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Electrochemical Formation of Aluminum Coagulants for Dairy Wastewater Treatment

MAKAROV Yevhen[1,a], ANDRONOV Vladimir[1,b], DANCHENKO Yuliya[2,c*]

[1]National University of Civil Defense of Ukraine, 94, Chernyshevska str., Kharkiv, 61023, Ukraine

[2]Lviv State University of Life Safety, 35, Kleparivska St., Lviv, 79007, Ukraine

[a]makarov1993@ukr.net, [b]va_andronov@ukr.net, [c]yulia.danchenko@ldubgd.edu.ua

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Abstract. Researches of chemical-technological parameters of electrochemical production of aluminum-based coagulants for electrocoagulation wastewater treatment of milk processing enterprises have been carried out. The impact of pH and the timing of the electrocoagulation process was studied in two cases of the implementation of the technological process: with the addition of an alkaline additive before and after the electrocoagulation treatment. The mechanism of the coagulation action of aluminum compounds formed as a result of electrocoagulation has been studied. It has been established that the addition of an alkaline additive after electrocoagulation is more effective. At the same time, the degree of wastewater treatment remains quite high. This will ensure energy savings and will positively affect the environmental and economic assessment of the technology.

Introduction

Factories and enterprises for the production of dairy food products are the source of the most dangerous wastewater, which in case of irrational and irresponsible use can significantly affect the state of surface and underground natural reservoirs. In addition, the ingress of these waters without prior treatment or treatment for treatment at urban treatment plants can cause disruption of biological treatment systems and the death of activated sludge [1-4].

Wastewater from dairy plants is a complex heterogeneous system that is a mixture of ionic and molecular solutions, suspensions, emulsions and colloidal solutions (sols). The dispersion medium is water, and the dispersed phase is represented by solid inorganic particles emulsified by insoluble fat droplets, particles of coagulated protein, organic acids, lactose, and colloidal particles of organic contaminants [1, 5, 6].

It is known that for the primary treatment of dairy wastewater are the most effective chemical methods or treatment with chemical reagents electrolytes – sulfates, chlorides, hydroxy salts of aluminum or iron, calcium chloride, etc. Crystal salts of metals, entering the water, dissolve, hydrate, dissociate and hydrolyze with the formation of colloidal particles of insoluble hydroxides of metals – coagulants. Charged colloidal hydroxide particles are characterized by excess surface energy and increased adsorption capacity, which allows you to effectively remove both dispersed and dissolved contaminants in wastewater [7]. The addition of salts provides not only the removal of major contaminants – fats, proteins, organic acids, lactose, suspended solids, but also nutrients – compounds of nitrogen and phosphorus, chlorides, sulfates, etc. [8-10]. The disadvantages of the chemical method of obtaining coagulants are the need for additional equipment for storage and dosing of chemical reagents, secondary contamination of wastewater with sulfates, chlorides, etc.

A more ecological and economical way to obtain coagulants – metal hydroxides, is electrochemical dissolution of metal (aluminum, iron, copper, zinc, etc.) anodes in electrolyte solutions, which is successfully used in electrocoagulation method of wastewater treatment of different chemical composition [11-15].

Literature Review

When using metal anodes, electrolytic dissolution occurs with the transition to a solution of metal ions, which subsequently form coagulants - insoluble metal hydroxides. Newly formed coagulants have increased adsorption activity to colloidal and suspended particles and are used in the processes of electrocoagulation of wastewater treatment. During electrocoagulation of wastewater, other electrochemical, physicochemical and chemical processes can take place in the following sequence: electrophoretic concentration (directed movement of dispersions as freely charged particles and their concentration near the electrode surface); electrolytic dissolution of anodes and formation of metal hydroxides; polarization coagulation of dispersed particles; packaging of primary units and flocculation coagulation; flotation of the formed aggregates by bubbles of electrolytic gases. All these processes in the complex provide a high degree of purification of contaminated wastewater, which are in different phase-dispersed states.

The process of electrochemical formation of coagulants is influenced by many factors: the material of dissolved anodes, the number of anodes in the cell, pH, current, the presence of other electrolytes in wastewater, voltage, duration of electrocoagulation, etc. [11, 12, 14-16]. The efficiency of electrocoagulation is usually assessed by the degree of wastewater treatment from a particular type of pollution, which is characterized by a certain indicator. For example, for dairy wastewater, these indicators may be chemical oxygen demand (COD), the amount of ethereal soluble substances (ESS), the amount of suspended solids, etc.

