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Досліджено процеси електрохімічного видалення іонів кадмію та цинку окремо і в суміші з розчинів сірчаної або соляної кислот в одно- та двокамерних електролізерах. Показано графічну залежність виходу за струмом важких металів від початкових характеристик розчинів та умов процесу. Доведена перспективність використання електролізу для селективного видалення важких металів із суміші з кислих розчинів

Ключові слова: іонний обмін, електрохімічні методи очищення води, стічні води, відпрацьований регенераційний розчин

Исследованы процессы электрохимического удаления ионов кадмия и цинка отдельно и в смеси из растворов серной или соляной кислот в одно- и двухкамерных электролизерах. Показана графическая зависимость выхода по току тяжелых металлов от начальных характеристик растворов и условий процесса. Доказана перспективность использования электролиза для селективного удаления тяжелых металлов из смеси из кислых растворов

Ключевые слова: ионный обмен, электрохимические способы очистки воды, сточные воды, отработанный регенерационный раствор

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ELECTROEXTRACTION OF HEAVY METALS FROM WASTEWATER FOR THE PROTECTION OF NATURAL WATER BODIES FROM POLLUTION

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1. Introduction

In the classic sense, the class of “heavy metals” includes zinc, chromium, copper, cadmium, cobalt, nickel, arsenic, selenium, silver, antimony, mercury, thallium and lead. Com-

pounds of these elements as well as the elements themselves are toxic [1]. About 70 % of toxic metals get into a human body with food. The most dangerous toxic elements in foods to be controlled are mercury, cadmium, lead, arsenic, copper, tin, zinc, and iron. High probability of population poisoning

with heavy metals is associated with the use of poor-quality drinking water [2], in which the concentration of heavy metals increases as a result of eutrophication of water bodies [3].

Unfortunately, water supply sources are at the same time the places of wastewater discharge. Typical urban water treatment stations do not include the stage of extraction of ions of heavy metals from wastewater. That is why these toxicants should be completely extracted at local water treatment plants. As a result of imperfection of water treatment technologies, a significant amount of industrial waste, including heavy metals [4], gets into water bodies. The main industrial productions that pollute the environment with heavy metals include metallurgical and chemical plants, metal treatment enterprises, ore concentration enterprises, cellulose and paper producing enterprises, power engineering, and mines. In the world and in particular in Ukraine, there is a considerable number of such enterprises. That is why removal of heavy metal ions from industrial wastewater is a relevant and global problem.

2. Literature review and problem statement

The methods, most often used for heavy metals removal from water, include the reagent [5], the sorption [6], the baromembrane [7] methods and the ion exchange method [8]. To remove iron compounds, one uses the methods of catalytic oxidation [9].

The benefits of reagent method [5] include simplicity of toxicants extraction and availability of reagents-precipitators, simplicity of equipment and the ease of the process control. The drawbacks include incomplete removal of contaminants, irreversible loss of valuable substances with sediments, and the problem of recycling of received sediments.

For deep purification of wastewater from weakly concentrated and heavy metals, it is advisable to use the baromembrane and sorption methods, as well as the ion exchange.

The advantages of sorption methods include the possibility of simultaneous wastewater purification from heavy metals ions, chromaticity, turbidity, chloral organic compounds, radionuclides, and oil products. In addition, positive sides of these methods are independence of the process efficiency on process fluctuations in concentrations of contaminants, possibilities of treatment at low temperatures of water, reduction of the use of chemical reagents, simplicity, efficiency and reliability of the technological process.

It is possible to clean water from ammonia and heavy metals by using mineral sorbents [10]. However, after exhaustion of the capacity of a sorbent, there arises the problem of regeneration or disposal of waste material, determining parameters of the desorption process in case of the sorbent reuse, and the methods of recycling of concentrated solutions.

Baromembrane processes are characterized by high quality of obtained water (although, for example, nanofiltration is highly selective to two-valence ions (up to 99 % and slightly selective to one-valence ions (40–60 %) [11]). In technological terms, these methods are characterized by small dimensions of equipment, relatively low maintenance and energy costs. Disadvantages of baromembrane methods include relatively low productivity, considerable capital costs, the need for thorough preliminary preparation of water, significant amounts of liquid wastes-concentrates (20–25 %), complexity of concentrates' recycling before dumping into the drain.

