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REMOVAL OF COPPER (II) IONS FROM SPENT SOLUTIONS BY GRANULAR GRAPHITE ELECTRODES

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Abstract: The most abundant heavy non-ferrous metals in the industrial wastewaters and spent solutions are lead, copper, zinc, nickel, however, it depends on the type of the industry. This work proposes the concepts of an electrochemical method of divalent copper removal from the spent solutions with the help of granular graphite electrodes. The study has been conducted, changing the meanings of the five major parameters including the current density (i), the concentration of copper (II) ions (C), the surface area of graphite electrodes (S), the concentration of sulfuric acid in the solution (M) and the electrolysis duration (τ), affecting Cu (II) ions removal percentage from the solution. The experimental results show that the current density, surface area of the granular graphite electrodes and the time are the main factors, which affect the removal percentage of Cu (II), while the changes in the sulfuric acid concentration in the solution have a minor effect. The highest copper removal value is 97% and 54 % current efficiency was observed in conditions: i =150A/m^2, τ = 1.5 h, [H_2SO_4] = 0.4 M, S = 150 cm^2 which is considered as an optimal condition for copper removal process by granular graphite electrode.

Key words: copper (II) ions, granular graphite electrode, spent solutions, heavy non-ferrous metals, removal degree, current efficiency

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1. Introduction

The industrial revolution with economic concerns has created some secondary problems such as heavy metal contaminated wastewater. And there has always been a need for a suitable, efficient, and cheap way of wastewater treatment with a high degree of success. Chemical precipitation, ion floatation, adsorption, coagulation, and some other chemical methods have been the most

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available methods for wastewater treatment [1].

Biopolymers and hydrogels are widely used for industrial applications because of their availability and safety. For instance, the modified biopolymer adsorbents, which are derived from chitosan, starch, and chitin, are proposed to be new material for water treatment from Cu^{2+} ions. Biosorption is highly effective for the aqueous solutions, containing low concentrations of Cu^{2+} and other metals because of its simplicity and high removal capacity [2]. Another adsorption method of wastewater treatment has been tested with magnetic/carbon nanocomposites by Andelescu A. and Nistor M.A. pH of the solution, a quantity of sorbent, the initial concentration of Cu (II), and temperature have been chosen as the main parameters. It has been observed that the removal efficiency of metal ions increases directly proportional to the absorbent's quantity and temperature, and inversely proportional to the initial metal concentration [3]. The adsorption experiments, using DTC-modified rGO-PDTC/Fe_3O_4nanocomposite, have achieved a high level of heavy metal removal. The spent nanocomposite after the adsorption and desorption process has been regenerated by the organic reaction. Nanocomposite has exhibited a good adsorption capability for the five cycles [4]. Manganese oxides are observed to be a good adsorbent for heavy metal ions, and they can be reused many times until the loss of the removal capacity. In his research, Yang X. used birnessite, which is the main manganese mineral. The research results have shown that the Cu^{2+} removal capacity of birnessite (44.3mg g^{-}1) can be remarkably increased to 372 mg g^{-1} with the electrochemical redox reactions [5].

The practical use of fibrous materials in heavy metal treatment has been shown in the research of Du Z. and Zheng T. Raw jute fiber and carboxyl-modified jute fiber have been taken as two types of sorbents and have been compared in the same process conditions. The results have shown that the CMJF has exhibited 4.2 times higher adsorption capacity [6]. Magnetic chitosan/graphene oxide nanocomposite (MCGON) can be used as an adsorbent of Cu^{2+} from the aqueous solutions. MCGON has a high specific area, large pore volume, small particle size, and strong saturation magnetization. MCGON exhibited an adsorption capacity of 217.4 mg/g^{-1}. The process has been practical and efficient due to the adsorbent's high saturation capacity [7].

Due to the use of the electrolysis-enhanced micro-electrolysis fluidized bed technology processes, it has been detected that copper is mostly removed in optimum conditions: flow rate – 22 mm/s, current-voltage -12V, initial pH=4, time-30 min [8]. Reusable and capable hollow magnetic polydopamine nanoparticles have been fabricated as an effective way of heavy water removal from the sewage and industrial effluents. The experiment results have shown that the heavy metal removal value has been above 70% and stayed the same after reusing the Fe_3O_4@PDA 5 times. Fe_3O_4@PDA nanoparticles have been introduced as a beneficial method of Cu (II) and Pb (II) recovery [9]. Cu (II) removal value reached a high of 99,9% by using mechanically activated $CaCO_3$. The sediment of treated wastewater $Cu_4(SO_4)(OH)_6*H_2O$ has been used as a copper-based antibacterial agent [10].