In [11], electrocoagulation of dairy wastewater was performed using aluminum electrodes and the efficiency of the process was evaluated by the value of COD and the amount of suspended solids. It was found that at the initial pH≈5 of wastewater, at an electric current density of 61.6 A/m^2, which was applied for 21 minutes, COD decreased by 57% and the total amount of suspended solids decreased by 97%. At the same time, the pH of treated (treated) wastewater increased to 10.

Electrocoagulation of palm oil production wastewater was studied in [16]. It was found that the optimal number of aluminum electrodes for maximum treatment of wastewater from dyes is 4, the optimal voltage is 15 V. The amount of added electrolyte NaCl for maximum efficiency of the treatment process is 1.67 g/dm^3.

In [17], the authors investigated the electrocoagulation treatment of wastewater from a paper processing plant. The efficiency of the process was determined by the following indicators of wastewater: chemical oxygen demand (COD), the amount of suspended solids, the amount of ammonia and color. To increase the efficiency of pollutant removal, a combination of four vertically arranged electrodes was used in the electrolyzer, in which two iron electrodes were located between two aluminum electrodes. The influence of the duration of the electrocoagulation process, electric voltage and initial pH of wastewater on the efficiency of wastewater treatment from the above pollutants is determined. It is established that the optimal parameters of electrocoagulation are the value of electric voltage 10 V, the initial pH of wastewater 7, the duration of the process – 60 minutes. Under these conditions, the removal efficiency of COD, suspended solids, color and ammonia is 79.5%, 83.4%, 98.5% and 85.3%, respectively.

The authors [18] conducted experiments on electrocoagulation of wastewater treatment of acetic acid production. The arrangement of the laboratory installation consisted of three vertically arranged aluminum and three iron electrodes, three of which were the cathode and three - the anode. The comparative characteristics of two cases were studied: aluminum electrodes - anodes and iron electrodes - anodes. The cathodes, respectively, were iron or aluminum electrodes. According to the technology, additional chemical reagents were added to wastewater - sodium sulfate to increase electrical conductivity, as well as high molecular weight polymeric substances of organic and inorganic nature to improve the coagulation process. The influence of electric current density, pH value and nature of the additive on the efficiency of the wastewater electrocoagulation process was studied. It was found that in the case of aluminum anodes, current density 20 mA/cm^2 and initial pH4, 90.91% of COD removal was achieved. At the same time, 42.42 kWh/m^3 of electricity was used for processing. It is established that in the case of using iron anodes, current density

22.5 mA/cm^2, initial pH~9, without any chemical additives, the removal of COD reaches 93.58%. 47.06 kWh/m^3 of electricity was used for processing.

Many scientific studies have studied the patterns of electrochemical formation of coagulants [18-22]. The main chemical reactions of aluminum hydroxide formation that occur in the process of electrocoagulation of wastewater are the following (in the case of aluminum anodes):

- on aluminum anodes of aluminum oxidation:

$$Al_{(solid)} \rightarrow Al^{3+}_{(aqua)} + 3e; \quad (1)$$

- on the cathodes of water reduction:

$$3H_2O + 3e \rightarrow 3/2\ H_{2\ (gas)} \uparrow + 3OH^-_{(aqua)}; \quad (2)$$

- formation of coagulant in acidic or neutral environment:

$$Al^{3+}_{(aqua)} + 3H_2O \rightarrow Al(OH)_{3(solid)} \downarrow + 3H^+_{(aqua)}; \quad (3)$$

- formation of coagulant in alkaline medium:

$$Al^{3+}_{(aqua)} + 3OH^-_{(aqua)} \rightarrow Al(OH)_{3(solid)} \downarrow. \quad (4)$$

According to the authors [12, 16, 19-21], in an alkaline environment monomeric are formed $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_4^-$ and polymer $Al_2(OH)_2^{4+}$, $Al_2(OH)_5^+$, $Al_6(OH)_{15}^{3+}$, $Al_{13}(OH)_{34}^{5+}$ aluminum complexes, which are able to increase the efficiency of electrocoagulation due to the fact that they have both positive and negative charges. However, experimental data [18, 22] show that increasing the initial pH value of wastewater can, conversely, reduce the efficiency of electrocoagulation. According to the authors [18], at pH>7 a gel layer is formed on the aluminum anode, which slows down the oxidation processes and, accordingly, the formation of coagulant.

Thus, it is established that the efficiency of electrochemical formation and chemical nature of coagulants (metal hydroxides, complex ions) for electrocoagulation treatment of dairy wastewater directly depends on the conditions of the process. First of all, the pH of the source wastewater, the presence of various pollutants, the strength or density of the electric current, the duration of the experiment. The mechanism of coagulant formation in media with different pH values has been found to be incompletely studied, especially the electrochemical formation of aluminum-based coagulants. Therefore, the study of chemical and technological parameters of electrochemical production of coagulants based on aluminum for electrocoagulation wastewater treatment of dairy enterprises is an important scientific and practical task.