The most common method of extraction of heavy metals ions [12] from low-concentrated solutions is ion exchange. The reasons why it takes the leading positions are:

- possibility of wastewater treatment to assigned concentrations;
- low power costs;
- concentration of pollutants to the degree that ensures the possibility of further disposal;
- absence of costs for expensive reagents;
- process controllability.

Similar to other described methods, the ion exchange method has its shortcomings, among which the main problem is recycling of eluates.

Under industrial conditions, recycling of the used regeneration solutions is performed by evaporation or by reagent methods [12, 13]. However, the use of evaporation is limited to significant power consumption, and restrictions for the use of the reagent method are described above. That is why the most promising methods of eluates recycling are electrolysis and electrodialysis [14], which are used for water desalting.

At the same time, possibilities of separation of metals in the process of recycling of the latter by electrolysis have not been sufficiently studied so far. The issue of reduction of ions of metals, which precede hydrogen in the electromotive series, in single-chamber electrolyzers in acidic medium, remains unresolved. The ionite is used inefficiently during separation of heavy metals ions on ionites in the sorption processes and large amounts of regeneration solutions with low concentrations of metals are formed [15]. This approach is important only in analysis of mixtures of metals. In addition, it is not applicable at cleaning water from ions of heavy metals, when the problems of metal concentration and complete extraction of the latter from eluates in the form of a metal powder become urgent [16].

Extraction of zinc, nickel and other metals that force hydrogen from aqueous solutions of acids in double- and three-chamber electrolyzers [16] is accompanied by the use of expensive membranes, low reliability of the latter and significant power consumption.

That is why nowadays the issues of separation of heavy metals during electroextraction of ions from water solutions are acute in the problems of waste-free water treatment. The issue of determining conditions of extraction of active metals from acidic aqueous media at single-chamber electrolyzers also remains unresolved.

It is known that ions of such heavy metals as copper, cadmium, lead and other metals, which follow hydrogen in the activity series, are easily reduced electrochemically, even from acidic solutions. Such metals as zinc and nickel are reduced from acidic solutions only at high concentrations of more than 90–100 g/dm³. Moreover, while zinc can be easily reduced in a neutral medium, nickel is reduced with high current efficiency only in weakly acid medium (pH 3–4) [16]. That is why selection of conditions for efficient removal of metals from the used regeneration solutions by electroextraction is an important and a relevant problem.

3. The aim and objectives of the study

The aim of present research was to create environmentally friendly processes of extraction of heavy metals from wastewater using ion exchange, to determine conditions of energy saving in processes of electroextraction of metals

from eluates and to establish parameters of their electrochemical separation.

To accomplish the set goal, the following tasks must be solved:

- to explore the processes of electroextraction of heavy metals from acidic regeneration solutions on condition of obtaining pure metals and solutions of acids, suitable for reusing, in order to create waste-free technologies of water purification from heavy metals;

- to determine dependence of electricity consumption on composition of solutions and the structure of electrolyzers in order to decrease power consumption in the processes of electroextraction of metals;

- to determine conditions for separation of heavy metals in processes of electroextraction in order to enable bringing valuable components back to the production.

4. Materials and methods for studying zinc and cadmium removal from aqueous solutions by electrochemical method

In the process of the studies, we applied single- and double-chamber electrolyzers, in which a cathode from stainless steel and a titanium anode, covered with ruthenium oxide, were used. The cathode and the anode areas in double-chamber electrolyzers were separated by the anion-exchange membrane MA-41.

During application of the double-chamber electrolyser, solution of cadmium sulfate or zinc sulfate was found in the cathode chamber. Solution of sulfuric acid with the concentration of 50 mg-equiv./dm³ was in the anode chamber.

