

У роботі були проведені дослідження процесів електрохімічного окиснення амонію в двокамерному електролізері в залежності від складу вихідних розчинів – аноліту і католіту, щільності струму, часу електролізу. Показано, що електрохімічне окиснення амонію у водних розчинах сульфату амонію проходить із швидкістю 14–55 мг/(дм³·год) при щільності струму 86,2–172,4 А/м² і вихідних концентраціях за даним іоном 10–120 мг/дм³. Швидкість окиснення амонію за даних умов зростає із підвищенням вихідних концентрацій амонію та із збільшенням щільності струму.

Вихід окисненого амонію за струмом та питома витрата електрики на очищення води від амонію також визначаються концентраціями даного іону та щільністю струму і зростають при збільшенні концентрації амонію та зниженні щільності струму.

Швидкість окиснення амонію зростає в 1,66 рази в розчинах сульфату амонію ($[NH_4^+] = 90 \text{ мг/дм}^3$, $j = 172,4 \text{ А/м}^2$) у водопровідній воді в порівнянні із дистильованою водою. Це обумовлено наявністю у водопровідній воді хлоридів, які відіграють роль каталізатора при окисненні амонію за рахунок проміжного утворення активного хлору. В даних умовах відмічено повне окиснення амонію в порівнянні з розчинами в дистильованій воді, де залишкові концентрації амонію сягають 1–3 мг/дм³.

Показано, що наявність хлоридів у католіті в концентрації 30 мг/дм³ практично не призводить до прискорення процесу окиснення амонію.

В роботі показано, що у всіх випадках при окисненні амонію рН розчинів знижується до 6,1–2,0, що обумовлено окисненням амонію до нітратів та підкисленням води утвореними азотною та сірчаною кислотами.

З наведених результатів можна зробити висновок, що електрохімічний метод є найбільш перспективним методом для вилучення іонів амонію з води. З його допомогою можна досягти 100 % очищення води

Ключові слова: іони амонію, електродіаліз, окислювально-відновні процеси, анодне окиснення, питома електропровідність, вихід речовини по току

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REMOVAL OF AMMONIUM IONS FROM AQUEOUS SOLUTIONS USING ELECTRODIALYSIS

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1. Introduction

Nitrogen-containing compounds in surface waters are in the dissolved, colloidal, and suspended state. Under the influence of physical-chemical and biochemical factors, these compounds can transfer from one state to another. The average concentration of total nitrogen in natural waters varies over a significant range and depends on the eutrophy of an aqueous object. For example, for oligotrophic waters, the content of total nitrogen varies within 0.3–0.7 mg/dm³; for mesotrophic waters, this indicator is 0.7–1.3 mg/dm³; for eutrophic water environments, 0.8–2.0 mg/dm³.

The ratio of different forms of nitrogen in water can serve the identifier of pollution time. Elevated concentrations of ions of ammonium and nitrites in water indicate fresh contamination, while a high content of nitrates in water confirms pollution over earlier period. The elevated concentrations of all forms of nitrogen in water indicate the permanent pollution of reservoirs with sewage waters.

In natural waters, ammonia forms as a result of the decomposition of nitrogen-containing organic substances of

both the natural and anthropogenic origin. It is well soluble in water with the formation of ammonium hydroxide.

The concentration of ammonium ions in non-contaminated surface waters is negligible and varies in the range of 10–200 mg/dm³ (recalculated for nitrogen). The presence of these ions in water is explained by the processes of biochemical degradation of protein substances, deamination of amino acids, decomposition of urea under the action of urease.

The main sources that deliver ammonium ions to water are the industrial-household sewage, agricultural waste water (cattle-breeding complexes, ammonia fertilizers), as well as sewage water from enterprises in several industries (chemical, food processing, coke-chemical, timber-chemical). The content of ammonium ions in industrial waste water reaches 1 mg/dm³, in household waste water – 2–7 mg/dm³. The industrial-household waste waters daily deliver to sewer systems up to 10 g of ammonium nitrogen per person.

The elevated content of ammonium ions in water can serve the indicator that points to the deterioration in the state of natural waters under the influence of anthropogenic load.

The maximum permissible concentration of ammonium in water of reservoirs for household water use is 2.6 mg/dm³.

Based on the requirements from the World Health Organization, the concentration of ammonium ions in drinking water is not standardized as the harmful effect of a given ion on human health is not determined. It is noted, however, that its content exceeding 1.5 mg/dm³ worsens the smell of water, and at concentrations larger than 35 mg/dm³ there is deterioration in the taste of water.

The content of ammonium in drinking water is not standardized in the USA. However, in the EU states, the concentration of ammonium ions in drinking water is limited to the value of 0.5 mg/dm³.

DSanPiN 2.2.4-171-10 [1] establishes that the content of ammonium in tap water should not exceed 0.5 mg/dm³.

Therefore, at present, one of the tasks on ensuring the standards of quality of drinking water for people implies the efficient removal of ions of ammonium from natural and waste waters. Specifically, at the first stage, this involves the selection of a method for purification, and at the second stage – establishing the optimal parameters for purification processes.

2. Literature review and problem statement

Depending on the output characteristics of water and the requirements to its quality, in order to remove ammonium ions from water, they use reagent [2, 3], sorption [4, 5], ion-exchange [6, 7], and biological [8] methods. All these methods have their advantages and disadvantages. For example, the ion-exchange methods are effective to remove ammonium at a complete desalination of water [7] and are ineffective in the presence of ions of hardness.