Materials and Methods of Research

Wastewater from a dairy plant in the Sumy region (Ukraine) was used for the study. For research during two working shifts, wastewater samples were taken from the milk collection area, laboratory, cheese shop, hardware department, butter shop, processed cheese shop and sales department. Taking into account the contribution to the total runoff of each section of the enterprise, the total runoff with the average composition of wastewater was formed.

Electrocoagulation treatment of wastewater was carried out in a laboratory installation, which includes an electrolyzer made of organic glass with dimensions of 18 cm × 15 cm × 4 cm. The volume of treated wastewater was about 1 dm^3. The area of aluminum electrodes was about 250 cm^3. Sodium hydroxide NaOH in the form of a 5% aqueous solution was used as an alkaline additive.

The efficiency of treatment was studied by the following indicators of wastewater: pH, transparency, amount of ether-soluble substances, content of orthophosphate ions PO_4^{3-} and ammonium nitrogen ions NH_4^+ [2, 23]. The pH was determined at a temperature of 18-20^{0}C using a portable pH meter brand SX 711 (China) with a measurement accuracy of ± 0.001pH. The transparency of the water was determined using a Snellen instrument, which is a glass cylinder with a flat bottom. The amount of essential soluble substances (fats and mineral oils) (ESS) was determined by the method of multiple extraction with petroleum ether as an extractant. After evaporation of the ether from the extract by weight, the mass of all soluble ether-soluble substances was determined. The content of orthophosphate ions and ammonium nitrogen ions was determined by photometric method using a laboratory photometer.

Discussion of the Research Results

To study the effect of pH on the patterns of coagulant formation and treatment efficiency, wastewater with an average composition was selected. Electrocoagulation was performed for 10 minutes at an electric current density of 0.005 A/cm^2. Before treatment, an alkaline additive was added to the wastewater, which allowed to vary the pH from 4.0 to 8.7. The results obtained are presented in Table 1.

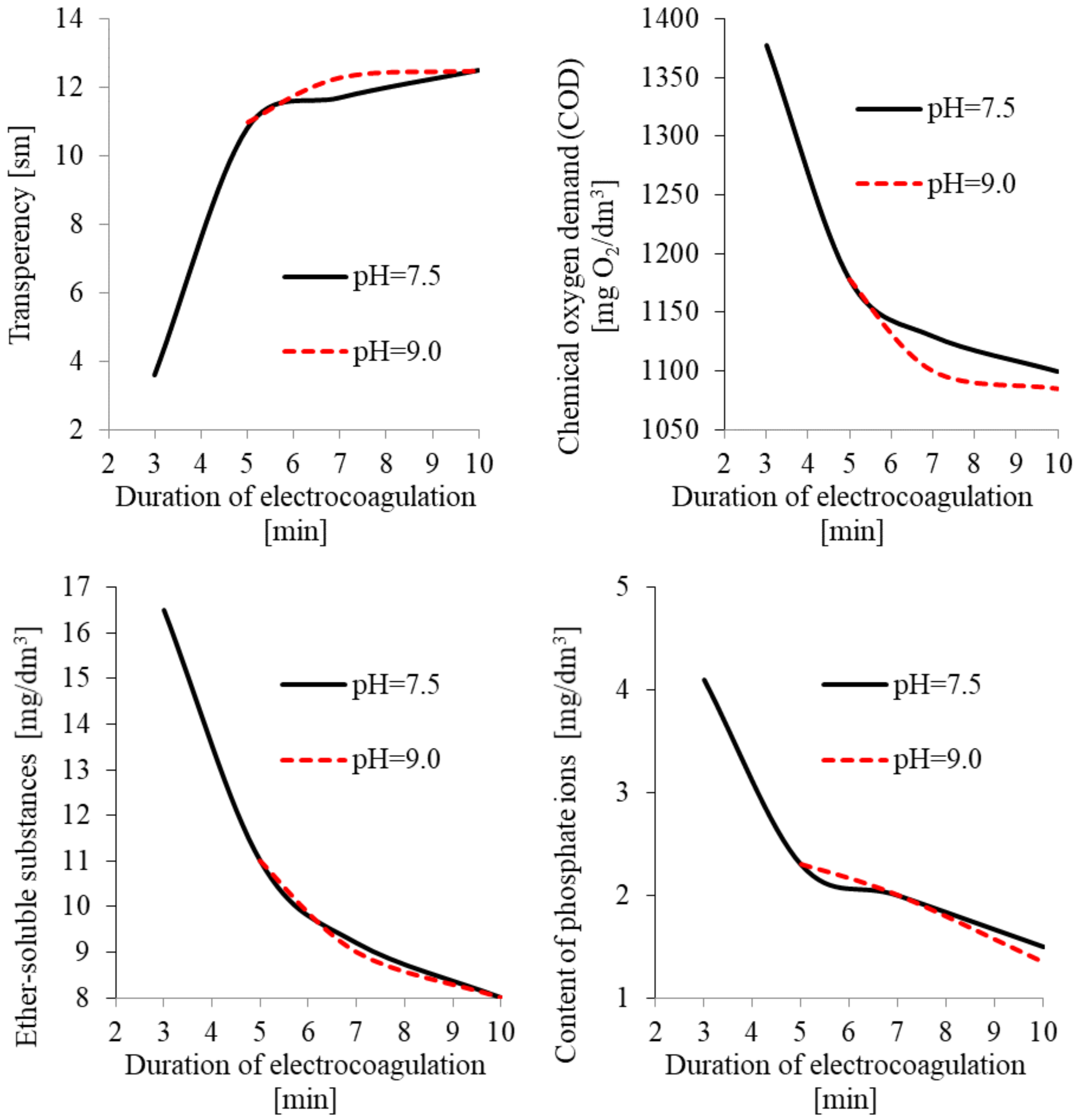
Table 1. The effect of pH on the patterns of coagulant formation and wastewater treatment efficiency

