduate student*

E-mail: jenny_666@live.ru

I. Radovenchuk

PhD, Associate Professor*

E-mail: r.yar@ukr.net

*Department of Ecology and Technology of Plant Polymers National Technical University of Ukraine

"Igor Sikorsky

Kyiv Polytechnic Institute"

Peremohy ave., 37,

Kyiv, Ukraine, 03056

1. Introduction

Heavy metals, as well as other chemical contaminants, penetrate the human environment as a result of a series of processes. These include not only natural events (volcanic eruptions, geochemical anomalies, etc.), but mostly those of anthropogenic nature. The content of heavy metals in the environment is growing rapidly as a consequence of the intensive industrial development, unsustainable use of natural resources, and the urbanization of society [1].

Poorly treated wastewater gets into natural bodies of water, where heavy metals accumulate in the water and bottom sediments, thereby becoming a source of secondary pollution. Compounds of heavy metals spread relatively quickly throughout an aqueous object. Part of them forms a sediment in the form of carbonates, sulphates, they partly adsorb on mineral and organic sediments. As a result, the content of heavy metals in the sediment is constantly increasing. When

the adsorption capacity of sediments is exhausted, heavy metals penetrate water. This leads to setting a dynamic equilibrium and to maintaining a stable concentration of metals even when their supply from wastewater decreases [2].

The main sources of penetration of heavy metals into natural water bodies is the wastewater from chemical, metallurgical industries. The wastewater from enterprises of extractive industry (mines' water), nuclear and thermal power plants, machine-building enterprises (galvanic production), agricultural runoffs (mineral fertilizers) is also an important source of heavy metals [3]. Heavy metals that act as biotrace elements are involved in the biochemical processes in plants and animals, as well as people [4].

Given the above, the task of purification of wastewater from ions of heavy metals is particularly relevant and necessitates the modernization of existing technologies of water purification and the search for new, more efficient, technological processes of water treatment.

2. Literature review and problem statement

At present, there are many methods for cleaning wastewater from heavy metals: reagent, diaphragm, electrochemical, sorption, ion exchange, biological methods, and others [5, 6]. An important task of wastewater purification is the application of the most energy-efficient methods, as well as returning the metals removed from wastewater back into production.

A traditional procedure of reagent water purification is based on the use of coagulants and flocculants [7]. The coagulants used are the salts of aluminum, iron, and compounds [8, 9]. The advantages of the reagent method include the ease of extraction of toxicants and affordability of deposition reagents, the simplicity of equipment and the ease to control the process. The disadvantages are an incomplete removal of contaminants, the irreversible loss of valuable substances with sediments, the problem of disposal of the obtained sediments [10].

Common methods of wastewater treatment are sorption methods. The advantages of this method include cost effectiveness, simplicity of hardware design and the capability to carry out deep cleaning of water, low-concentrated in terms of the ions of heavy metals. The authors of work [11] considered a method for obtaining a composite sorbent and studied its sorption properties in relation to heavy metals' ions. The effectiveness of treatment at a starting concentration of 10 mg/dm³ for copper amounted to 80 %.

Sorption methods are more cost-effective only if the sorbents are used many times. The regeneration of sorbents is followed by the creation of a large amount of highly toxic and highly-concentrated eluates that must be exposed to additional neutralization and disposal. In addition, there is a problem on the disposal of the used sorption material.

Increasing attention has been given to purification methods that are based on ion exchange using natural and synthetic materials. Such methods make it possible to not only remove heavy metals' ions from wastewater, but also to reuse wastewater in a circular water supply [12, 13].

The main disadvantage of the ion-exchanging method is the necessity to feed the ion-exchanging plants with wastewater that was pre-purified from suspended substances, cyanides, iron ions, petroleum products, and other organic substances, with a low temporary hardness. In addition, the disadvantage is the formation, following the regeneration, of highly toxic and highly-concentrated eluates, which must be exposed to additional decontamination [14].

When there are large volumes of industrial wastewater, it is advisable to employ at treatment plants the electrochemical and membrane water purification methods (electroflotation, electrolysis, ultrafiltration, nanofiltration, reverse osmosis). For the maximum efficiency of wastewater treatment, it is necessary to build combined systems: reagent pre-treatment, electroflotation, filtering, sorption, membrane concentration, vacuum evaporation [15].

The best variant when removing heavy metals from washing waters of galvanic production is the application of ion exchange and the electroextraction of heavy metals while processing regeneration solutions [10]. In this case, the cationites concentrate the cations of heavy metals, while during electroextraction restored metals are obtained from the used regeneration solutions in the form of a powder and solutions of acids that are suitable for reuse [16]. However, when using two- and three-chamber electrolyzers, when ac-

ids are concentrated in the anodic or intermediate chamber, and metals are recovered on the cathode, there is an issue related to deep purification of catholyte.