We used separately solutions of cadmium sulfate and zinc sulfate in different concentrations of ions of heavy metals ($[Cd^{2+}] = 92\text{--}5,508$ mg/dm³, $[Zn^{2+}] = 120\text{--}128$ mg/dm³) and sulfuric acid ($[H_2SO_4] = 98\text{--}540$ mg-equiv./dm³) as model solutions. In addition, we used a mixture of chlorides of cadmium and zinc in different ratios of ions of metals and hydrochloric acid ($[Cd^{2+}] + [Zn^{2+}] = 244\text{--}254$ mg/dm³, $[HCl] = 106\text{--}530$ mg-equiv./dm³). Subsequently, we used the mixture of sulfates of cadmium and zinc in different ratios of ions of metals and sulfuric acid ($[Cd^{2+}]:[Zn^{2+}] = 400:400$ mg/dm³, $[H_2SO_4] = 0\text{--}624$ mg-equiv./dm³).

In the course of the study, acidity and concentration of heavy metals ions in solutions were determined in the same intervals of time [16].

Current efficiency (B, %) was calculated as the ratio of the determined amount of metals, removed from the solution of cadmium and zinc, to theoretically estimated amount of metals.

5. Results of the study of electrochemical release of heavy metals ions from used regeneration solutions

At the first stage of the research, we carried out the studies of removal of metallic cadmium and obtaining an acid from cadmium sulfate solutions of different initial concentration and varying acidity in a single-chamber electrolyser (Fig. 1, 2). In the figures hereinafter, the lines, connecting experimental points, are not approximating curves, but are rather given for clarity and improved visualization of results.

As Fig. 1, 2 show, release of cadmium in a single-chamber electrolyser flows quite effectively at the voltage of 5V. The

bulk of metal is released from the solution within two hours, and at concentration of sulfuric acid of 490 mg-equiv./dm³, the bulk of cadmium is removed within one hour. This is caused by the fact that electric conductivity of the solution increases with the increased concentration of acid, which enables an increase in current strength.

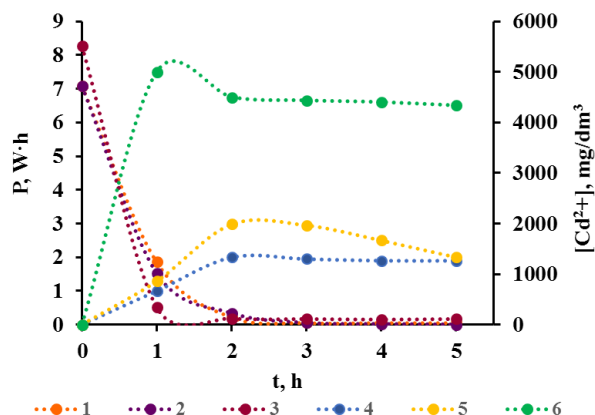


Fig. 1. Dependence of cadmium concentration (1; 2; 3) and electric power consumption for cadmium reduction (4; 5; 6) on duration of electrolysis of acidic solution of cadmium sulfate at voltage of 5 V in single-chamber electrolyser ($V=0.1$ dm³) at initial cadmium concentrations (mg/dm³) and sulfuric acid (mg-equiv./dm³): 1, 4 – 4,721, 98; 2, 5 – 4,721, 250; 3, 6 – 5,508, 490

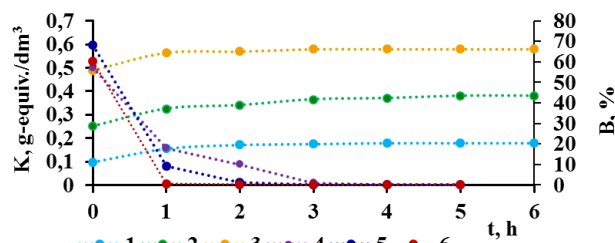


Fig. 2. Dependence of acidic solution (1; 2; 3) and current efficiency of metallic cadmium (4; 5; 6) on duration of electrolysis of acidic solution of cadmium sulfate at voltage of 5 V in single-chamber electrolyser ($V=0.1$ dm³) at initial cadmium concentrations (mg/dm³) and sulfuric acid concentrations (mg-equiv./dm³): 1, 4 – 4,721, 98; 2, 5 – 4,721, 250; 3, 6 – 5,508, 490

At a decrease in cadmium concentration in the solution, acidity increases, which generally ensures relatively high values of current strength, however, current efficiency at reduction of cadmium significantly decreases. It is explained only by the concentration factor.

