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ELECTROCOAGULATION OF MODEL WASTEWATER USING IRON ELECTRODES

ELEKTROKOAGULACJA ŚCIEKÓW MODELOWYCH NA ELEKTRODACH ŻELAZNYCH

Abstract: This paper presents the results of electrocoagulation of model wastewater using iron electrodes under laboratory conditions. The investigated wastewater was susceptible to electrolytic treatment, and the model system supported the performance of analyses in seven replications, generating a database for reliable statistical and mathematical processing. Wastewater was treated by chronopotentiometric electrocoagulation in a static system at constant current intensity $I = 0.3$ A. Changes in supply voltage for $I = \text{const}$ were registered over time. Changes in pH, turbidity, chemical oxygen demand (COD), suspended solids and total phosphorus concentrations in the treated wastewater were determined. A new method for determining the optimal dosage of the iron electrocoagulant was proposed by relying on the third degree polynomial function rather than the parabolic equation. The proposed method, justified theoretically and demonstrated practically, enabled precise determination of the electrocoagulant dose. An increase in the electrocoagulant dose increased the share of sweep electrocoagulation in the wastewater treatment process.

Keywords: model wastewater, dose of iron electrocoagulant

Wastewater is popularly treated with the involvement of mechanical and biological methods. Their effectiveness may be limited, therefore supplementary treatment methods are often deployed. One of such methods involves chemical coagulation which supports the biological treatment of wastewater. Chemical coagulation is used to remove excess orthophosphate ions from industrial and municipal effluents with the application of the following reagents: aluminum and iron sulfates, iron(III) chloride, other iron coagulants [1] and polyaluminum chloride (PAC) [2]. The results generated by treatment models [3] and simulations [4, 5] continue to expand our knowledge about the chemical coagulation process.

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Electrocoagulation poses an alternative to chemical coagulation in the treatment of water and effluents. Electrocoagulation methods generally involve iron or aluminum anodes that undergo electrolytic dissolution. Iron and aluminum ions are introduced to the processed water or effluent where they act as electrocoagulants. In the process of oxygen cathodic polarization, the introduction of coagulating Fe^{2+} ions which undergo oxidation to Fe^{3+} increases the system's pH [6], whereas conventional chemical coagulation always lowers pH due to the hydrolysis of Fe^{3+} cations (PIX) [7]. In chemically coagulated and electrocoagulated wastewater, Fe^{3+} cations create positive micelles $\{\text{Fe}(\text{OH})_3\}$ that act as colloidal sorbents [8] for wastewater pollutants such as suspended solids, phosphorus compounds and substances responsible for the COD load.

In markets characterized by cheap energy and high cost of transporting chemicals, electrocoagulation poses a vital alternative to chemical coagulation since iron electrodes are much lighter than coagulating substances, *eg* PIX. Electrocoagulation requires simple equipment and is easy to operate. The addition of sea water, which is characterized by a high content of NaCl as the conductor of electricity, to wastewater or water [9,10] significantly lowers electricity consumption during electrocoagulation. Chloride compounds, the by-products of the process, additionally disinfect the treated effluents.

The experiment described in this study supported the development of a new method for the quantitative interpretation of the electrocoagulation process and the determination of the optimal iron electrocoagulant dose. It also attempted to explain the mechanism of treating model wastewater by electrocoagulation using iron electrodes in a static system.

Metods

The chronopotentiometric electrocoagulation process was carried out at constant current intensity ($I = \text{const}$) with the use of iron electrodes in a device shown in Fig. 1.

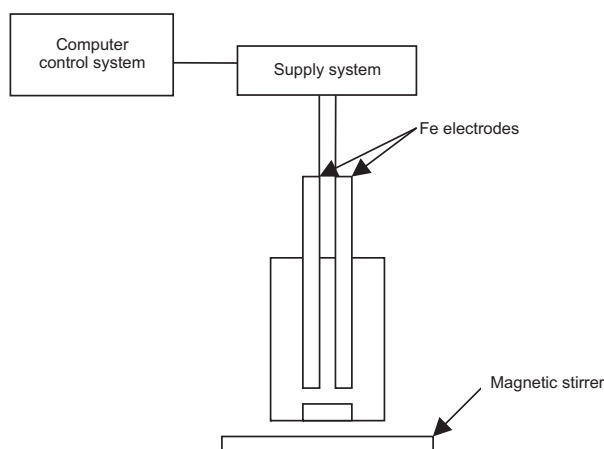


Fig. 1. Laboratory device for static electrocoagulation of wastewater

100 cm³ of freshly prepared model wastewater with a phosphate buffer was poured into six laboratory beakers. Saturated NaCl solution was added to each beaker in quantities (usually 11 drops) that increased specific conductivity to $\kappa \approx 4$ mS. To ensure the equivalence of wastewater electrocoagulation, the anticipated electrocoagulant dose m was input each time into Faraday's equation