The advanced methods of treating Cu (II), containing the wastewater experiments by combining the internal micro-electrolysis (IME) and electrocoagulation processes have been conducted by Fu Chen, Zhanbin Luo. The effects of pH, time, current density, and Fe/C mass ratio have been tested during the experiment. As a result, by IME, 92% of Cu, 88% of Pb, and 72% of Zn have been removed within 30 min at initial pH=3. As a result of the coagulation process 99% of Cu, 99% of Pb, and 98% of Zn have been removed [11].

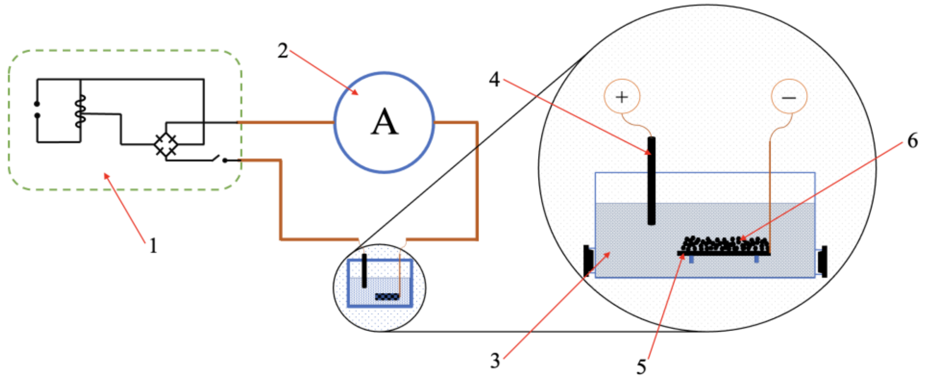
The electrochemical methods of wastewater treatment can be grouped into three categories as the transformation methods, separation methods, and combined methods. These methods are compact and efficient as they do not require a lot of space and have a high value of metal removal [12]. Our previous research results reveal the effectivity of the electrochemical method via using the granular graphite electrodes in wastewater treatment from Pb (II) ions [13]. Electrolytic recovery of copper from wastewater has been experimented and the effects of temperature, current density, anode material, organic contaminants have been measured. As a result of the 2D and 3D electrodes comparison, it has been observed that 2D electrodes used about 27.3 kWh while 3D electrodes used only 5.86 kWh for the same amount of copper recovery (1.443kg) [14]. I.A. Khattab and M.F. Shaffei have done some research for the electrochemical removal of Cu^{2+} from the effluent wastewater. A direct current has been used as a power supply and a graphite material has been used as an electrode. The experiment has been conducted in an electrolyte with an initial Cu^{2+} concentration of 100–350 mg/l and 750 ml/min flow rate. 0.5 M NaCl has been used as a supporting electrolyte and the pH value of the electrolyte has been 3. The current density range has been between 100-500 A/m^2. As a result, under the optimal conditions (current density-500 A/m^2, electrolysis time = 30 min, pH = 3, initial [Cu] = 100 mg/l) removal percent has reached 96% [15].

Heavy metal-containing wastewater can be regenerated by two-stage electrochemical treatment. It is determined that the process of bioleaching heavy metals from sediment emits the processed water with a high level of dissolved metals and sulfate. The model cell with a platinum anode with an effective electrode area of 10 cm^2 and a graphite cathode with an effective area of 10 cm^2 has been used to achieve a high level of heavy metal treatment. The treatment process has consisted of two stages. The main load of heavy metals has been eliminated by cathode in the first stage and excessive sulfuric acid which is 3-4 g/l has been decreased to about 1 g/l with help of anode. The pH level has risen from 3.0 to 4–5. As a result of electrolyte with a time duration of 5.5 hours, an electric current density of 0.1 A/m^2, more than 99% of Cu, Pb, Zn, and Cd have been removed [16].

Although it is possible to achieve a high value of Cu (II) ions removal, some methods cannot be widely used for the industrial purposes. The main reasons are high price and low efficiency. As the electrochemical way of Cu (II) ions removal with granular graphite electrodes has a high removal value and high current efficiency, it can be a promising approach for the effective treatment of industrial spent solutions.