In the case of cadmium reduction in a double-chamber electrolyser (Table 1), at the use of acidic solution of cadmium sulfate, intensity of reduction of metal increases at an increase in acidity of the solution, like in a single-chamber electrolyser. In this case, at acidity of 250 and 540 mg-equiv./dm³, almost complete removal of cadmium was achieved respectively in 5 and 3 hours.

Zinc reduction does not take place during electrochemical reduction of zinc from the used acid regeneration solution in a single-chamber electrolyser. Only water electrolysis with release of hydrogen and oxygen takes place.

Table 1

Dependence of effectiveness of cadmium release in double-chamber electrolyser (membrane MA-41) on duration of electrolysis at voltage of 25 V at acidity of solutions (H_2SO_4) mg-equiv./dm³: 100 (I), 250 (II), 540 (III)

<i>t</i> , h	[Cd ²⁺], mg/dm ³			<i>P</i> , W·h			<i>K</i> , mg-equiv./dm ³						<i>B</i> , %		
							catholyte			anolyte					
	I	II	III	I	II	III	I	II	III	I	II	III			
0	92.0	92.0	96.0	—	—	—	100	250	540	50	50	50	—	—	—
1	32.0	31.0	32.5	3.75	4.50	9.00	114	270	540	96	100	264	100	100	98.7
2	16.1	14.0	5.2	1.75	2.00	4.60	120	270	420	100	118	316	77.4	80.3	9.5
3	8.0	1.4	2.1	1.25	1.75	1.25	128	255	370	106	136	375	42.8	69.6	1.5
4	4.0	0.8	0.0	0.75	1.00	1.00	130	250	—	106	141	—	35.7	8.4	—
5	2.0	0.4	—	0.50	0.75	—	132	250	—	108	142	—	26.8	5.2	—
6	1.8	0.0	—	0.25	0.25	—	124	250	—	114	142	—	5.4	5.2	—
7	1.6	—	—	0.25	0.00	—	124	250	—	116	142	—	5.2	—	—
8	1.2	—	—	0.25	—	—	108	—	—	130	—	—	5.0	—	—

Zinc is reduced quite effectively in a double-chamber electrolyser (Table 2). In this case, at the first stage of the process, acidity in the catholyte decreases from 100–560 mg-equiv./dm³ to 30–60 mg-equiv./dm³ followed by zinc reduction.

Acidity increases at zinc reduction and sulfates diffusion in the anode area during electrolysis.

As a result of studying effectiveness of cationites regeneration depending on ions of heavy metals, it is observed that hydrochloric acid ensures higher effectiveness of desorption of metal ions in comparison with sulfuric acid. However, the main drawback of hydrochloric acid is complexity of recycling of the used regeneration solutions. Electrodes are quickly destroyed in the process of electrochemical reduction of heavy metals in the presence of chlorides. In addition, release of active chlorine occurs on the anode [16].

However, acidity of the solution decreases at oxidation of chlorides in a single-chamber electrolyser or at diffusion of chlorides from catholyte in two- and three-chamber electrolyses, which contributes to effective reduction of zinc ions.

Interesting results were obtained during electrolysis of the solution of a mixture of hydrochloric zinc and cadmium in the presence of hydrochloric acid in a single-chamber electrolyser. In this case, both cadmium ions and zinc ions are released from the solution almost completely (Fig. 3–5). Cations concentration was controlled by trilonometry, which makes it possible to determine only the total concentration of metals.

It should be noted that at the initial acidity of the solution of 106 mg-equiv./dm³ within the first two hours of

electrolysis, acidity increases up to 130–134 mg-equiv./dm³. Subsequently, due to release of hydrogen on the cathode and of chlorine on the anode, concentration of hydrochloric acid in solution decreases up to 50–60 mg-equiv./dm³. Zinc ions are reduced quite effectively under such conditions, which enables efficient removal of metals from the solution. Current efficiency of metals is not high and reaches 30–68 %.