$$m = k \cdot I \cdot t,$$

where: m – weight of the iron electrocoagulant in grams,
 k – electrochemical gram equivalent of Fe(II); $k = 56/2 = 28$ g,
 I – electric current in amperes,
 t – and the planned electrocoagulation time was determined
at $I = 0.3$ A = const, electrolysis time in seconds.

Current I was kept constant at 0.3 A, and higher doses of electrocoagulant required longer electrocoagulation time t . The iron electrocoagulant was dosed as follows:

- beaker 1 = 512 s electrolysis,
- beaker 2 = 768 s,
- beaker 3 = 1024 s, etc.

Electrocoagulation was carried out with the use of two iron electrodes measuring $100 \cdot 10 \cdot 1$ mm each. The electrodes were immersed at a depth of 5 cm, with a precise spacing of 1 cm, in 100 cm³ beakers containing model wastewater. Wastewater was continuously stirred with an electromagnetic stirrer. Treatment took place at constant current of $I = 0.3$ A and registered voltage V . Every 256 s, the control system automatically changed the direction of current flow on the electrodes to enable cathode self-cleaning [11]. A contaminated cathode was thus transformed into a soluble anode, and it was purified by anode dissolution. The entire process was controlled by a computer. A unique hardware and software system had been designed and built for the needs of the experiment.

After electrolysis, samples were collected from the supernatant layer, and the following wastewater parameters were determined after 30 min of sedimentation with the application of standard HACH methods [12]: pH, COD, total phosphorus, turbidity and suspended solids concentrations. Electrocoagulation was performed in seven replications, and the two highest and the two lowest values were rejected. The remaining three values were used to compute the mean value and the standard deviation (SD). The results were presented in graphic form.

Results

The changes in supply voltage V for constant $I = 0.3$ A were registered over time t . The average values of function $V = f(t)$ are shown in Fig 2.

A clear change in current direction can be observed every 256 s. This value guarantees electrode (cathode) self-cleaning and it minimizes polarization loss, therefore it was adopted as the optimum parameter for electrocoagulation in model systems [11].

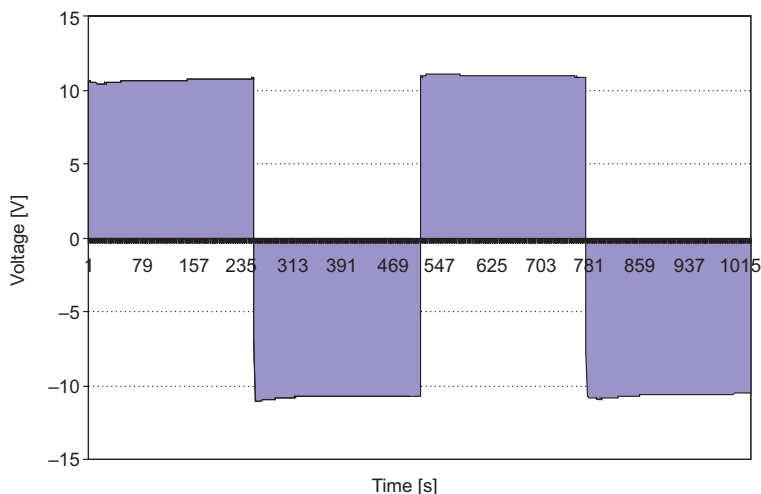


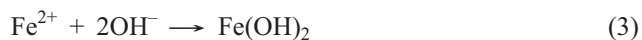
Fig. 2. Changes in voltage over time producing $I = \text{const} = 0.3 \text{ A}$

During electrolysis time of 256 s, voltage did not exceed 11 V, + or –, respectively. In semi-technical and industrial tests investigating natural wastewater, the above data would support the full determination of electrocoagulation parameters, including electric power, power consumption, etc.