2. Experimental part

The necessary methods and appropriate methods were selected for conducting the research. A direct current was used to study the rules of the copper (II) ions removal process. A rod graphite electrode was taken as the anode and a granular graphite electrode as the cathode for the electrolyzer with a volume of 200 ml (Figure 1). A model solution containing 1g/l of Cu^{2+} ions, acidified with 0.2 M of sulfuric acid was used as an electrolyte. Current density (i), electrolysis time (τ), the surface area of a granular graphite electrode (S), the molar concentration of sulfuric acid (M), and concentration of Cu (II) ions were taken as the main parameters affecting the electrolysis during the study.



1− rectifier; 2− amperemeter; 3−model solution; 4− rod graphite anode; 5− bed graphite electrode; 6− granular graphite cathode.

Figure 1 − Model of the electrolyzer used for research.

A voltammeter CTA-1 was used to determine the low concentrations of Cu^{2+} ions in a solution from 0.001mg/l and above, with high accuracy. The process of determining the mass concentration of Cu^{2+} ions in electrolyzed solution with a CTA-1 analyzer was shown in Figure 2.

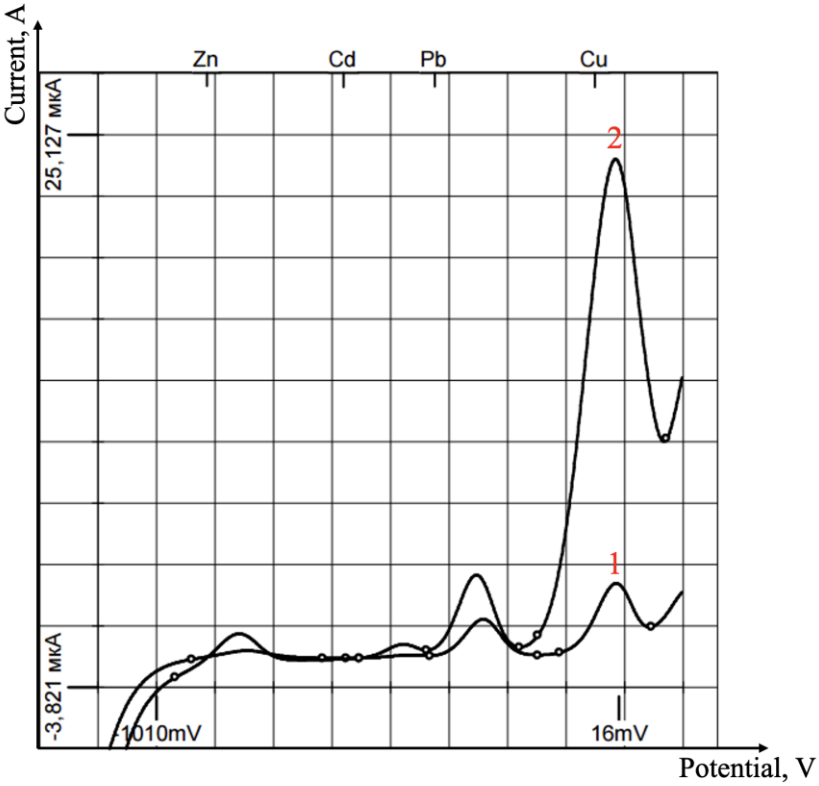


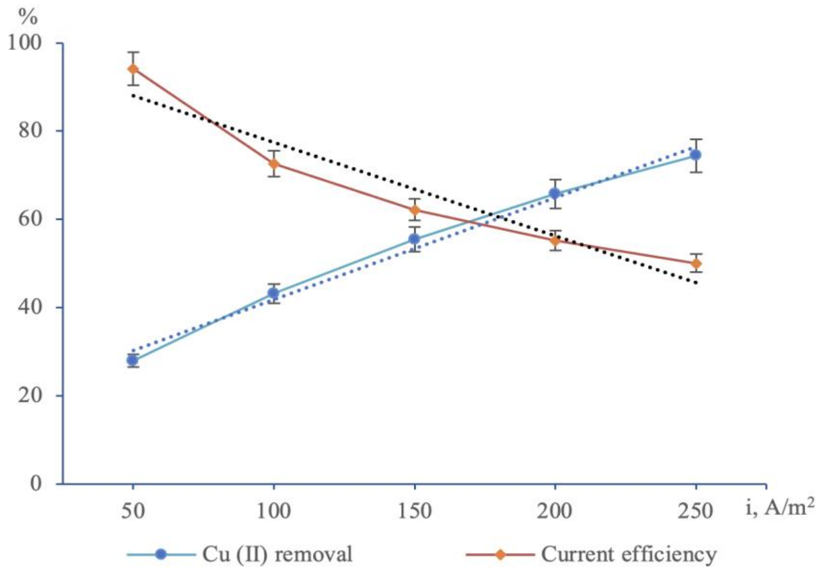
Figure 2 − The expression of reduction maximum of Cu^{2+} ions during voltametric analysis: 1− voltametric curve of background solution; 2− voltametric curve of sample solution containing Cu^{2+} ions