pH		COD, [mgO/dm^3]	ESS, [mg/dm^3]	Purification effect, [%]	
to electrocoagulation	after electrocoagulation			from COD	from ESS
4.0	-	12000	1260	-	-
4.0	5.0	1200	22	90.0	98.3
4.9	5.6	1200	9	90.0	99.3
5.8	6.2	1200	7	90.0	99.4
6.7	7.2	1100	7	90.9	99.4
7.6	7.2	1100	5	90.9	99.6
8.7	7.2	1080	2	91.0	99.9

As can be seen from the presented results, after electrocoagulation of wastewater without the addition of alkaline additives, the degree of purification by COD and ESS is 90 and 98.3%, respectively. Addition before treatment of an alkaline additive to the pH of the source water 4.9-5.8 does not affect the degree of purification by COD and slightly increases (approximately 1%) the degree of purification by ESS. The pH of the water after electrocoagulation increases. Therefore, it can be stated that electrochemical processes (1-3) occur in electrocoagulation in acidic and weakly acidic (pH ≈ 4.0-5.8) medium. The process of oxidation of water at the cathode (2) with the formation of OH^- ions predominates, which leads to a slight increase in the pH at the end of electrocoagulation. It is obvious that in such conditions the formation of aluminum complexes does not occur, which would inevitably lead to a decrease in pH. Therefore, it can be concluded that the electrocoagulation of acidic and weakly acidic wastewater ($4<pH<6$) mainly produces particles of molecular structure $Al(OH)_3$, which perform the main coagulating action and provide a certain degree of purification. At the same time the adsorption mechanism of removal of pollutants is realized to a greater extent.

If an alkaline additive is added before electrocoagulation to form a neutral and slightly alkaline medium, the following is observed after treatment. The degree of wastewater treatment is slightly higher, both for COD (by 1%) and for ESS (by 1.6%). The pH of the water after treatment remains neutral and does not depend on the amount of added alkaline additive. Obviously, this is due to additional acidification of the solution due to hydrolysis of monomeric $AlOH^{2+}$, $Al(OH)_2^+$ and polymeric $Al_2(OH)_2^{4+}$, $Al_2(OH)_5^+$, $Al_6(OH)_{15}^{3+}$, $Al_{13}(OH)_{34}^{5+}$ aluminum complexes formed in excess of OH^- ions. Electrochemical processes take place in water during neutral and weakly alkaline electrocoagulation (1,2,4). But the process of coagulant formation in the form of $Al(OH)_3$ (4) obviously does not occur. Therefore, in the electrocoagulation of neutral and weakly alkaline wastewater (9>pH>6) as coagulating substances are monomeric and polymeric aluminum complexes, which are charged particles. This provides a higher degree of wastewater treatment. At the same time the mixed mechanism of removal of pollutants is realized: along with adsorption electrostatic coagulating action is possible.