Biological methods are appropriate to be applied for sewage purification under certain concentrations of biogenic substances and micro elements [9]. In recent years, the ANAMMOX technologies have been very popular [10]. The most significant advantages of this technology [11] is a reduction in the emission of carbon dioxide into the atmosphere, by 85–90 %, in comparison with traditional technologies, as well as the low cost of the process [12]. However, the mentioned processes proceed very slowly and remain ineffective under low ammonium concentrations. That is why biological methods are almost not employed to clean natural waters.

The reagent method should be used for the purification of wastewater containing high concentrations of ammonium compounds. To remove ammonium ions from the anaerobically treated wastewater, magnesite is used as a source of magnesium ions [13]. It is also appropriate to use when treating the regeneration solutions containing ammonium and phosphates [14]. The result of such a water treatment [15] is struvite MgNH₄PO₄·6H₂O, which can be used as a mineral fertilizer [16]. However, a given process is accompanied by significant consumption of reagents and a partial secondary pollution of water [17].

The application of natural sorbents in order to remove ammonium using a sorption method has a number of limitations. For example, duration of the process, low sorption capacity at small concentrations of ammonium ions in water, low efficiency of purification under dynamic conditions. To improve efficiency of the sorption process, it is proposed to use the modified ceramic adsorbents to remove ammonium ions with the subsequent utilization of used sorbents as fertilizers [18]. An alternative method of water purification from ammonium

compounds might be biosorption [19]. However, these methods are inefficient at low concentrations of ammonium.

When applying the reverse osmosis and electro dialysis [20], selectivity is not high enough, and there occurs a task on processing the concentrates obtained.

Based on an analysis of the scientific literature, we can conclude that at present there is a lack of actually effective methods for extracting ammonium ions from water.

Above all, most such methods as biological, reagent, sorption, are quite complex, long, and do not provide for the required level of water purification at low concentrations of ammonium. Insufficiently effective as well are the destructive, baro-membrane methods and electro dialysis methods. In general, the methods considered here do not provide for the required reliability of water purification from ammonium impurities.

Much more prospects are offered by the processes of electrochemical oxidation of ammonium. First of all, when using inert anodes (titanium, covered with ruthenium oxide, platinum, etc.), the water is not added with foreign substances. In addition, regardless of the concentration of ammonium, it is oxidized to nitrogen or nitrates. Nitrogen is an inert substance. Permissible concentration of nitrates, even in drinking water, reaches 45 mg/dm³, whereas for ammonium this level for bottled water is 0.5 mg/dm³. And the most important aspect is the simplicity and reliability of the method. The proper selection of process parameters ensures complete destruction of ammonium ions regardless of the composition of water.

3. The aim and objectives of the study

The aim of this work was to design a highly effective process of electrochemical oxidation of ammonium compounds in a two-chamber electrolyzer, to determine a dependence of the process efficiency on the electrolysis parameters (current density, electrolysis duration), taking into consideration the composition of water and composition of the catholyte used.

To accomplish the aim, the following tasks have been set:

- to determine a dependence of the process parameters of ammonium ions oxidation in the anode region of a two-chamber electrolyzer (membrane MA-41) (degree of conversion, process intensity, output for current) on current density (voltage and current strength, respectively) and duration of electrolysis;
- to estimate effect of the water environment composition on oxidation efficiency of the ammonium sulfate solutions;
- to determine influence of chloride-anion concentration in catholyte on ammonium oxidation efficiency in the anode region.

4. Materials and methods to study the oxidation of ammonium from aqueous solutions of ammonium sulfate

In this work, we used the two-chamber electrolyzer with an anion-exchange membrane MA-41 (Ukraine, Russia), which employed the cathode made from stainless steel ($S_k=0.12$ dm²) and the titanium anode covered with ruthenium oxide ($S_a=0.12$ dm²) (Fig. 1). The anode chamber contained model solutions of ammonium sulfate with the ammonium ions concentration from 10 to 120 mg/dm³. Model solution were prepared both in distilled and tap water. The cathode chamber contained 0.1 N of alkaline solution;

for some experiments, in a mixture with chlorides at a concentration of 30 mg/dm³.

During experiments, over an equal period, we determined the residual concentration of ammonium ions and pH in anolyte. All indicators of water quality were determined according to the procedures given in [21].

The output for current (*B*, %) was calculated as the ratio of the determined amount of ammonium removed from solution to its theoretically estimated amount:

$$B = \frac{q_p}{q_T} \cdot 100 = \frac{m_f}{m_t} \cdot 100, \tag{1}$$

where *q_p* is the amount of electricity that is actually spent to transport a gram-equivalent of the substance; *q_t* is the theoretically calculated amount of electricity, which is needed to transport a gram-equivalent of the substance; *m_f* is the amount of actually transported substance, g; *m_t* is the theoretically estimated amount of the transported substance, g.

The theoretical amount of the transported substance was derived from formula:

$$m_T = K_E \cdot I \cdot t, \tag{2}$$

where *K_E* is the electrochemical equivalent (0.03731 [g-equiv./ (A·h)]); *I* is the current strength, A; *t* is time, h.