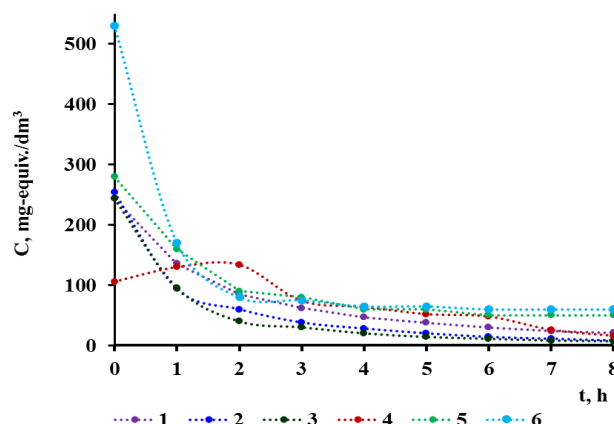


Fig. 3. Change in total concentration of zinc and cadmium ions (1; 2; 3), hydrochloric acid (4; 5; 6) over time of electrolysis of solutions of cadmium, zinc chlorides and hydrochloric acid 5 V at total concentration of zinc, cadmium and hydrochloric acid, mg-equiv./dm³: 1, 4 – 244, 106; 2, 5 – 254, 280; 3, 6 – 244, 530

Table 2

Dependence of effectiveness of zinc release in double-chamber electrolyser (membrane MA-41) on duration of electrolysis at voltage of 25 V at acidity of solutions (H_2SO_4), mg-equiv./dm³: 100 (I), 250 (II), 540 (III)

<i>t</i> , h	[Zn ²⁺], mg/dm ³			<i>P</i> , W·h			<i>K</i> , mg-equiv./dm ³						<i>B</i> , %		
							catholyte			anolyte					
	I	II	III	I	II	III	I	II	III	I	II	III			
0	128	127	120	—	—	—	100	250	560	50	50	50	—	—	—
1	75.0	83	85	8.00	12.25	13.25	32	60	60	171	284	585	42.5	17.3	14.0
2	20.0	29	32	4.75	9.75	9.25	33	45	50	221	327	628	72.7	76.4	67.9
3	15.0	20	16	0.75	1.75	3.50	32	35	40	226	339	640	80.4	61.6	72.7
4	13.0	14	13	0.25	1.25	1.25	29	35	40	231	343	641	53.7	52.4	45.5
5	12.0	10	12	0.25	0.75	0.75	29	30	35	234	342	643	26.9	35.7	13.4
6	11.7	8	8	0.25	0.75	0.75	28	30	30	238	343	642	26.9	17.9	8.6
7	11.5	6	2	0.25	0.75	0.75	26	30	30	239	344	642	16.1	16.9	8.4
8	11.5	4	1	0.25	0.75	0.75	24	30	30	239	343	641	10.8	16.5	8.2

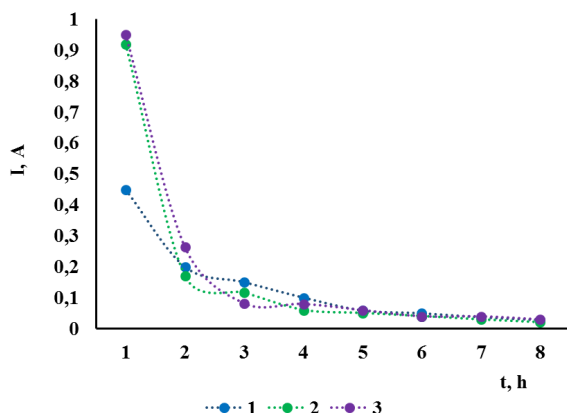


Fig. 4. Change in current strength over time of electrolysis of solutions of cadmium, zinc chlorides and hydrochloric acid at voltage of 5 V at total concentration of zinc and cadmium at acidity, mg-equiv./dm³: 1 – 244, 106; 2 – 254, 280; 3 – 244, 530

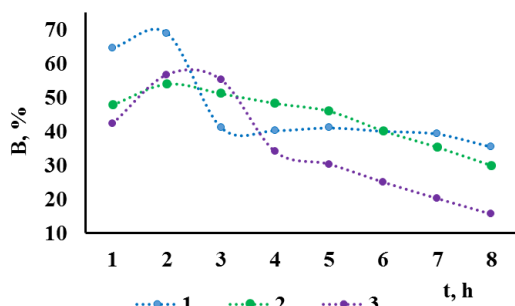


Fig. 5. Dependence of current efficiency of reduced metals (cadmium and zinc) on duration of electrolysis at voltage of 5 V from acidic solutions of metals at the total concentration of zinc and cadmium at acidity, mg-equiv./dm³: 1 – 244, 106; 2 – 254, 280; 3 – 244, 530

Important results on separation of cadmium and zinc were obtained when we used single-chamber electrolyzers. The process is based on the property of cadmium to be reduced in acidic medium, in which zinc at concentrations of up to 50 g/dm³ is not reduced. Electrolysis was carried out at current strength of 1 A (Fig. 6) and of 2.5 A (Fig. 7). The concentration of acid changed from 0.0 to 624.0 mg-equiv./dm³. Current efficiencies at different current strengths are shown in Fig. 8.