In the investigated processes of electroextraction, authors achieved a decrease in the content of ions of heavy metals to 10–300 mg/dm³. That would suffice for the one-chamber electrolyzers because sulfuric acid forms in catholyte, which is repeatedly used for regeneration. However, in the case of two- and three-chamber electrolyzers, there is a problem on the disposal of solutions with low concentrations of heavy metals' cations. One of the directions to resolve this issue is to prolong the duration of electrolysis in order to achieve permissible concentrations for the ions of heavy metals.

In [17], authors examined cathode processes of electroextraction of lead from a trilonate electrolyte. It was established that the maximum output for current for lead is implemented in the alkaline medium with pH=10. Note that the concentration of electrolyte for the lead ions must be maintained at a level of 40 g/dm³. Authors in [18] investigated performance of the electrocoagulation using six iron electrodes for the simultaneous removal of heavy metals: Cu, Ni, Zn, and Mn, from wastewater. The results revealed that at a starting concentration of 250 mg/dm³ for each metal, the removal achieved reached the level of 96 %, and for Mn – 72.6 %.

Similar studies were undertaken by authors in [19, 20] using an electrocoagulation method on aluminum electrodes for the removal of heavy metals at a starting concentration of 50–800 mg/dm³. The residual concentrations of metals were at the level of 2 mg/dm³ and higher.

Thus, results of an analysis of the scientific literature allow us to conclude that these are the simple processes of electrolysis that have not been explored in detail, those that are implemented without the use of expensive membranes and without additional reagents. Many authors studied the processes of electrochemical removal of heavy metal ions at high starting concentrations. However, the processes of electroextraction of heavy metals from water at low initial concentrations have remained almost unexamined up to now. And this is particularly important not only for the post-purification of technological solutions, but also to clean natural waters that contain traces of heavy metals.

3. The aim and objectives of the study

The aim of our study was to determine the effectiveness of removal of heavy metals' cations from diluted aqueous solutions via electrolysis in one- and two-chamber electrolyzers. In addition, the ultimate goal was to estimate the prospects of a method for cleaning and post-purification of tap and waste water, as well as circulating waters from galvanic production.

To achieve the set aim, the following tasks have been solved:

- to explore the processes of electroextraction of ions of copper, zinc and lead in the one-chamber electrolyzers from low-concentrated solutions;
- to determine the effect of medium's pH and hardness on the efficacy of electroextraction of ions of heavy metals from diluted solutions in the one- and two-chamber electrolyzers;
- to assess the efficiency of extraction of heavy metals' ions from diluted solutions by an electrolysis method in the two-chamber electrolyzers.

4. Materials and methods to study the removal of copper from aqueous solutions using an electrochemical method

We used one- and two-chamber electrolyzers (with a volume of the chamber being 100 cm³), which included a cathode made of the stainless steel 12H18N10T and a titanium anode covered with ruthenium oxide. The area of the electrodes and the membrane area is 0.11 dm². Electrolysis was carried out at a current of 0.1–1 A, a voltage of 5–33 V.

While conducting a study in the two-chamber electrolyzer, the cathode and anode regions were separated by the anion-exchanging membrane MA-40 (Ukraine). The cathode chamber contained a working solution of metal with a concentration for the ion of heavy metal of 10 mg/dm³. The anode chamber contained a 0.5 N solution of sulfuric acid. The study was carried out using the distilled and tap water from the city of Kyiv. In addition, we conducted a study using the tap water, which was preliminary softened with a soda solution. When using distilled water, Na₂SO₄ was added to the solution in a concentration of 100 and 200 mg/dm³ in order to increase the conductivity of the solution.

During electrolysis, we controlled in equal time intervals the residual concentration of the metal, the alkalinity in a cathode chamber, and the acidity in the anode chamber.

The degree of removal of heavy metal ions from solutions was calculated from formula:

$$Z = \frac{(C_s - r)}{C_s} \cdot 100\%, \tag{1}$$

where C_s is the starting concentration of metal ions; C_r is the residual concentration of metal ions.

The output for current was computed as a ratio of the theoretical amount of electricity to the amount of electricity that is used to transport an equivalent of a substance [21].

$$\beta = \frac{q_s}{q_t} \cdot 100\% = \frac{m_a}{m_t} \cdot 100\%, \tag{2}$$

where q_s is the amount of electricity that is actually used to transport an equivalent of a substance; q_t is the theoretical amount of electricity, which is used to transport a substance; m_a is the amount of an actually transported substance; m_t is the theoretically determined amount of a transported substance.