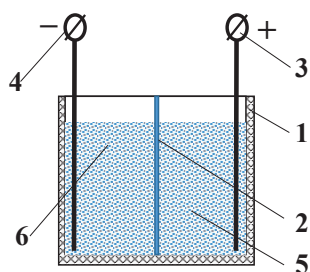


Fig. 1. Schematic of a two-chamber electrolyzer:
1 – body, 2 – membrane MA-41, 3 – anode, 4 – cathode,
5 – model solution of ammonium sulfate, 6 – alkaline solution

The actual amount of the transported substances was calculated from formula:

$$M_f = V_p \cdot (C_0 - C_i), \tag{3}$$

where *V_p* is the volume of solution, dm³; *C₀* is the starting concentration of ions in solution, g/dm³; *C_i* is the concentration of ions in the *i*-th sample upon sorption, g/dm³.

Specific electric conductivity (*χ*, Ohm⁻¹·m⁻¹) was calculated as the product of current strength and the distance between electrodes divided by the product of voltage and anode:

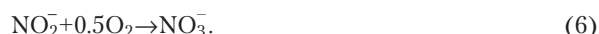
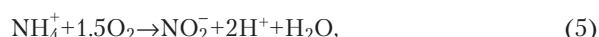
$$\chi = \frac{I \cdot l}{U \cdot S}, \tag{4}$$

where *I* is the current strength, A; *l* is the distance between electrodes, m; *U* is voltage, V; *S* is the area of the anode, m².

5. Results of research into electrochemical oxidation of ammonium ions

It is known that in the presence of chlorides in anolyte there is the formation of active chlorine, which affects the process of ammonium oxidation. However, it is unknown whether ammonium would oxidize in the absence of chlorides. Therefore, in this work we investigated the processes of electrochemical oxidation of ammonium sulfate. Fig. 2 shows that in this case there is also the degradation of ammonium ions.

Obviously, a reduction in the concentration of ammonium ions in electrolyzer occurred as a result of oxidation of ammonium nitrogen with oxygen that forms on the anode:



At the first stage of experiments we used solutions of ammonium sulfate in the range of concentrations 10–40 mg/dm³ (Fig. 2, 3).

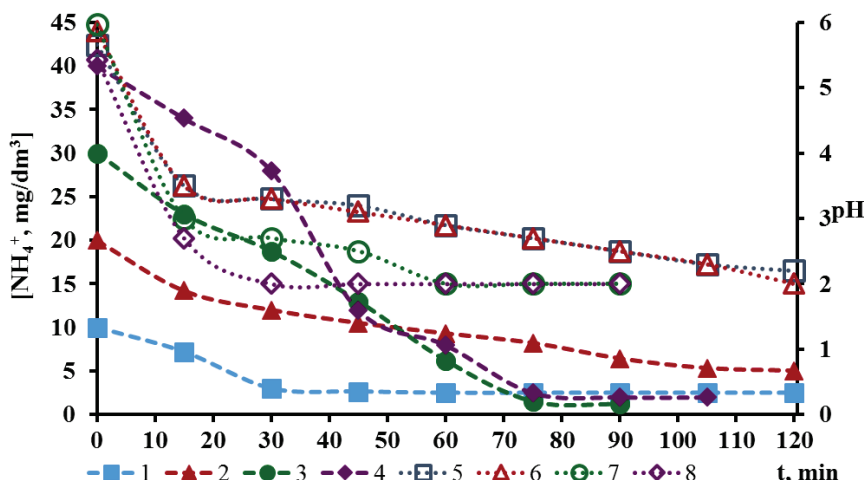


Fig. 2. A change in the concentration of ammonium ions (1, 2, 3, 4) and pH (5, 6, 7, 8) in the anolyte of a two-chamber electrolyzer (membrane MA-41) during electrolysis at a current density of 86.2 A/m² (1, 2, 5, 6) and 172.4 A/m² (3, 4, 7, 8) at starting concentrations of ammonium ((NH₄)₂SO₄) in a solution of distilled water, mg/dm³: 10 (1, 5), 20 (2, 6), 30 (3, 7), 40 (4, 8)

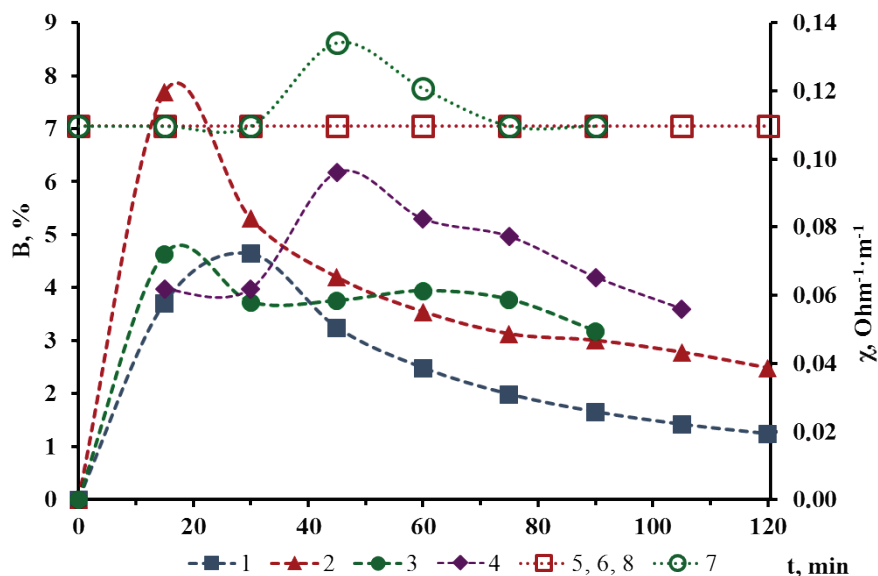


Fig. 3. Dependence of the output for current (1, 2, 3, 4) and specific electrical conductivity (5, 6, 7, 8) at the ammonium ions oxidation in a two-chamber electrolyzer (membrane MA-41) on duration of electrolysis at a current density of 86.2 A/m² (1, 2, 5, 6) and 172.4 A/m² (3, 4, 7, 8) at the starting concentrations of ammonium ((NH₄)₂SO₄) in a solution of distilled water, mg/dm³: 10 (1, 5), 20 (2, 6), 30 (3, 7), 40 (4, 8)