The changes in wastewater pH during electrocoagulation with the use of iron electrodes are presented in Fig. 3. The electrocoagulation process always increased the pH of treated wastewater to around 9.2. One of the reasons for the pH increase during electrocoagulation is hydrogen ion secretion resulting from water reduction at the cathode:



The electrocoagulation process with the use of iron electrodes, at $\text{pH} > 7$, leads to the following reactions at the phase boundary:



Depending on wastewater pH during electrocoagulation, iron may form the following ions:



subsequently converted to $\text{Fe}(\text{OH})_3$ [6]. The type of the resulting ions and wastewater pH may significantly influence treatment effectiveness.

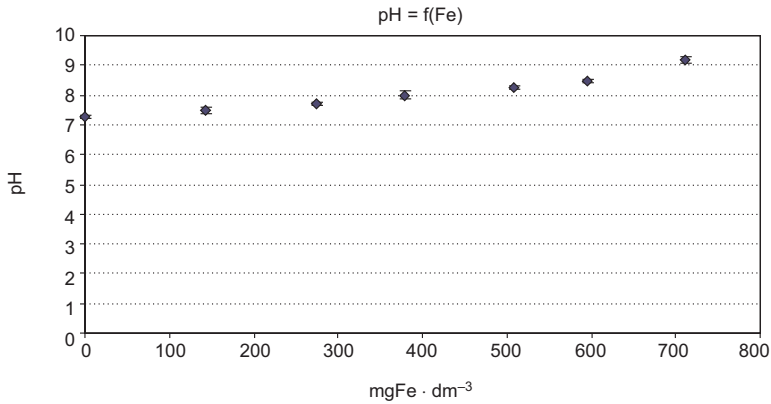
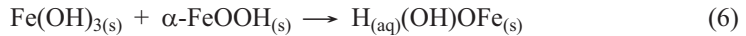


Fig. 3. Changes in wastewater pH

In experiments involving iron electrodes, iron(II) ions were generated into the system, and they were partially oxidized to iron(III). The above was demonstrated by the color of the treated wastewater and supernatant which changed from grayish green to reddish brown. At high pH and in aerobic conditions, Fe^{2+} ions and their hydroxyl complexes are easily converted to $\text{Fe}(\text{OH})_3$ and FeOOH , the co-products of the process. Those co-products may be transformed into hydrogenated iron(III) hydroxy species in the following reaction [13]:



The resulting species are electrically neutral, and they are unable to destabilize negatively charged wastewater pollutants. Owing to their surface charge, they can absorb pollutants on the surface, scavenge them and form complexes with those impurities.

The removal of suspended solids from wastewater coagulated with the use of an iron electrocoagulant is presented in Fig. 4. In the above third-degree polynomial curve, the

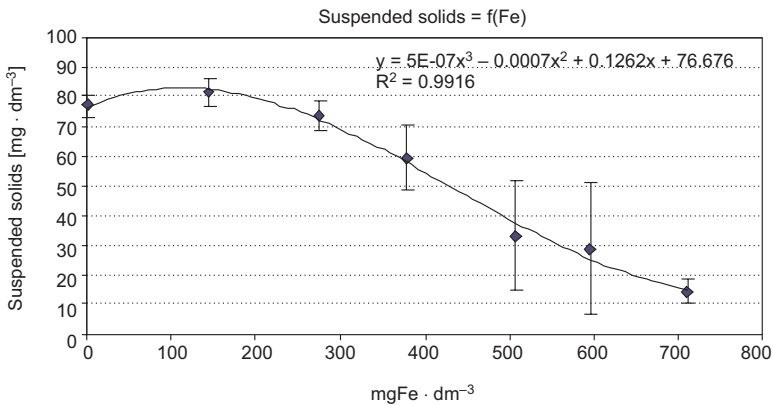


Fig. 4. Removal of suspended solids from wastewater

point of inflection is determined at an electrocoagulant dose of $550 \text{ mgFe} \cdot \text{dm}^{-3}$. The effectiveness of the applied mathematical model is demonstrated by the high value of the coefficient of determination $R^2 = 0.9916$. Significant standard deviation values could be attributed to very long flocculation times and the resulting difficulty in collecting water samples above the sediment layer. A small portion of flocs was always sampled together with a specimen of treated waste.