The actual amount of a transported substance was determined by a change in its concentration in the full volume of a solution.

The theoretical amount of a transported substance was determined according to the Faraday's law:

$$m_t = K_e \cdot I \cdot t, \tag{3}$$

where K_e is the electrochemical equivalent; I is the amperage, A; t is time, h.

Characteristics of tap water are:

H=5.2 mg-equiv./ dm³;

A=5.1 mg-equiv./dm³;

[Cl⁻]=73.5 mg/dm³;

[SO₄²⁻]=57 mg/dm³;

pH=7.272.

Characteristics of softened water are:

H=1.75 mg-equiv./dm³;

A=31 mg-equiv./dm³;

[Cl⁻]=72 mg/dm³;

[SO₄²⁻]=55.7 mg/dm³;

pH=10.3.

The concentration of ions of heavy metals was determined by the method of inverse chronopotentiometry [22].

5. Results of research into electrochemical removal of heavy metals from water

5.1. Processes of electroextraction of heavy metals in the one-chamber electrolyzers from low-concentrated solutions

During the electrolysis of solutions of sulfates of copper and zinc in distilled water in the presence of sodium sulfate at a starting concentration of ions of metals of 10 mg/dm³, we observed a gradual reduction in concentration over the period of electrolysis (Fig. 1). In this case, the process is more efficient in the case of zinc ions, as in the electrolysis of a solution of copper sulfate. In the first case, over 4 hours the concentration of zinc decreases to 1.63 mg/dm³, while that of copper – only to 3.18 mg/dm³. That may be due to the higher power of current in the case of zinc. Although we observed for the latter slightly higher output values for current than those for copper.

In general, the process differs from electrolysis from the more concentrated solutions [10], where the extraction of copper proceeds more efficiently. It should be noted that due to the low concentrations of ions and the course of the competing reaction of electrochemical decomposition of water with the evolution of hydrogen and oxygen, the outputs for currents were very low in both cases. At the same time, while the output for current in the concentrated solutions, when recovering these metals, amounted to 50–90 % and dramatically decreased with a decrease in the concentration of metals, in the diluted solutions it reached (4–20)·10⁻⁴ % and changed little with a change in concentration. This is due to the fact that the concentration of ions was so low that the bulk of electric power was used for competing processes – mainly on the electrolysis of water.

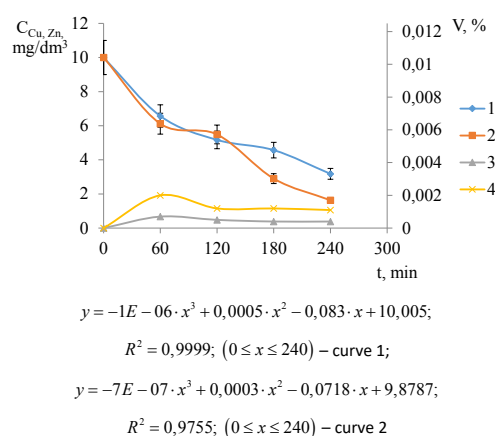
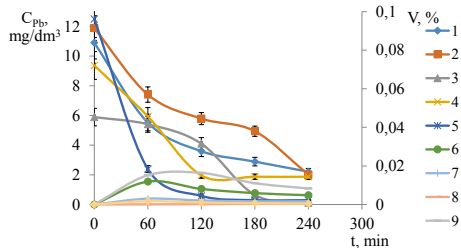


Fig. 1. A change in the concentration of copper (1) and zinc (2), in the output for current (3; 4) in a solution of distilled water over the duration of electrolysis at initial pH of the solution 5.94 (1; 3) and 7.17 (2; 4), voltage 31 V (1; 3) and 25 V (2; 4) at amperage 0.4 A (1; 3) and 1.57 A (2; 4)

Similar results were obtained during electrolysis of solutions of lead chloride in distilled water (Fig. 2). In this case,

at a starting concentration of lead of 10 mg/dm³, its residual concentrations decreased to 2.01–2.21 mg/dm³, and at a starting concentration of 5.89 mg/dm³, its residual concentration was 0.12 mg/dm³. The output for current was also the same as for copper and quite low for zinc.