The initial concentration of ions of zinc and cadmium was approximately 400 mg-equiv./dm³. Cadmium ions were the first to be reduced during electrolysis, which contributes to acidification of the solution. Even in the absence of sulfuric acid in the initial solution, acidity of the solution increases up to 95 and 138 mg-equiv./dm³ respectively after 30 minutes at current strength of 1 A, and after 15 minutes at current strength of 2.5 A. But at such levels of acidity, zinc ions are not reduced. Moreover, acidity of the solution subsequently increases. As a result, concentration of cadmium ions decreases to trace values and concentration of zinc ions in the solution remains unchanged.

Judging from current efficiency of reduced cadmium, it should be noted that indicators are high at current strength of 1 A. The bulk of cadmium is extracted within the first 30–45 minutes at current strength of 2.5, which is why current efficiency subsequently decreases up to 6–42 %.

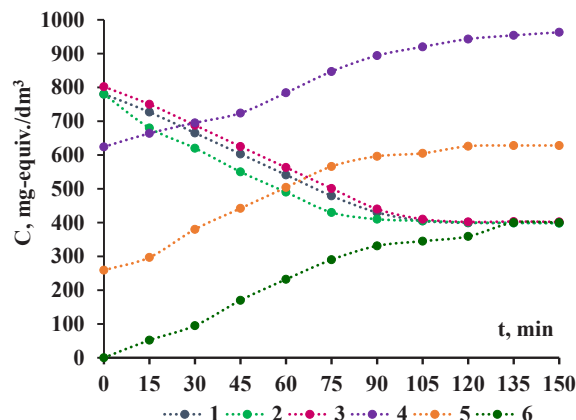


Fig. 6. Dependence of total concentration of cadmium and zinc ions (1; 2; 3) and acidity of solution (4; 5; 6) on duration of electrolysis at current strength of 1 A of the solution, containing ions of zinc, cadmium and sulfuric acid in concentrations, mg-equiv./dm³: 1, 4 – 399, 381, 624; 2, 5 – 399, 381, 259; 3, 6 – 400, 402, 0

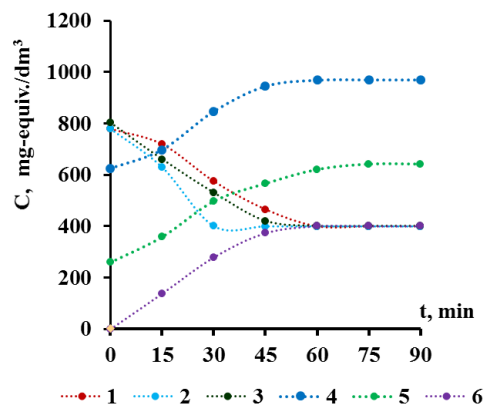


Fig. 7. Dependence of total concentration of ions of cadmium and zinc (1; 2; 3) and acidity of solution (4; 5; 6) on duration of electrolysis at current strength of 2.5 A of solution, containing ions of zinc, cadmium and sulfuric acid in concentrations, mg-equiv./dm³: 1, 4 – 399, 381, 624; 2, 5 – 399, 381, 259; 3, 6 – 400, 402, 0