The most effective dose that removed nearly 81 % of suspended solids was around $710 \text{ mgFe} \cdot \text{dm}^{-3}$. A much lower dose of approximately $590 \text{ mgFe} \cdot \text{dm}^{-3}$ resulted in 63 % efficiency, which is a relatively satisfactory result in the initial phase of chemical wastewater treatment. The use of PIX in similar conditions reduced suspended solid concentrations by 63 % [8].

Treatment effectiveness is largely determined by the form of ions which emerge as “primary” ions in the electrocoagulation system. Based on the Pourbiax diagram [14], it can be assumed that the predominant monomeric forms of iron in the experiment were colloidal $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_4^-$ ions. Those ions do not destabilize negatively charged pollutants, and they merely bridge positively charged impurities. It can be assumed that at low initial doses of the electrocoagulant, the predominant process during wastewater treatment is sorption on colloidal micelles of iron hydroxide, whereas the share of sweep electrocoagulation increases gradually at higher electrocoagulant doses [15].

The removal of turbidity from model wastewater coagulated with the use of iron electrocoagulant is presented in Fig. 5. The curve shows a high degree of similarity to function $\text{Suspended solids} = f(\text{Fe})$. The noted similarity validates the control function, *ie* the correlation between wastewater turbidity and suspended solids. Similarly to the removal of suspended solids, the most effective dose of around $710 \text{ mgFe} \cdot \text{dm}^{-3}$ removed turbidity in nearly 62 %. The highest dose of $710 \text{ mgFe} \cdot \text{dm}^{-3}$ was only 2 % more efficient than the dose of $590 \text{ mgFe} \cdot \text{dm}^{-3}$.

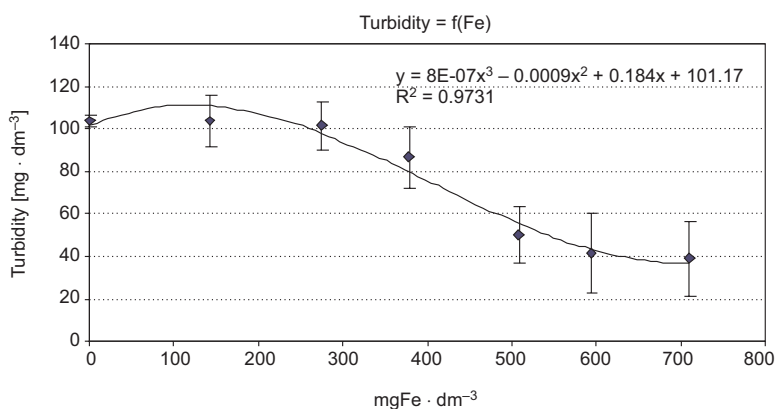


Fig. 5. Removal of wastewater turbidity

Such high coagulant doses resulted probably from the high pH levels of treated wastewater. Similarly as with suspended solids, an increase in pH after electrocoagulation caused a decrease in the sorption on colloidal micelles of iron hydroxide

and an increase in the sweep of pollutants as a result of their direct contact with sedimenting flocs of iron(II) and iron(III) hydroxides.

The third-degree polynomial curve in Fig. 6 illustrates the removal of phosphorus compounds from wastewater coagulated with an iron electrocoagulant. Significant standard deviation values can probably be attributed to the slow sedimentation of iron hydroxide flocs. Due to sedimentation (or flotation), not all flocs with absorbed pollutants are removed from treated wastewater, and they may be sampled together with the analytical specimen. Samples are rarely filtered before analysis for practical reasons. Relatively high standard deviation values were reported as a result of the sedimentation procedure. Despite the above, the curve shown in Fig. 6 is characterized by a high coefficient of determination $R^2 = 0.9792$, thus further validating the choice of the applied mathematical model.