$$y = 0,0002 \cdot x^2 - 0,084 \cdot x + 10,543; \quad R^2 = 0,9797; (0 \leq x \leq 240) - \text{curve 3};$$

$$R^2 = 0,9758; (0 \leq x \leq 240) - \text{curve 1}; \quad y = 0,0002 \cdot x^2 - 0,083 \cdot x + 9,5517;$$

$$y = -2E-06 \cdot x^3 + 0,0008 \cdot x^2 - 0,1145 \cdot x + 11,901; \quad R^2 = 0,9778; (0 \leq x \leq 240) - \text{curve 4};$$

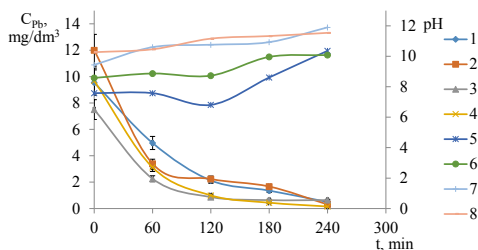
$$R^2 = 0,9998; (0 \leq x \leq 240) - \text{curve 2}; \quad y = -3E-06 \cdot x^3 + 0,0015 \cdot x^2 - 0,2434 \cdot x + 12,421;$$

$$y = 1E-06 \cdot x^3 + 0,0006 \cdot x^2 - 0,0285 \cdot x + 5,7984; \quad R^2 = 0,996; (0 \leq x \leq 240) - \text{curve 5}$$

Fig. 2. A change in the concentration of lead (1; 2; 3; 4; 5), in the output for current (6; 7; 8; 9; 10) over the duration of electrolysis of a solution of lead chloride in distilled water (1; 2; 3; 6; 7; 8) at concentration of Na₂SO₄ 100 mg/dm³ (1; 6) and 200 mg/dm³ (2; 3; 7; 8), tap (4; 9) and softened tap water (5; 10) at initial pH 5.81 (1; 2; 3; 6; 7; 8); 7.15 (4; 9); 10.31 (5; 10) and amperage 0.012 A (1; 6); 0.040 A (2; 7); 0.14 A (3; 8); 0.06 A (4; 9); 0.156 A (5; 10)

5. 2. Influence of pH of the medium on the effectiveness of electroextraction of ions of heavy metals from diluted solutions

Solutions had a starting pH value at the level of 5.81. When increasing the pH of solutions, lead removal efficiency increased (Fig. 3). At pH 7.58 and 8.58, the concentration of lead decreased over 4 hours from 10 mg/dm³ to 0.50 and 0.31 mg/dm³, respectively. At pH=10.27, the concentration decreased to 0.155 mg/dm³.



$$y = 0,0002 \cdot x^2 - 0,0815 \cdot x + 9,4026; \quad R^2 = 0,9922; (0 \leq x \leq 240) - \text{curve 1};$$

$$y = -3E-06 \cdot x^3 + 0,0014 \cdot x^2 - 0,2119 \cdot x + 11,922; \quad R^2 = 0,9951; (0 \leq x \leq 240) - \text{curve 2};$$

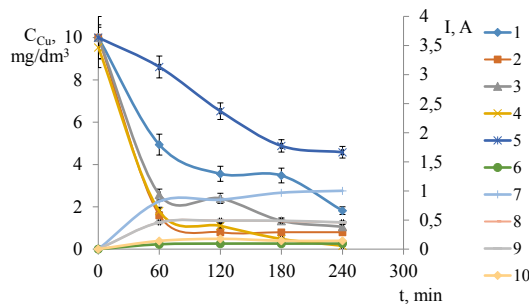
$$y = 0,0002 \cdot x^2 - 0,081 \cdot x + 7,1129; \quad R^2 = 0,9608; (0 \leq x \leq 240) - \text{curve 3};$$

$$y = 0,0003 \cdot x^2 - 0,1034 \cdot x + 9,24; \quad R^2 = 0,9719; (0 \leq x \leq 240) - \text{curve 4}$$

Fig. 3. A change in the concentration of lead (1; 2; 3; 4) and pH (5; 6; 7; 8) of the solution of distilled water, containing 200 mg/dm³ of Na₂SO₄ due to the duration of electrolysis at a voltage of 20 V at initial pH 7.5 (1; 5); 8.5 (2; 6); 9.5 (3; 7); and 10.5 (4; 8)

The extraction of ions of lead in tap water (Fig. 2) also occurs quite effectively, similar to this process in softened water.