3. Results and discussions

The research work is based on the removal of copper (II) ions by the electrolytic reduction from the spent solutions to metallic copper at the granular graphite cathode:

$$Cu^{2+} + 2e^{-} \rightarrow Cu^{0} \qquad E^{0} = +0.34\ V$$

The effect of current density on the copper (II) ions removal degree has been investigated by direct current. The current density interval was 50-250 A/m^2. It has been observed that an increase in current density has resulted in a steady rise in the removal of Cu^{2+} ions from electrolytes (Figure 3). Despite the high removal level at a high current density, an erosion of graphite electrode and a reduction of current efficiency have been noted at a high 200-250 A/m^2. This is due to an increase in the hydrogen emission rate which is electrolyzed at the same time with a copper at the cathode at high current densities. Therefore, the current density of 150 A/m^2 has been assumed to be an optimal value.



τ= 0.5 h., $[H_2SO_4]$ =0.2 M, S=100 cm^2, $[Cu^{2+}]$ = 1 g/l

Figure 3 − Influence of the current density on the copper removal degree.

The dependence of copper (II) ions removal degree from the solution on the initial Cu^{2+} ions concentration has been studied. As a result of electrolysis carried out for 0.5 hours at a current density of 150 A/m^2 and the initial copper (II) ions concentration between 0.5 and 2.5 g/l, it has been observed that the removal percentage of Cu^{2+} ions decreases as the concentration increases. However, it has been revealed that the value of current efficiency increases directly proportional to the initial copper (II) ions concentration (Table 1).

Table 1 − Influence of the initial copper (II) ions concentration on the copper removal degree, i = 150A/m^2, τ = 0.5 h., $[H_2SO_4]$ =1.0 M, S=100 cm^2

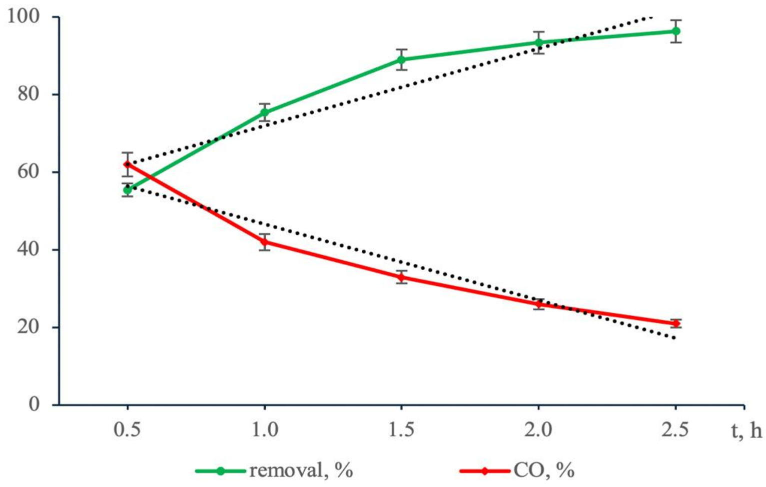
$[Cu^{2+}]$ g/l	0.5	1.0	1.5	2.0	2.5
Copper (II) ions removal percentage, %	62.5 ± 0.5	55.5 ± 0.4	42.0 ± 0.2	36.5 ± 0.2	31.8 ± 0.2
Current efficiency, %	35.0 ± 0.2	70.6 ± 0.5	80.6 ± 0.4	81.8 ± 0.4	89.1 ± 0.5

The result of experiments, which have been conducted to study the influence of the concentration of the sulfuric acid in the solution has shown that an increase in the acid concentration results in a slight growth of copper (II) ions removal level. This circumstance can be attributed to the high electrical conductivity of sulfuric acid with increasing acid concentration (Table 2).