Fig. 2 shows that the oxidation of ammonium ions proceeds quite intensely. Over 30 minutes, at a current density of 86.2 A/m², at the starting concentration of ammonium ions of 10 mg/dm³, the content of ammonium ions in the sample reduces by 7.0 mg/dm³. Under the same conditions, but at the starting concentration of ammonium ions of 20 mg/dm³, the concentration decreases by 8 mg/dm³.

At a higher current density of 172.4 A/m² and the consumption of electricity of 1.42 A·h/dm³, at the initial concentrations of ammonium ions of 30 mg/dm³ and 40 mg/dm³, over 30 minutes, 11.2 mg/dm³ and 12 mg/dm³ are oxidized, respectively.

In all cases (Fig. 2), there is a decrease in pH of the environment in the process of electrolysis. Note that the output for current at ammonium oxidation is low and does not exceed 9 % (Fig. 3).

Electrical conductivity of the solution varies insignificantly over time.

The oxidation of ammonium in anolyte from solutions of ammonium sulfate, prepared on tap water, at concentrations of 10–40 mg/dm³, proceeds faster than that from solutions prepared on distilled water (Fig. 4, 5), which is apparently due to the catalytic action of chlorides present in tap water.

Fig. 4 shows that the complete oxidation of ammonium occurs over 45–90 minutes at a current density of 86.2 A/m². The output for current of the oxidized ammonium is low, though it is higher than that in distilled water (Fig. 5). Note that the output for current increases with increasing the concentration of ammonium ions while the consumption of electricity in this case is declining (Table 1). No significant increase in the electrical conductivity of solutions in tap water, compared with distilled water, observed.

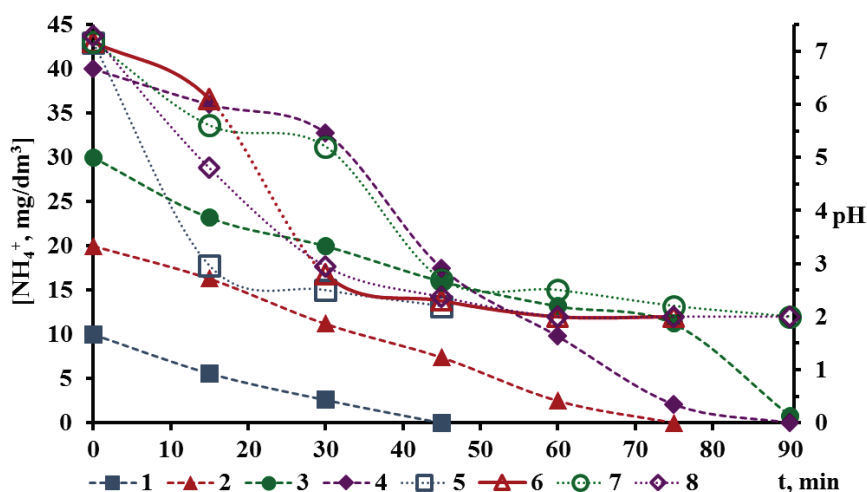


Fig. 4. A change in the concentration of ammonium ions (1, 2, 3, 4) and pH (5, 6, 7, 8) in the anolyte of a two-chamber electrolyzer (membrane MA-41) during electrolysis at a current density of 86.2 A/m² at the starting concentrations of ammonium ((NH₄)₂SO₄) in a solution of tap water, mg/dm³: 10 (1, 5), 20 (2, 6), 30 (3, 7), 40 (4, 8)

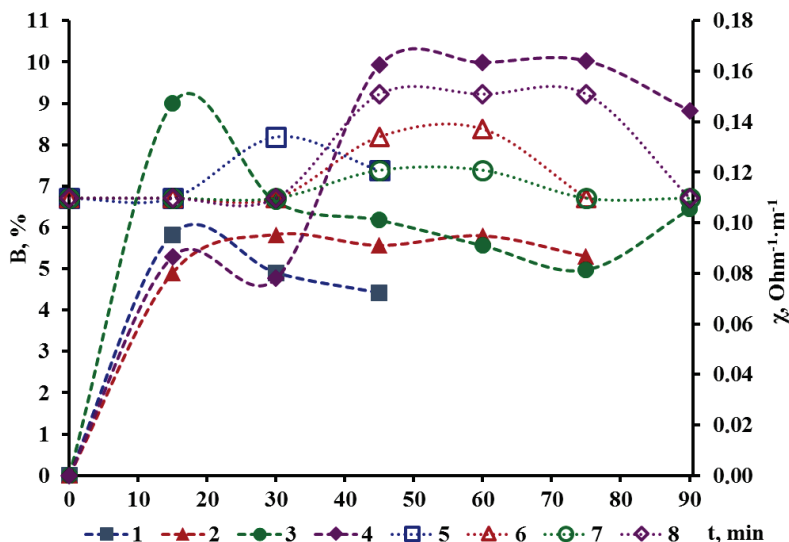


Fig. 5. Dependence of the output for current (1, 2, 3, 4) and specific electrical conductivity (5, 6, 7, 8) at the oxidation of ammonium ions in a two-chamber electrolyzer (membrane MA-41) on electrolysis duration at a current density of 86.2 A/m² at the starting concentrations of ammonium ((NH₄)₂SO₄) in a solution of tap water, mg/dm³: 10 (1, 5), 20 (2, 6), 30 (3, 7), 40 (4, 8)