Similar results were obtained during electrolysis of copper sulfate in tap water and softened tap water (Fig. 4). It is obvious that this is due to an increase in pH in tap water, as well as a reduction of the negative impact of hardness ions, which, during hydrolysis on the cathode, reduce the electrical conductivity of the system. Note that the output for current is not significantly affected because this indicator is very low at the expense of a concentration factor.



$$y = -2E-06 \cdot x^3 + 0,0009 \cdot x^2 - 0,1311 \cdot x + 10,007; \quad R^2 = 0,9999; (0 \leq x \leq 240) - \text{curve 1};$$

$$y = -3E-06 \cdot x^3 + 0,0014 \cdot x^2 - 0,2066 \cdot x + 9,9143; \quad R^2 = 0,9921; (0 \leq x \leq 240) - \text{curve 2};$$

$$y = -2E-06 \cdot x^3 + 0,0012 \cdot x^2 - 0,1728 \cdot x + 9,8603; \quad R^2 = 0,9751; (0 \leq x \leq 240) - \text{curve 3};$$

$$y = -3E-06 \cdot x^3 + 0,0012 \cdot x^2 - 0,1848 \cdot x + 9,4305; \quad R^2 = 0,988; (0 \leq x \leq 240) - \text{curve 4};$$

$$y = 5E-05 \cdot x^2 - 0,0368 \cdot x + 10,208; \quad R^2 = 0,9812; (0 \leq x \leq 240) - \text{curve 5}$$

Fig. 4. Dependence of the residual concentration of copper ions (1; 2; 3; 4; 5) and amperage (6; 7; 8; 9; 10) during electrolysis of the solution of copper sulfate in softened tap water (1; 2; 3; 4; 6; 7; 8; 9) and tap water (5; 10) at initial pH: 10.30 (1; 2; 3; 6; 7; 8); 8.00 (4; 9); 7.15 (5; 10)

5. 3. Removal of ions of heavy metals from diluted solutions using an electrolysis method in two-chamber electrolyzers

It should be noted that in a two-chamber electrolyzer the efficiency of removal of ions of heavy metals increases, independent of pH of the medium and the concentration of hardness ions (Fig. 5). Thus, the concentration of copper ions in tap water at pH=6.82 decreases over 4 hours from 10 to 0.28 mg/dm³, whereas in softened water at pH=10.3 it reduces from 10 to 0.67 mg/dm³. The concentration of zinc is reduced to 0.07 mg/dm³, below the permissible norms for discharge into sewage, in drinking water or natural water for domestic purposes.

In general, a given electrolyzer makes it possible to not only post-purify wastewater to acceptable levels, but also provides an opportunity to clean natural water to a drinking water quality. In this case, water can be effectively purified regardless of the level of water hardness and pH of the medium.

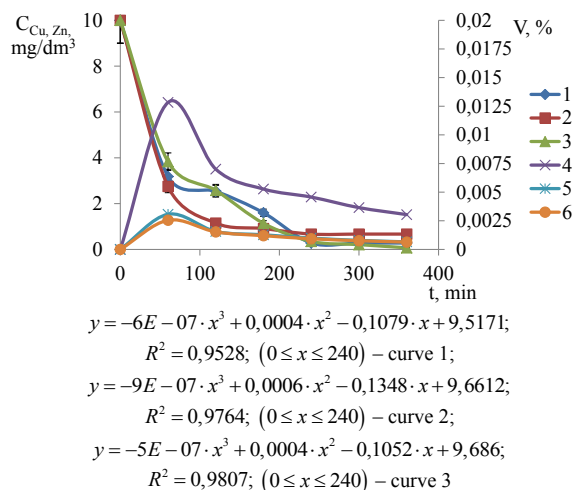
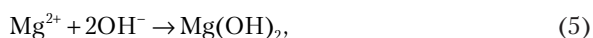


Fig. 5. A change in the concentration of copper ions (1; 2) and zinc (3), in the output for current (4; 5; 6) over the duration of electrolysis of the solution of ions in tap water (1; 4), softened tap water (2; 3; 5; 6) in a two-chamber electrolyzer at initial pH 6.82 (1; 4) and 9.55 (2; 3; 5; 6) at amperage 0.045 A (1; 4); 0.2 A (2; 3; 5; 6)

6. Discussion of results of studying the electrochemical removal of heavy metals from water

As one can see from the results shown in Fig. 1, 4, 5, in the course of electrolysis of aqueous solutions of heavy metals we observed a decrease in the residual concentration of metals over the duration of electrolysis. Though, as it is known from [23], when determining heavy metals polarographically, the recovery on cathodes occurs at considerably lower concentrations, to 10^{-5} mg/dm³. However, in this case specific electrodes are employed – mercury, silver, gold, platinum. The electrodes are cleaned from impurities in certain ways.