Table 2 − Influence of sulfuric acid concentration on the copper (II) ions removal degree, i = 150 A/m^2, τ = 0.5 h., [Cu^{2+}] =1.0 g/l, S=100 cm^2

[H_2SO_4], M	0.2	0.4	0.6	0.8	1.0
Copper (II) ions removal percentage, %	55.5 ± 0.3	58.6 ± 0.2	62.8 ± 0.2	65.1± 0.3	66.4 ± 0.4
Current efficiency, %	62.2 ± 0.4	65.6 ± 0.3	70.4 ± 0.3	72.9 ± 0.4	74.4 ± 0.4

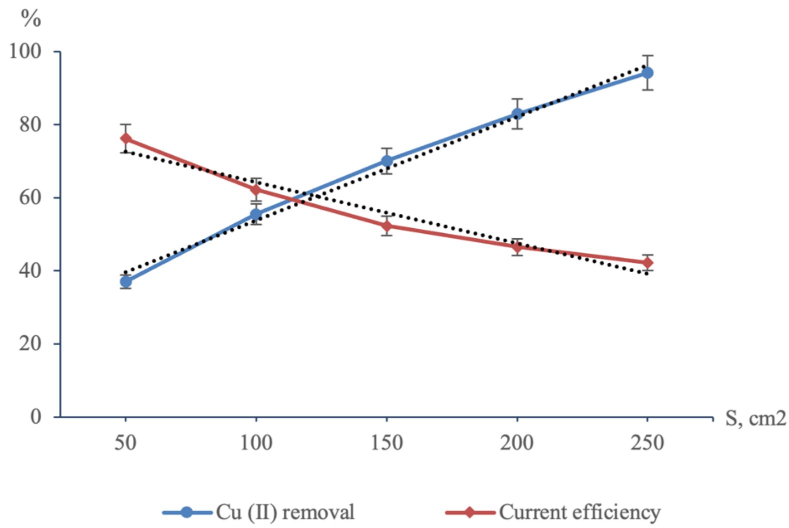
The influence of the duration of electrolysis has been studied by direct current under the conditions of current density 150 A/m^2, [H_2SO_4] = 0.2 M, [Cu^{2+}] = 1.0 g/l and surface area of granular graphite electrode has been 100 cm^2. As a result of the experiment, it has been found that as the electrolysis duration increases, the degree of copper (II) ions removal also increases. The maximum value of copper (II) ions removal degree has been 96.3% in 2.5 hours of the electrolysis process (Figure 4). After the electrolysis for 0.5 hours duration, the current efficiency of copper (II) ions removal has reached 62%, while the current efficiency of copper (II) ions removal after the electrolysis for 2.5 hours has been 21%. The reduction of current efficiency can be attributed to the decrease in the initial copper (II) ions concentration in the solution over time.



i = 150 A/m^2, [H_2SO_4] = 0.2 M, [Cu^{2+}] = 1.0 g/l, S= 100 cm^2

Figure 4 −Influence of electrolysis duration on the copper (II) ions removal degree.

The following research work has been carried out to determine the influence of the surface area of a granular graphite electrode on the copper (II) ions removal percentage at a current density of 150 A/m^2 with an electrolysis duration of 0.5 hours (Figure 5). It has been observed that copper (II) ions removal value is proportionate to the surface area of the electrode. The results have shown that electrolysis with the participation of the granular graphite electrodes with a surface area of 50 cm^2 has had a 76.2% current efficiency, and the current efficiency decreases as the surface area of granular graphite electrode increases. The efficient surface area of granular electrodes decreases as volume increases in size.



i = 150 A/m^2, [H_2SO_4] = 0.2 M, [Cu^{2+}] = 1.0 g/l, τ = 0.5 h.

Figure 5 –Influence of the surface area of the granular graphite electrode on the copper (II) ions removal degree.

By comparing the obtained results, the values obtained as the optimal point of each parameter are - i =150 A/m^2, S=150 cm^2, τ=1.5 h, [H_2SO_4] = 0.4 M, [Cu^{2+}] =1.5 g/l. Electrolysis by the given values has shown 97% copper (II) ions removal degree, and 54% current efficiency.

4. Conclusion

As a result of the scientific research, the influence of the main factors affecting the degree of copper removal from electrolytes has been determined. It has been noted that:

- Cu^{2+} removal percentage decreases and current efficiency raises as the initial concentration of Cu^{2+} ions increases;
- Cu^{2+} ions removal percentage and a current efficiency raise as the concentration of sulfuric acid in the solution increases;
- The removal percentage of Cu^{2+} ions increases, and current efficiency reduces as the duration of electrolysis gradually increases;
- The removal percentage of Cu^{2+} ions increases, and current efficiency decreases as the surface area of granular graphite electrode expands;
- The removal percentage of Cu^{2+} ions rises, and the current efficiency reduces as the current density increases. Comparing the results, it has been found

that the method of using granular graphite electrodes is a very effective way of cleaning the spent solutions with a high copper concentration.