Table 1
Dependence of electricity consumption for the oxidation of ammonium ((NH₄)₂SO₄) on electrolysis duration and composition of the solution

t, min	Electricity consumption, kW·h/g-equiv.				
	[NH ₄ ⁺] mg/dm ³ , distilled water			[NH ₄ ⁺] mg/dm ³ , tap water	
0	10	50	90	10	90
15	39.75	7.73	4.31	25.30	13.76
30	31.80	12.14	5.63	24.61	4.13
45	45.43	13.34	5.20	30.36	4.53
60	59.37	16.19	5.97	–	5.07
75	74.21	–	8.53	–	5.98
90	89.05	–	11.14	–	8.20
105	103.89	–	14.47	–	14.25
120	118.73	–	20.01	–	–

When performing the electrolysis of solutions of ammonium sulfate (50–120 mg/dm³ for NH₄⁺) in distilled water in a two-chamber electrolyzer, the complete oxidation of ammonium is achieved at a current density of 172.4 A/m² over 1–2.5 hours (Fig. 6). In this case, the output for current of the oxidized ammonium reaches 8–31 % (Fig. 7).

Ammonium sulphate in tap water with a concentration of 90 mg/dm³ oxidizes for ammonium significantly faster than in the case of a solution in distilled water (Fig. 6, 8). In this case, the output for current reaches 6.6–16.2 % (Fig. 9). In addition, a solution of ammonia in tap water has a higher electrical conductivity than the ammonium solution in distilled water.

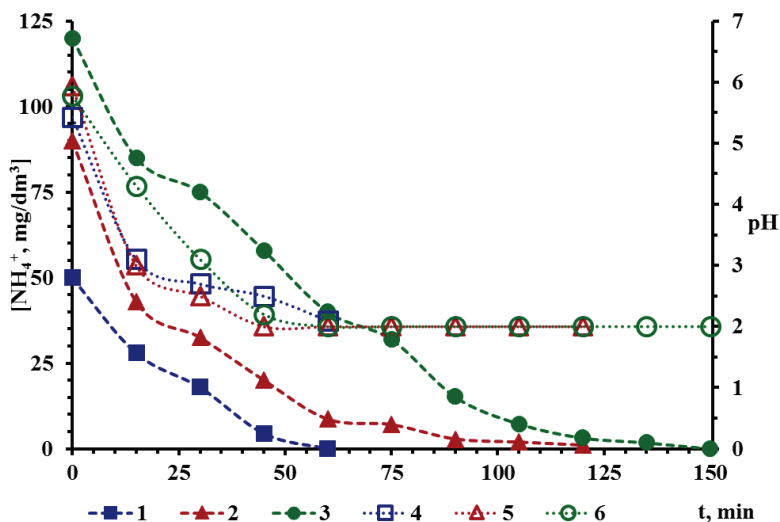


Fig. 6. A change in the concentration of ammonium ions (1, 2, 3) and pH (4, 5, 6) in the anolyte of a two-chamber electrolyzer (membrane MA-41) during electrolysis at a current density of 172.4 A/m² at the starting concentrations of ammonium ((NH₄)₂SO₄) in a solution of distilled water, mg/dm³: 50 (1, 4), 90 (2, 5), 120 (3, 6)

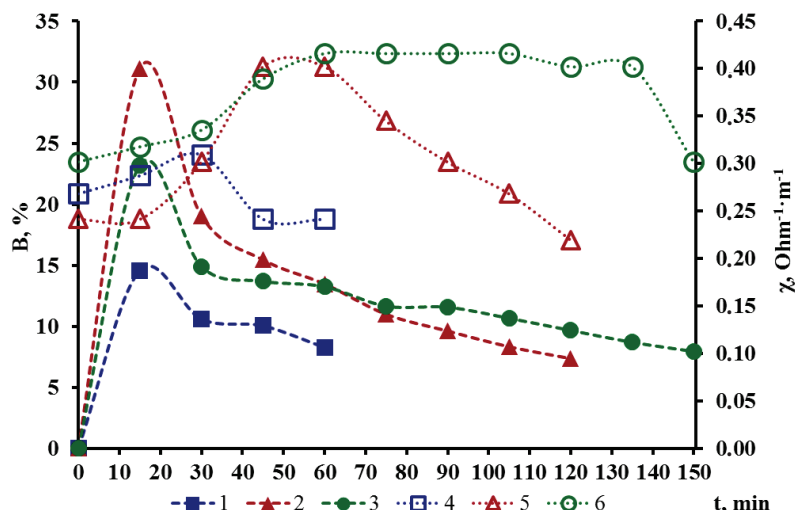


Fig. 7. Dependence of the output for current (1, 2, 3) and specific electrical conductivity (4, 5, 6) at the ammonium ions oxidation in a two-chamber electrolyzer (membrane MA-41) on electrolysis duration at a current density of 172.4 A/m² at the starting concentrations of ammonium ((NH₄)₂SO₄) in a solution of distilled water, mg/dm³: 50 (1, 4), 90 (2, 5), 120 (3, 6)