We used a standard electrode made of stainless steel, which can be partially covered with the products of metal oxidation. In addition, the tap and partially softened water always contain the hardness ions. As a result of the medium alkalization on the cathode due to reaction (4), they can deposit on the cathode in the form of metal hydroxides (reactions 5; 6). This process leads to the passivation of the cathode and impedes the recovery of metals in reaction (7).



where M^{2+} are the ions of metals Zn^{2+} , Cu^{2+} , Pb^{2+} .

Removal of trace amounts of heavy metals can occur by the hydrolysis on the cathode as well. In this case, there are no visible deposits of a metal hydroxide or a free metal. It is known that heavy metals' ions pass into the state of hydroxides at pH>8.5–9.5. However, when treating tap water that contained lead in a concentration of 10 mg/dm³

with a solution of soda with the consequent taking the pH to 10.5, settling and filtration, the residual concentration of lead was 8.46 mg/dm³. That is, despite the high content of carbonate and hydroxide ions in water, the bulk of lead remained in the solution. That occurs even though the product of solubility of $PbCO_3$ is $7.5 \cdot 10^{-14}$, $Pb(OH)_2 - 1 \cdot 10^{-24}$.

Similar results were obtained when using solutions of sulfates of zinc and copper in softened water whose pH was 9.53–10.35. In these solutions, the concentrations of ions of copper and zinc reached ≈ 10 mg/dm³. Most likely, the result of electrolysis was the reduction of heavy metals' ions regardless of the degree of hydrolysis, while residual concentrations in water were determined by the content of unhydrolyzed and hydrolyzed ions. This is confirmed by the results of post-purification of the solution of lead chloride, treated in the electrolyzer, in softened water at an ultrafiltering installation (Table 1). We used the ultrafiltering membrane OPMN-P. The voltage was 6 V, the amperage was 0.1 A. A starting concentration of lead was 10 mg/dm³, pH of the solution was 10.28, $H=1.2$ mg-equiv./dm³, $A=30$ mg-equiv./dm³.

At the beginning, when the degree of recovery (removal) of lead (Z) was 5.6 %, the residue of the metal in water was in the hydrolyzed state and it was removed from the ultrafiltering membrane by 99 %. Next, with an increase in the degree of lead recovery to 85 %, its part in the ion state in a solution increased to 0.85–1.015 mg/dm³ or to 85–99 %, while the degree of cleaning via electrolysis and ultrafiltration decreased to 90 %.

Even though at hydrolysis and ultrafiltration the removal of lead ions occurs faster than that during electrolysis, a given method has advantages. First of all, the concentrates that are difficult to recycle do not form. In addition, there is no need to wash the membranes and there is a possibility to purify water under continuous mode in a wide range of medium's pH. Moreover, the application of ultrafiltration to remove copper and zinc was less effective.

Table 1

Dependence of purification efficiency of a lead chloride solution on electrolysis duration

t , hours		0	1	2	3	4
pH	I	10.27	10.23	10.36	10.46	10.55
	II	10.27	10.08	10.20	10.25	10.34
C_{Pb} , mg/dm ³	I	10.00	9.44	5.28	3.47	1.47
	II	10.00	0.08	0.85	0.99	1.015
H, mg-equiv./dm ³	I	1.20	1.18	1.08	1.02	0.99
	II	1.20	0.80	0.52	0.44	0.36
Purification degree Z, %	I	0.00	5.60	47.20	65.30	85.30
	II	0.00	99.18	91.50	90.10	89.85

Note: I – after electrolysis; II – after electrolysis and ultrafiltration

When applying electrolysis at the concentrations of heavy metals at the level of 10 mg/dm³, the degree of removal in the one-chamber electrolyzers amounted to 68–89 % for copper, 84 % for zinc, and 95–98.5 % for lead (Table 2). In the two-chamber electrolyzers, the degree of removal of zinc amounted to 99.3 %, lead – 97.2 %.

Table 2
Dependence of the degree of extraction of heavy metals' ions from aqueous solutions in a one-chamber electrolyzer

t, hours	Purification degree Z, %											
	Water	Distilled							Tap		Softened	
	Metal	Zn	Cu	Pb				Cu	Pb	Cu	Pb	
	pH	7.17	5.98	6.82	7.58	8.51	9.44	10.3	7.16	7.10	10.32	10.31
1	38.8	34.3	8.3	50.3	66.0	77.4	68.8	50.6	40.6	74.2	76.1	
2	45.1	48.3	30.5	78.7	77.6	91.3	90.0	64.4	80.4	76.0	94.2	
3	71.0	54.3	89.1	86.4	83.3	93.6	95.6	65.7	81.3	86.6	97.1	
4	83.7	68.2	98.0	95.0	96.9	93.6	98.5	81.8	84.9	89.4	97.1	

It is interesting to note that during electrolysis, or electrolisis and ultrafiltration, there occurs the partial softening of water (Table 1).