The results of the experiments suggested that the addition of alkaline additives may be more effective after the process of electrocoagulation of wastewater. To test this hypothesis, studies on electrocoagulation of wastewater with different process times – 3, 5, 7 and 10 minutes. The addition of alkaline additive to pH=7.5 and pH=9.0 was carried out after the electrocoagulation process. The treated water with the added alkaline additive was mixed. After filtration, the filtrate was determined for transparency, COD, ESS, the amount of phosphate ions and the amount of ammonium nitrogen ions. The results obtained are presented in Fig. 1 and in Table 2.



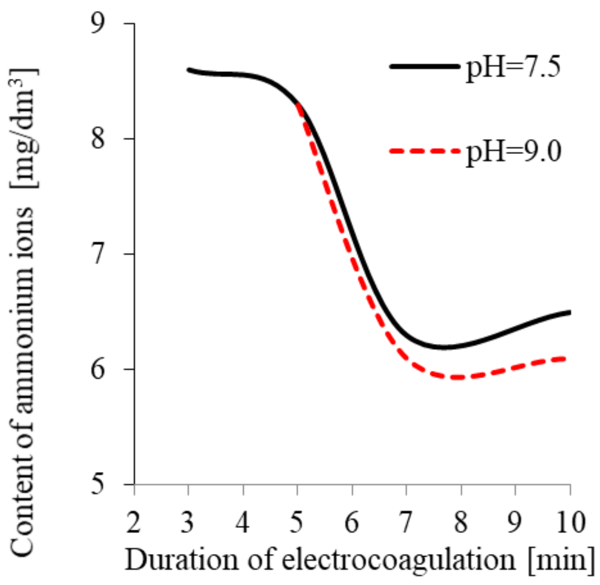


Fig. 1. Regularities of pH and electrocoagulation term influence on chemical composition of wastewater

Table 2. The effect of pH and electrocoagulation time on the degree of wastewater treatment

Duration of electrocoagulation [min]	pH	Purification effect [%]				
		for transparency	for COD	for ESS	for phosphate ions	for ammonium ions
3	7.5	83.2	73.1	97.5	97.2	14.3
5	7.5	94.4	77.1	98.3	98.4	17.5
7	7.5	94.9	78.0	98.6	98.6	37.7
10	7.5	95.2	78.6	98.8	99.0	35.0
5	9.0	94.5	77.1	98.3	98.4	17.5
7	9.0	95.1	78.6	98.6	98.6	39.0
10	9.0	95.2	78.8	98.8	99.1	39.0

Based on the results of the experiment, the following conclusions can be drawn. Regularities of the effect of pH and electrocoagulation time on the chemical composition of wastewater can be divided into two periods. The first period is limited to the period of electrocoagulation from 3 to 5 minutes. During this time, the degree of wastewater treatment from any contaminants does not depend on pH. The second period is limited to the period of electrocoagulation from 5 to 10 minutes. In this case, the pH value affects the degree of purification: with increasing pH, the degree of purification of wastewater from contaminants increases. Therefore, as can be seen from the presented data, the addition of alkaline additives after electrocoagulation is more efficient and will reduce the processing time. The degree of wastewater treatment will remain quite high (98-99%). This will save electricity and have a positive impact on the environmental and economic assessment of technology. Also from the obtained results it can be concluded that the pH value does not significantly affect the patterns of coagulant formation, the mechanism of coagulating action and the degree of wastewater treatment.

Conclusions

Researches of chemical-technological parameters of electrochemical production of coagulants on the basis of aluminum for electrocoagulation treatment of sewage of dairy processing enterprises are carried out. It is established that the efficiency of electrochemical formation and chemical nature of coagulants (metal hydroxides, complex ions) for electrocoagulation treatment of dairy waste directly depends on the process conditions: wastewater pH, the presence of various pollutants, strength or density of electric current, duration of electrocoagulation. The influence of pH and terms of the electrocoagulation process was studied in two cases of the technological process: when adding an alkaline additive before and after electrocoagulation treatment. In the case of the first case, the following conclusions can be drawn. Electrocoagulation of acidic and weakly acidic wastewater ($4<pH<6$) mainly produces particles of molecular structure $Al(OH)_3$, which perform the main coagulating action and provide a certain degree of purification. At the same time the adsorption mechanism of removal of pollutants is realized to a greater extent. In electrocoagulation of neutral and weakly alkaline wastewater ($9>pH>6$) as coagulating substances are monomeric and polymeric aluminum complexes, which are charged particles. This provides a higher degree of wastewater treatment. At the same time the mixed mechanism of removal of pollutants is realized: along with adsorption electrostatic coagulating action is possible. It was found that the addition of alkaline additives after electrocoagulation is more effective and will reduce the processing time. The degree of wastewater treatment remains quite high (98-99%). This will save electricity and have a positive impact on the environmental and economic assessment of technology.

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