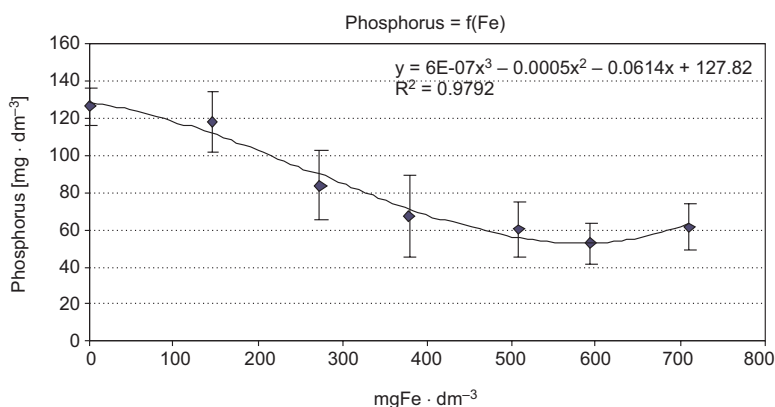


Fig. 6. Removal of phosphorus compounds from wastewater

In the analyzed curve, the point of inflection was determined at a electrocoagulant dose of approximately $380 \text{ mgFe} \cdot \text{dm}^{-3}$, which was much lower than that in suspended solids and turbidity diagrams. Unlike in those diagrams, a dose increase to $710 \text{ mgFe} \cdot \text{dm}^{-3}$ in the discussed curve did not lead to changes in phosphorus concentrations in treated wastewater. It could be expected that a further increase in the electrocoagulant dose would inhibit the sorption-coagulation process, leading to an insignificant destabilization (peptization) of sludge and a drop in phosphorus concentrations above the sludge.

The highest of the three applied doses were marked by similar phosphorus removal efficiency in the range of 51–58 %. Electrocoagulation with iron electrodes was characterized by phosphorus removal efficiency similar to that delivered by PIX [8]. The differences in the doses of chemical coagulants and electrocoagulants result from the effect of the system's pH and the direction of changes in pH on the treatment process. The pH of wastewater significantly influences the structure of active ionic forms of iron, and treatment effectiveness is largely determined by the "primary" forms. In this experiment, the lowest dose of the iron electrocoagulant raised pH to

approximately 7.5 (Fig. 3), and a further increase in electrocoagulant doses resulted in $\text{pH} > 9$. At such high pH levels, the system is characterized by a predominance of monomeric iron species [6], *ie* colloidal iron hydroxides and $\text{Fe}(\text{OH})_4^-$ ions. The above ions are unable to destabilize negatively charged phosphates. It should be noted that a Fe : P molar ratio higher than 1 : 3, which guarantees the removal of phosphorus from wastewater, rules out a simple precipitation reaction, such as: $\text{Fe}_3(\text{PO}_4)_2\downarrow$, $\text{FePO}_4\downarrow$, $(\text{FeOH})_3(\text{PO}_4)_2\downarrow$, $(\text{FeOH})_3\text{PO}_4\downarrow$, as a process of removing phosphorus from wastewater by electrocoagulation with the use of iron electrodes.

The removal of substances responsible for the COD load from model wastewater coagulated with the use of iron electrocoagulant is presented in Fig. 7. The COD curve is characterized by a high coefficient of determination $R^2 = 0.9916$ and low standard deviation values. The above confirms the analyzed wastewater's susceptibility to electrolytic treatment and high goodness of fit of the applied mathematical model (third degree polynomial) for the resulting experimental data.

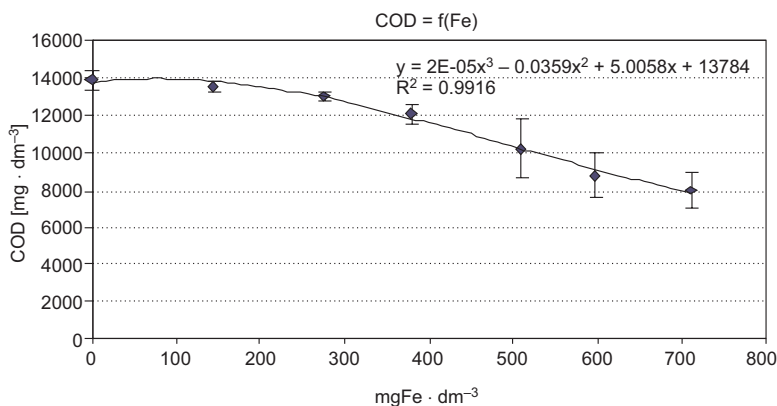


Fig. 7. Removal of substances responsible for the COD load

The most satisfactory results were reported for the highest dose of $710 \text{ mgFe} \cdot \text{dm}^{-3}$ which removed 43 % of substances responsible for the COD load. The noted results are superior to PIX [8], but the required dose is 1.5-fold higher. The higher efficiency of the iron electrocoagulant than PIX resulted from differences in the system's pH and the direction of changes in pH values during wastewater treatment.