The results of the study have shown that with the help of granular graphite electrodes it is possible to remove 97% of copper (II) ions from a solution and make the spent solution suitable for technical use.

The results of scientific research can be used in the cleaning areas of the high Cu^{2+} ions containing solutions.

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ҚОЛДАНЫЛҒАН ЕРІТІНДІЛЕРДІ МЫС (II) ИОНДАРЫНАН ТҮЙІРШІКТІ ГРАФИТТІ ЭЛЕКТРОДТАР КӨМЕГІМЕН ТАЗАЛАУ

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Түйіндеме. Өндіріс түріне қарай қолданылған ерітінділер мен ақаба сулар құрамында ең көп кездесетін ауыр және түсті металдар қорғасын, мыс, мырыш, никель болып табылады. Берілген зерттеу жұмысында түйіршікті графит электродтар көмегімен қолданылған ерітінділерден мыс (II) иондарынан тазартудың электрохимиялық әдісі ұсынылды. Зерттеуде қолданылған ерітінді құрамындағы мыс (II) иондарының тазалану дәрежесіне әсер ететін негізгі бес параметрдің, оның ішінде ток тығыздығы (i), мыс (II) иондарының концентрациясы (C), графит электродтарының беттік ауданы (S), ерітіндідегі күкірт қышқылының концентрациясы (M) және электролиз ұзақтығы (τ) мәндерін өзгерте отырып жасалды. Тәжірибе нәтижелері ток тығыздығы, түйіршікті графит электродтарының беттік ауданы және электролиз уақытының ерітіндінің мыс (II) иондарынан тазалану дәрежесіне ең көп әсер ететін факторлар екендігі, ал ерітіндідегі күкірт қышқылының концентрациясы айтарлықтай әсер етпейтіндігі көрсетті. Мыс (II) иондарынан тазалану дәрежесінің ең жоғары мәні 97% және ток бойынша шығымы 54 % мәні келесі шарттарда анықталды: - $i = 150 А/м^2$, $\tau = 1.5$ сағ., $[H_2SO_4] = 0.4$ M, $S = 150$ $см^2$ және осы мәндер қолданылған ерітіндіні мыс (II) иондарын түйіршікті графит электродтары қатысында тазалаудың оңтайлы жағдайы ретінде белгіленді.

Түйінді сөздер: мыс (II) иондары, түйіршікті графит электроды, қолданылған ерітінділер, ауыр түсті металдар, тазалану дәрежесі, ток бойынша шығым.

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ОЧИСТКА ОТРАБОТАННЫХ РАСТВОРОВ ОТ ИОНОВ МЕДИ (II) ГРАНУЛИРОВАННЫМИ ГРАФИТОВЫМИ ЭЛЕКТРОДАМИ

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Резюме. Наиболее распространенными тяжелыми цветными металлами в отработанных растворах и сточных водах в зависимости от типа промышленности являются свинец, медь, цинк, никель. В данной работе предложено электрохимический способ очистки ионов меди (II) из отработанных растворов с помощью гранулированных графитовых электродов. Исследование было проведено с изменением значений пяти основных параметров, включая плотность тока (i), концентрацию ионов меди (II) (C), площадь поверхности графитовых электродов (S), концентрацию серной кислоты в растворе (M) и продолжительности электролиза (τ) влияющую на степень извлечения ионов Cu (II) из раствора. Результаты экспериментов показывают, что плотность тока, площадь поверхности графитовых электродов и время являются основными факторами, влияющими на степень очистки Cu (II), в то время как изменения концентрации серной кислоты в растворе оказывают незначительное влияние. Наибольшее значение очистки от ионов меди 97% и выход по току 54 % установлено в условиях: i =150 А/м^2, τ = 1,5 ч, [H_2SO_4] = 0,4 М, S = 150 см^2, что предложено оптимальным условием для процесса очистки меди гранулированными графитовыми электродами.

Ключевые слова: ионы меди (II), гранулированные графитовые электроды, отработанные растворы, тяжелые цветные металлы, степень очистки, выход по току

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