In general, the effectiveness of water purification from the ions of heavy metals via electrolysis increases with an increase in pH of the medium and a decrease in water hardness. In the two-chamber electrolyzers, these factors almost do not affect the effectiveness of water purification.

The results obtained indicate the prospects of using a method of electrolysis for the selective removal of heavy metals from tap water, softened, or natural water. This method of purification will not only make it possible to post-purify wastewater to the maximally permissible concentrations for heavy metals' ions, but also to purify water from natural sources to the quality of drinking water. The main draw-

backs of the method are the low values of the output for current, due to the low starting concentrations of solutions. That is why, when treating large volumes of solutions, such a method will be characterized by high energy consumption. Effective application of a given method can be considered appropriate only when treating small volumes of solutions.

7. Conclusions

1. It is shown that the degree of removal of ions of zinc, copper and lead from aqueous solution when using an electrolysis method at concentrations of 10 mg/dm³ in one- and two-chamber electrolyzers is from 68 % to 99.3 %.

2. It was established that the effectiveness of electroextraction of metals from aqueous diluted solutions in one-chamber electrolyzers increases with a decrease in water hardness and an increase in pH of the medium, and in two-chamber electrolyzers it is high regardless of pH of the medium and water hardness.

3. It is shown that at low concentrations of heavy metals' ions in water (≈ 10 mg/dm³) when removing using the method of electroextraction the output for current is low ($\approx 10^{-2}$ – 10^{-4} %) and changes little over the duration of electrolysis and at a change in the residual concentration of metals in water, the efficiency of zinc extraction amounted to 99.3 %, that of lead – 97.2 %.

References

- Dubinina A. A., Ovchinnikova I. E., Petriv V. O. Vyznachennia vmistu vazhkykh metaliv u vynohradnomu vyny "Kahor" vitchyznianoho vyrobnytstva // Prohresyvni tekhnika ta tekhnolohiyi kharchovykh vyrobnytstv restorannoho hospodarstva i torhivli. 2012. Issue 1. P. 224–229.
- Ramazanov A. Sh., Esmail G. Q., Sveshnikova D. A. Kinetics and thermodynamics of sorption of heavy metal ions on the clay containing montmorillonite // Sorbcionnye i hromatograficheskie processy. 2015. Vol. 15, Issue 5. P. 672–682.
- Homelia M. D., Malin V. P., Halimova V. M. Kontsentruvannia ioniv midi ta vyznachennia efektyvnosti yii desorbtsiyi z kationitiv v dynamichnykh umovakh // Problemy vodopostachannia, vodovidvedennia ta hidravliki. 2016. Issue 27. P. 78–84.
- Novel adsorbent based on silkworm chrysalides for removal of heavy metals from wastewaters / Paulino A. T., Minasse F. A. S., Guilherme M. R., Reis A. V., Muniz E. C., Nozaki J. // Journal of Colloid and Interface Science. 2006. Vol. 301, Issue 2. P. 479–487. doi: <https://doi.org/10.1016/j.jcis.2006.05.032>
- Heavy metal ions removal from metal plating wastewater using electrocoagulation: Kinetic study and process performance / Al-Shannag M., Al-Qodah Z., Bani-Melhem K., Qtaishat M. R., Alkasrawi M. // Chemical Engineering Journal. 2015. Vol. 260. P. 749–756. doi: <https://doi.org/10.1016/j.cej.2014.09.035>
- Arbabi M., Hemati S., Amir M. Removal of lead ions from industrial wastewater: A review of removal methods // International Journal of Epidemiologic Research. 2015. Vol. 2, Issue 2. P. 105–109.
- Ekologiya ochistki stochnykh vod fiziko-himicheskimi metodami / Serpokyrov N. S., Vil'son E. V., Getmancev S. V., Marochkin A. A. Moscow, 2009. 264 p.
- Lukasheva G. N., Butkevich D. M. Analiz sravnitel'nykh ispytaniy koagulyantov pri ochistke vody // Tekhnologiya nefi i gaza. 2008. Issue 4. P. 16–20.
- Gomelya N. D., Krasil'nikova T. N. Ocenka effektivnosti alyuminievykh koagulyantov pri ochistke stochnykh vod // Ekotekhnologii i resursoberezhenie. 2007. Issue 1. P. 53–56.
- Electroextraction of heavy metals from wastewater for the protection of natural water bodies from pollution / Gomelia N., Trokhymenko G., Hlushko O., Shabliy T. // Eastern-European Journal of Enterprise Technologies. 2018. Vol. 1, Issue 10 (91). P. 55–61. doi: <https://doi.org/10.15587/1729-4061.2018.123929>
- Izvlachenie kationov Pb i Cu iz rastvorov s pomoshch'yu kompozitsionnogo sorbenta na osnove PETF / Buharova E. A., Tatarinceva E. A., Ol'shanskaya L. N., Shayhiev I. G. // Vestnik Kazanskogo tekhnologicheskogo universiteta. 2014. Vol. 17, Issue 3. P. 34–37.