Experimental conditions supported sweep coagulation. Higher electrocoagulant doses raised pH which, in turn, increased the share of sweep coagulation. In chemical coagulation, an increase in chemical coagulant doses lowered the system's pH and contributed to the destabilization of wastewater colloids. The drop in pH was also accompanied by the risk of sludge peptization. The above attests to the parabolic character of changes in suspended solid concentrations, turbidity, phosphorus concentrations and COD levels as a function of the coagulant dose. High pH levels during electrocoagulation significantly minimize the risk of sludge peptization, suggesting that the third-degree polynomial curve better fits electrocoagulation data than a parabola.

The observed changes in turbidity, suspended solids and phosphorus compound concentrations and substances responsible for the COD load in electrocoagulated wastewater indicate that experimental conditions supported sweep coagulation. Growing pH during treatment and a high final pH prevented the generation of effective iron cations that ensure high treatment effectiveness at the stage of latent and slow coagulation. The iron species produced in the presence of excess electrocoagulant ions in an alkaline environment supported:

a) sorption of substances responsible for the COD load on the surface of colloidal iron hydroxide,

b) bridging of positively charged impurities with the involvement of, for example $\text{Fe}(\text{OH})_4^-$,

c) sweeping of neutral as well as positively and negatively charged impurities that remained in direct contact with sedimenting iron hydroxide flocs.

Conclusions

The investigated model wastewater was susceptible to electrocoagulation treatment with the use of iron electrodes. In every experimental area, turbidity removal values fully validated the results reported in respect of suspended solids removal. The third degree polynomial method was used to plot curves showing changes in COD, total phosphorus concentrations, turbidity and suspended solids concentrations during wastewater treatment and to calculate the relevant electrocoagulant doses. Every increase in the iron electrocoagulant dose raised the pH of treated wastewater and minimized the probability of destabilization of negatively charged wastewater colloids. The share of sweep coagulation in the treatment process increased with a rise in the applied electrocoagulant dose. The noted values of the Fe : P molar ratio suggest that phosphorus removal from the treated wastewater did not involve the precipitation of iron phosphate sludge, and that the substances responsible for the COD load as well as phosphates are adsorbed by colloidal micelles of iron hydroxide.

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ELEKTROKOAGULACJA ŚCIEKÓW MODELOWYCH NA ELEKTRODACH ŻELAZNYCH

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Abstrakt: W pracy przedstawiono wyniki badań laboratoryjnych procesu elektrokoagulacji ścieków modelowych na elektrodach żelaznych. Użyte ścieki okazały się podatne na oczyszczanie elektrolityczne i tym samym, jako układ modelowy, umożliwiły prowadzenie badań aż w 7 powtórzeniach, co z kolei zapewniło bazę danych nadającą się do wiarygodnej obróbki statystyczno-matematycznej. Oczyszczanie ścieków prowadzono w statycznych warunkach chronopotencjometrycznych, tj. przy stałym prądzie $I = 0,3$ A. Każdorazowo rejestrowano zmiany napięcia zasilania w czasie zapewniające $I = \text{const}$. Oznaczano zmiany pH, zawiesin i mętności, ChZT oraz fosforu ogólnego w oczyszczanych ściekach. W odróżnieniu od metody wyznaczania dawki koagulantu z równania odpowiedniej paraboli, dla badanego procesu elektrokoagulacji zaproponowano oryginalną, nową metodę obliczania dawki optymalnej elektrokoagulantu żelazowego z równania wielomianu III stopnia. Metoda ta, uzasadniona teoretycznie i praktycznie, umożliwiła każdorazowo bardzo precyzyjne określenie takiej dawki. Stwierdzono, że wzrost dawki elektrokoagulantu żelazowego w układzie prowadzi do zwiększenia udziału elektrokoagulacji „zamiatającej” w badanym procesie oczyszczania ścieków.

Słowa kluczowe: ścieki modelowe, dawka elektrokoagulantu żelazowego