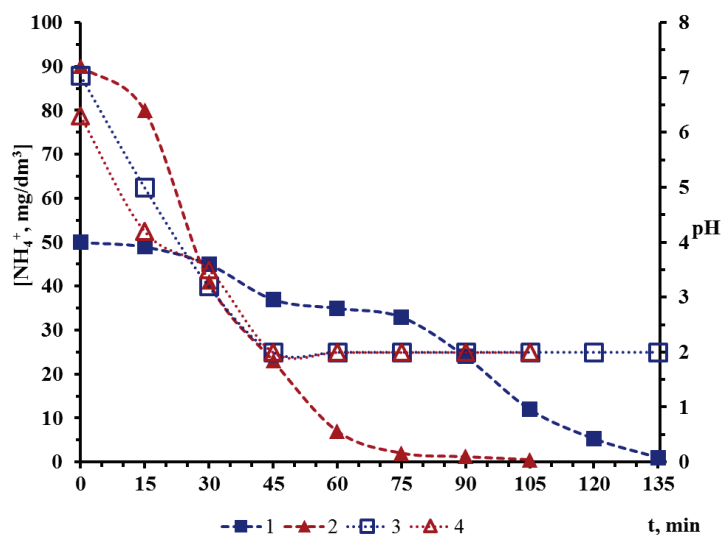


Fig. 8. A change in the concentration of ammonium (1, 2) and pH (3, 4) in the anolyte of a two-chamber electrolyzer (membrane MA-41) during electrolysis at a current density of 172.4 A/m² at the starting concentrations of ammonium ((NH₄)₂SO₄) in a solution of tap water, mg/dm³: 50 (1, 3), 90 (2, 4)

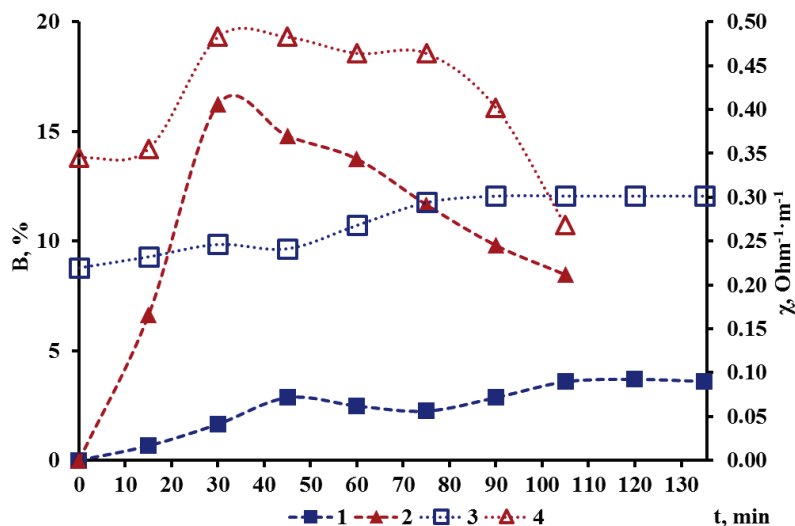


Fig. 9. Dependence of the output for current (1, 2) and specific electrical conductivity (3, 4) at the ammonium oxidation in two-chamber electrolyzer (membrane MA-41) on electrolysis duration at a current density of 172.4 A/m² at the starting concentrations of ammonium ((NH₄)₂SO₄) in a solution of tap water, mg/dm³: 50 (1, 3), 90 (2, 4)

Next, in our study, we comprehensively investigated the influence of water quality (distilled, tap water) and the presence of chlorides in the catholyte on the the oxidation process of ammonium sulfate (Fig. 10, 11). Fig. 10 shows that the presence of chlorides ($C=30\text{ mg/dm}^3$) in catholyte promotes a certain acceleration of the process of ammonium oxidation. In this case, the amount of chlorides in the system is sufficient for the catalysis of ammonium oxidation process.

The results reported here demonstrate that there is almost no difference between the rate of oxidation of ammonium ions in the solutions of distilled or tap water. Changes in pH of solutions (Fig. 10) and in the output of the oxidized ammonium for current (Fig. 11) are almost the same both in tap and distilled water.

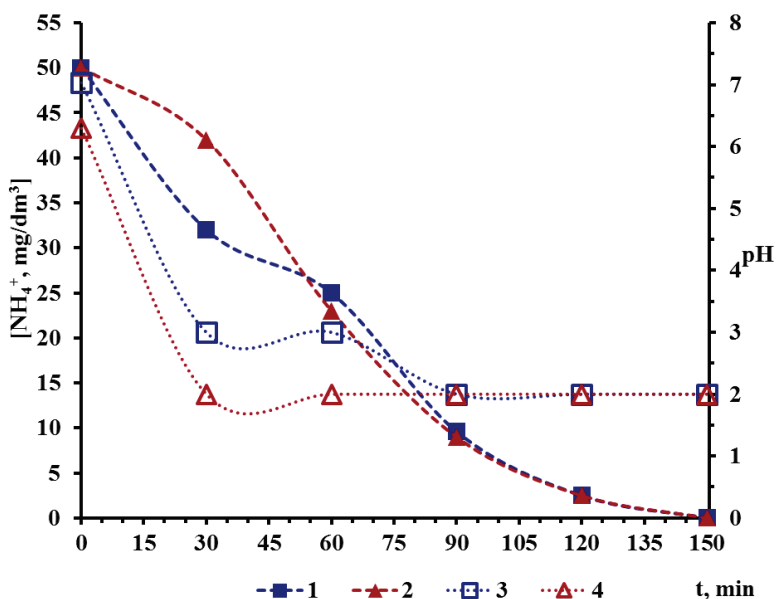


Fig. 10. A change in the concentration of ammonium (1, 2) and pH (3, 4) in the anolyte of a two-chamber electrolyzer (membrane MA-41) during electrolysis at a current density of 172.4 A/m^2 in a solution of distilled water (1, 3) and tap water (2, 4), $[(\text{NH}_4)_2\text{SO}_4]=50\text{ mg/dm}^3$ for ammonium, at $[\text{Cl}^-]=30\text{ mg/dm}^3$ in the catholyte