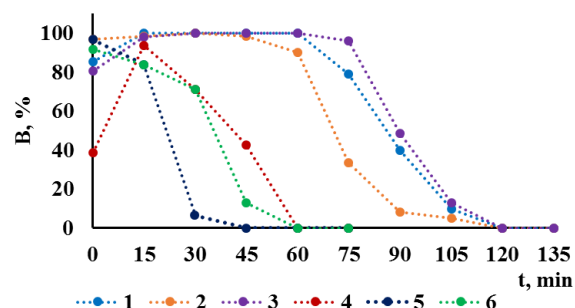


Fig. 8. Dependence of current efficiency of reduced cadmium on duration of electrolysis at current strength of 1 A (1, 2, 3) and of 2.5 (4, 5, 6) of the solution, containing ions of zinc, cadmium and sulfuric acid in concentrations, mg-equiv./dm³: 1, 4 – 399, 381, 624; 2, 5 – 399, 381, 259; 3, 6 – 400, 402, 0

6. Discussion of results of reduction of the used regeneration solutions by electrochemical method with release of heavy metals

Based on the results, obtained during electrolysis of the solution of cadmium sulfate of in the single-chamber electrolyser, it is possible to draw the following conclusion. If it is taken into account that the solution of acid, obtained after electroextraction of cadmium is reused for regeneration of the cation in the Cd^{2+} form, complete extraction of cadmium during electrolysis is not required. That is why electrolysis can be completed after release of bulk of cadmium after 1–2 hours.

When applying a double-chamber electrolyser for recycling solution of cadmium sulfate, acidity in the cathodic area not only does not decrease but partially increases at the first stage of electrolysis, at which the major cathode process is reduction of cadmium. This is explained by formation of acid instead of extracted cadmium at the insufficient rate of diffusion of sulfates in the anodic area. Subsequently, when the rate of hydrogen reduction on the cathode increases at a decrease in cadmium concentration due to diffusion of sulfates, acidity in the anodic area increases. Oxidation of water on the anode with release of oxygen and formation of protons occurs.

In addition to solving the problem of electroextraction of metals from acid solutions, a very important aspect is to determine power consumption for these processes and to compare the latter when using single- and double-chamber electrolyzers. Based on the data, shown in Fig. 1, Table 1 and Table 2, electricity consumption for release of 1 g-equiv. of metal in the form of a metallic powder was calculated. The results are shown in Table 3.

As Fig. 2 and Table 1, 2 show, the bulk of cadmium or zinc is released within 1–2 hours. In this case, yield of metal is optimal within the first hour, sometimes within first three hours. Subsequently, electricity consumption is largely determined by electrolysis of water.

As Table 3 shows, power consumption at extraction of 1 g-equiv. of cadmium is by 2–3 times lower in a single-chamber electrolyser, compared to a double-chamber electrolyser. An increase in power consumption in a single-chamber electrolyser is caused mainly by a sharp decrease in concentration of cadmium ions in the solution. Cadmium is reduced more slowly in a double-chamber electrolyser, so power consumption within the second hour increases slightly. However, power consumption sub-

sequently increases by more than an order of magnitude at a decrease in concentration of cadmium cations in the solution.

It should be noted that at an increase in acidity of resulting solution, power consumption increases due to an increase in resistance of the solution.

Power consumption is slightly higher at zinc electroextraction in a double-chamber electrolyser compared with cadmium reduction. This is caused by flowing of a parallel process of sulfates diffusion to the anode area, which is accompanied by hydrogen reduction on the cathode and water oxidation on the anode. Zinc is not reduced at high acidity values. That is why these two processes, zinc reduction and hydrogen reduction, flow in parallel, which increases electricity consumption.

It should be noted that it is necessary to carry out reduction of zinc from the used regeneration solution, containing zinc sulfate, only in double-chamber electrolyzers, because, due to high acidity of the solution, only electrolysis of water with release of hydrogen and oxygen takes place in single-chamber plants.

In the case of zinc reduction in a double-chamber electrolyser, the maximum yield of reduced zinc is observed during the 2nd–4th hour of electrolysis. This is significantly different from the process of cadmium reduction, where acidity does not affect the reaction of metal release and the yield of metal is maximal within the 1st hour. As mentioned above, this is due to the competing process of hydrogen reduction on the cathode, accompanied by diffusion of sulfates to the anode area. Intensity of zinc reduction increases only after a decrease in acidity in the cathode area.