12. Removal of nickel(II) ions from aqueous solutions using the natural clinoptilolite and preparation of nano-NiO on the exhausted clinoptilolite / Rajic N., Stojakovic D., Jovanovic M., Logar N. Z., Mazaj M., Kaucic V. // *Applied Surface Science*. 2010. Vol. 257, Issue 5. P. 1524–1532. doi: <https://doi.org/10.1016/j.apsusc.2010.08.090>
13. Strategies based on silica monoliths for removing pollutants from wastewater effluents: A review / Rodrigues D., Rocha-Santos T. A. P., Freitas A. C., Gomes A. M. P., Duarte A. C. // *Science of The Total Environment*. 2013. Vol. 461-462. P. 126–138. doi: <https://doi.org/10.1016/j.scitotenv.2013.04.091>
14. Filatova E. G. Wastewater treatment from heavy metal ions, based on the physico-chemical processes // *Izvestiya vuzov. Prikladnaya himiya i biotekhnologiya*. 2015. Issue 2 (13). P. 97–109.
15. Fedorova E. K., Bil'chenko N. G. Ochistka stochnykh vod gal'vanicheskikh proizvodstv // *Vestnik magistratury*. 2014. Issue 12-1 (39). P. 66–68.
16. Elektroliticheskoe izvlechenie ionov tyazhelykh metallov iz solyanokislykh rastvorov / Gomelya N. D., Glushko E. V., Gomelya N. D., Trohimenko A. G. // *Energotekhnologii i resursoberezhenie*. 2017. Issue 1. P. 60–67.
17. Elektroekstrakciya svinca iz svincovo-trilonatnogo rastvora / Anisimova O. S., Sergeev V. A., Mamyachenkov S. V., Karelov S. V., Sergeeva Yu. F. // *Izvestiya vuzov. Cvetnaya metallurgiya*. 2013. Issue 1. P. 17–21.
18. Al Aji B., Yavuz Y., Koparal A. S. Electrocoagulation of heavy metals containing model wastewater using monopolar iron electrodes // *Separation and Purification Technology*. 2012. Vol. 86. P. 248–254. doi: <https://doi.org/10.1016/j.seppur.2011.11.011>
19. Hanay Ö., Hasar H. Effect of anions on removing Cu^{2+} , Mn^{2+} and Zn^{2+} in electrocoagulation process using aluminum electrodes // *Journal of Hazardous Materials*. 2011. Vol. 189, Issue 1-2. P. 572–576. doi: <https://doi.org/10.1016/j.jhazmat.2011.02.073>
20. Treatment of electroplating wastewater containing Cu^{2+} , Zn^{2+} and Cr(VI) by electrocoagulation / Adhoum N., Monser L., Bellakhal N., Belgaied J. // *Journal of Hazardous Materials*. 2004. Vol. 112, Issue 3. P. 207–213. doi: <https://doi.org/10.1016/j.jhazmat.2004.04.018>
21. Shabliy T. O., Homelia M. D., Panov Ye. M. Elektrokhimichna pererobka vidpratsovanykh rozchyniv, shcho utvoriuiutsia pry reheneratsiyi kationitiv // *Ekologiya i promyshlennost'*. 2010. Issue 2. P. 33–38.
22. Determination of heavy metals in water ecosystem on the basis of method inversion chronopotentiometric / Surovtsev I. V., Galimova V. M., Mank V. V., Kopilevich V. A. // *Himiya i tekhnologiya vody*. 2009. Vol. 31, Issue 6. P. 677–687.
23. Malin V. P., Galimova V. M., Gomelya N. D. Evaluating the effectiveness of KU-2-8 at extraction copper ions from water in the presence of hardness ions // *Voda i vodoochysni tekhnologiyi. Naukovo-tekhnicni visti*. 2016. Issue 2. P. 10–18.