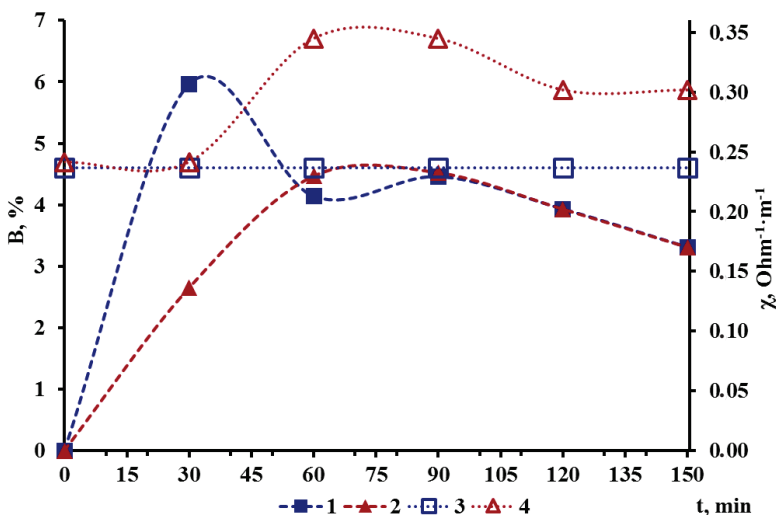


Fig. 11. Dependence of the output for current (1, 2) and specific electrical conductivity (3, 4) at the ammonium oxidation in a two-chamber electrolyzer (membrane MA-41) on electrolysis duration at a current density of 172.4 A/m^2 in a solution of distilled water (1, 3) and tap water (2, 4), $[(\text{NH}_4)_2\text{SO}_4]=50\text{ mg/dm}^3$ for ammonium, at $[\text{Cl}^-]=30\text{ mg/dm}^3$ in the catholyte

6. Discussion of results of the electrochemical oxidation of ammonium ions in solutions of ammonium sulfate

Based on the results obtained during the electro dialysis of solution of ammonium sulfate in a two-chamber electrolyzer with membrane MA-41, one can draw the following conclusion.

Electrochemical oxidation of ammonium ions in aqueous solutions of ammonium sulfate proceeds rather actively and without the presence of chlorides in anolyte. However, under the same conditions (0.5 hours, a current density of 86.2 A/m^2), the concentration of ammonium ions in samples reduces disproportionately relative to the starting concentrations. Thus, at the starting ammonium concentration of 10 mg/dm^3 , under the specified conditions, 70 % of ammonium present in water are oxidized ($C_f=3\text{ mg/dm}^3$). At the initial concentration of ammonium of 20 mg/dm^3 , its amount reduces by 40 % ($C_f=12\text{ mg/dm}^3$) (Fig. 2). This relates to the consumption of electricity, which in both cases was 0.71 A·h/dm^3 (Fig. 3). Therefore, at the same consumption of electricity one receives almost the same amount of the oxidized ammonium – 7 and 8 mg/dm^3 .

The maxima along curves in Fig. 3, 5, 7, 9, 11 emerge due to an increase in the output for current at the initial stage, which is associated with a higher concentration of ammonium ions in the solution at the beginning of the process with its subsequent reduction over electrolysis duration. Greater conversion of ammonium ions in the second case is explained by the higher initial concentration of ammonium in solution and the higher output for current of the oxidized ammonium (Fig. 3).

When increasing all output parameters: current density to 172.4 A/m^2 , consumption of electricity to 1.42 A·h/dm^3 , starting concentrations of ammonium ions to 30 mg/dm^3 and 40 mg/dm^3 , a larger amount of the substance is oxidized. It is obvious that an increase in the concentration of ammonium leads to a certain increase in the output for current, although this indicator decreases with an increase in current density (Fig. 3).

Lowered pH of the environment in the anolyte during electrolysis (Fig. 2) is predetermined by the decay of ammonium and transition of sulfuric acid into solution. Formation of nitrogen dioxide is not ruled out as well, which also leads to the acidification of water. Electrical conductivity of solutions in all cases is low, which is due to a low concentration of salts in anolyte and alkali in catholyte.