Removal of ions of cadmium and zinc occurs differently depending on the acid (hydrochloric or sulfuric). The joint removal of metals occurs in the case of electrolysis of a mixture of cadmium and zinc chlorides in a single-chamber electrolyser. Cadmium is removed at the first stage. It is due to the fact that cadmium is well reduced in the acidic medium, which ensures high effectiveness of metal release at the beginning of the electrolysis process. Acidity subsequently decreases due to decomposition of HCl with release of H_2 and Cl_2 , which contributes to effective reduction of zinc ions. However, current efficiency of metals is low and reaches 30–68 %. This is caused by significant electricity consumption for decomposition of hydrochloric acid and water. This is a shortcoming of the process. The benefit of the process is its simplicity, absence of expensive and deficient membranes in the structure.

Table 3

Dependence of electricity consumption for reduction of metal on composition of solution, type of electrolyser and duration of electrolysis

t, h	Electricity consumption, kWt·h/g-equiv.								
	Single-chamber			Double-chamber					
	$[\text{Cd}^{2+}]/[\text{H}_2\text{SO}_4]$, mg-equiv./dm ³ /mg-equiv./dm ³			$[\text{Cd}^{2+}]/[\text{H}_2\text{SO}_4]$, mg-equiv./dm ³ /mg-equiv./dm ³			$[\text{Zn}^{2+}]/[\text{H}_2\text{SO}_4]$, mg-equiv./dm ³ /mg-equiv./dm ³		
	84/98	84/250	98/490	92/100	92/250	96/540	128/100	128/250	120/5560
1	0.15	0.17	0.81	0.36	0.42	1.84	0.86	1.10	2.04
2	1.12	1.68	–	0.63	0.67	1.99	0.94	1.11	2.06
3	–	–	–	0.89	0.91	2.50	1.02	1.25	2.25
4	–	–	–	1.07	10.7	2.72	1.47	1.59	2.38
5	–	–	–	1.43	11.71	–	4.81	2.14	4.28
6	–	–	–	7.14	12.50	–	7.15	–	4.51

Removal of cadmium alone was observed during electrolysis of the mixture of cadmium and zinc sulfates in a single-chamber electrolyser, since this element is reduced in acidic medium. Unlike cadmium, zinc is not reduced at low pH and its concentration in the solution remains constant. Thus, separation of cadmium and zinc ions is possible in the used sulfuric-acidic regeneration solutions. Current efficiency of cadmium at the first stages of electrolysis is 100 %. After extraction of cadmium in a single-chamber electrolyser at the first stage, zinc is removed from the solution in a double-chamber electrolyser with obtaining metallic zinc and sulfuric acid.

A qualitative analysis of the process of extraction of heavy metals from wastewater was performed in the course of this research. It is necessary to carry out additional series of studies and perform their mathematical processing and modeling in order to obtain adequate kinetic equations, describing the processes of reduction of heavy metals from eluates.

7. Conclusions

1. We determined conditions for extracting heavy metals from the used eluates with obtaining chemically pure metals and solutions of acids, suitable for reusing, in order to create waste-free processes of ion-exchange cleaning of water from heavy metals. It is advisable to apply single-chamber

electrolysers in the case of using the resulting acid to regenerate cationite in Cd^{2+} -form. The intensity of the process increases at an increase in acidity of the resulting solution. It is recommended to use double-chamber electrolysers for complete extraction of cadmium. It is appropriate to perform zinc reduction in double-chamber electrolysers. Selection of conditions for release and separation of ions of zinc and cadmium from eluates depends on the acid, which is used during regeneration. It is necessary to apply single-chamber electrolysers in case of using hydrochloric solutions. Single-chamber electrolysers for cadmium removal are used for sulfuric acid solutions at the first stage, double-chamber electrolysers are used for zinc removal at the second stage.

2. It was shown that power consumption of electroextraction increases at an increase in acidity of solutions. During transition from single- to double-chamber electrolysers, power consumption increases by 2–3 times. However, effectiveness of extraction of metals from eluates in double-chamber electrolysers is higher compared to single-chamber electrolysers. That is why selection of the electrolyser's design is associated with the prospects of using the products of electroextraction.

3. It was found that effectiveness of separation of zinc and cadmium in the processes of electrolysis depends on acidity of solutions. Electrochemical reduction of cadmium occurs at acidity of more than 80 mg-equiv./dm³. Zinc is released at acidity that is lower than 60 mg-equiv./dm³.

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