The use of solutions of ammonium sulfate in tap water greatly affects the rate and efficiency of the process of electrochemical oxidation of ammonium ions (Fig. 4, 5). The tap water in Kyiv, Ukraine, is characterized by the following parameters: $[\text{Ca}^{2+}]=3.1\text{--}3.3\text{ mg-equiv./dm}^3$, $[\text{Mg}^{2+}]=0.8\text{--}1.2\text{ mg-equiv./dm}^3$, $[\text{HCO}_3^-]=3.9\text{--}4.5\text{ mg-equiv./dm}^3$, $[\text{SO}_4^{2-}]=15\text{--}50\text{ mg/dm}^3$, $[\text{Cl}^-]=10\text{--}37\text{ mg/dm}^3$. Hydro carbonate-ions ensure neutral pH values in the starting solutions of ammonium sulfate. However, during

electrolysis, values of pH for anolytes reduce to 6.1–2.0 (Fig. 4). Ions of calcium and magnesium do not affect the redox processes in anolyte. The acceleration in the process of oxidation is probably associated with the presence of chloride ions in tap water and oxidation of the latter in acidic and weakly-acidic environment. It should be emphasized that in distilled water the residual concentration of ammonium is 1.2–2.5 mg/dm³ while in tap water it is possible to completely remove ammonium ions.

The efficiency of ammonium oxidation in distilled water increases with an increase in the starting concentration of solutions. Thus, at a current density of 172.4 A/m², over 1–2.5 hours, in a two-chamber electrolyzer, the concentration of ammonium ions decreases from 50–120 mg/dm³ for ammonium to zero. An increase in the intensity of ammonium oxidation is due to a concentration factor and an increase in the electrical conductivity of solutions. Curves in Fig. 7 describe a change in voltage in the process of electrolysis. The chart demonstrates distinct regions of the increased conductivity and reduced voltage. This is due to an increase in the number of ions in anolyte at the beginning of the process and a decrease in the concentration of ions at its end, which is associated both with the oxidation of ammonium ions and a possible removal of nitrogen oxides from water.

The process of oxidation of ammonium sulfate (90 mg/dm³ for ammonium) proceeds even faster in the case of preparing solutions on tap water (Fig. 6, 8, 9).

It should be noted that the consumption of electricity for the oxidation of ammonium ions decreases with an increase in the concentration of ammonium in the solution, although there is no significant difference when using tap or distilled water (Table 1). If we assume that it is the insignificant concentration of chloride ions in anolyte that catalyzes the process of ammonium oxidation, then it is possible, in order to gradually dose chlorides into the anode chamber, to add chloride-ions to the catholyte. From the catholyte, chlorides together with hydroxide-anions would pass the anion membrane into the anode chamber.

It is possible that the formation of oxidized compounds of chlorine contributes to the acceleration of the complex processes of ammonium oxidation. And an increase in the starting concentration of sulfates slightly slows at the same time the degradation of ammonia. That could be explained by the progress of a side reaction – formation of persulfate-anions on the anode. Persulfate almost do not oxidize ammonium, and this leads to a certain slowdown in the process of degradation of ammonia by electrolysis.

Further studies (Fig. 10, 11) have shown that chlorides in catholyte in a concentration of 30 mg/dm³ lead to a certain acceleration of the process of ammonium oxidation. Such indicators of the process as changes in pH of solutions and outputs of the oxidized ammonium for current are almost indistinguishable for both distilled and tap water. This is predetermined by a sufficient concentration of chlorides in both cases. The advantage of the process of electrochemical oxidation of ammonium in tap water is the higher electrical

conductivity of the system that helps reduce energy consumption for its oxidation.

In general, it should be noted that a given method is promising for conditioning the water for household purposes and preparation of bottled water. This relates, first of all, to conditioning the artesian waters, which are quite often contaminated with ammonium although the content of the latter is low. It is the application of electrolysis that would safely purify water from ammonium with no significant negative impact on water quality. In this case, even in the presence of chlorides in water in small concentrations (up to 15–20 mg/dm³) the ammonium oxidation process proceeds efficiently. In the case of total absence of chloride ions, the intensification of the process can be achieved by adding chlorides to catholyte. During treatment in the anode area, water will be purified not only from ammonium, but it would be disinfected at the expense of forming atomic oxygen, peroxide compounds and microquantities of active chlorine or chlorine dioxide. These substances form at the anode. The processes of cleaning and disinfection of water are easily controlled by adjusting current density and water flow rate through the anode chamber.

7. Conclusions

1. It is shown that the efficiency of electrochemical oxidation of ammonium in solutions of ammonium sulfate in the anode region of a two-chamber electrolyzer depends both on the concentrations of ammonium and current density. The intensity of oxidation (the amount of decomposed NH₄⁺) increases with increasing concentrations of ammonium and with increasing current density current. Specific consumption of electricity ((kW·h/g-equiv.) decreases with increasing ammonium concentration and decreasing current density. In all cases, we observed a decrease in pH of the environment with an increase in the degree of conversion of ammonium (to 6.1–2.0) at the expense of formation of oxides of nitrogen and sulphuric acid.

2. It was established that during electrolysis in solutions of ammonium sulfate in tap water at the starting concentration of ammonium of 90 mg/dm³ at a current density of 172.4 A/m², the rate of ammonium oxidation process is 1.66 times larger compared to the solution on distilled water. The acceleration in the process of oxidation is obviously due to the presence of chlorides in tap water and the catalytic effect of these ions. In this case, in distilled water, the residual ammonium concentration is 1–3 mg/dm³, while in tap water its complete removal is achieved.

3. It is shown that in the presence of chlorides in catholyte at a concentration of 30 mg/dm³, there is almost the disappearance of the dependence of rate and efficiency of the oxidation of ammonium on environment – tap water or distilled water, which is predetermined by a sufficient concentration of chlorides in both cases: in the process of electrolysis, chlorides would enter the anolyte through the anion membrane together with hydroxide-anions.

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