Vol. 18, No. 7 2011

Beata ZAŁĘSKA-CHRÓST[1], Lech SMOCZYŃSKI[1]
and Regina WARDZYŃSKA[1]

TREATMENT OF WASTEWATER FROM THE PULP AND PAPER INDUSTRY BY ELECTROCOAGULATION IN A STATIC SYSTEM

OCZYSZCZANIE ŚCIEKÓW CELULOZOWO-PAPIERNICZYCH METODĄ ELEKTROKOAGULACJI W SYSTEMIE STATYCZNYM

Abstract: Results of the electrochemical treatment of pulp and paper wastewater have been described. The electrolysis was conducted in static system on aluminium electrodes. The wastewater purification was carried out at two values of the current density 3.125 mA/cm^2 and 6.25 mA/cm^2. After electrocoagulation the COD, turbidity, suspended solids and color of the supernatant were measured. The fractal dimension of the aggregates-flocs of the sludge obtained was determined, too. The examined process of statical electrocoagulation turned out to be an efficient method for pulp and paper wastewater purification. The aggregates-flocs measured were recognized as self-simil objects.

Keywords: electrocoagulation, pulp and paper wastewater, fractal dimension

Electrocoagulation is an increasingly popular method of wastewater treatment. According to numerous authors, it is a highly effective technique for treating farming and industrial wastewater as well as municipal sewage from populated areas. The referenced sources describe attempts at the electrolytic treatment of wastewater from textile plants [1–3], fabric dyeing plants [4], tanneries [5], pulp and paper plants [6], as well as the use of the electrocoagulation process in theoretical models [7, 8]. In most cases, the discussed treatment technique involves Al or Fe electrodes [3, 9–11]. The findings of the cited studies suggest that electrochemical coagulation provides a viable alternative to conventional treatment methods involving chemical coagulation [7, 12, 13].

Owing to the specific production technology, the pulp and paper industry significantly contributes to environmental pollution. It increases the total volume of dust and gas

[1] Department of Chemistry, Faculty of Environmental Management and Agriculture, University of Warmia and Mazury, pl. Łódzki 4, 10–957 Olsztyn, Poland, phone: +48 89 523 48 01, fax: +48 89 523 48 01, email: bezetka@uwm.edu.pl

emissions as well as the total quantity of industrial effluents. Pulp and paper wastewater can be treated by biological and chemical methods, but the applied techniques often fall short of increasingly stringent criteria, in particular those pertaining to organic compound removal efficiency. Further research is required to develop improved methods that best suit various types of waste materials so as to optimize wastewater treatment efficiency in observance of the local conditions.

The characteristic features of sludge, including post-coagulation sludge, are an important consideration in the process of optimizing wastewater treatment methods. For this reason, the aim of this study was also to determine the fractal dimension D [14] of aggregates produced by electrocoagulation. Fractal dimension is a source of valuable information about the aggregation mechanism. The fractal nature of aggregates has been studied in various experiments. In a study investigating aggregates formed during biological treatment of water and sewage, Da Hong Li and Ganczarczyk [15] noted that aggregates comprising active sludge particles and particles washed out of the filter bed have fractal properties. Various morphological characteristics of such aggregates could be determined by their fractal dimension. Aggregates formed in a coagulation model involving silica suspension and aluminum coagulants were investigated by Smoczynki and Wardzynska [16]. Their fractal dimension was closely correlated with the coagulants' chemical properties. The aggregates produced in the process of electro-flocculation were studied by Harif and Adin [17].

This study presents the results of the static electrocoagulation process using aluminum electrodes as a method for treating wastewater from the pulp and paper industry.

Materials and methods

Pulp and paper wastewater was obtained from the pulp and paper plant in Swiecie. The sampled wastewater was characterized by the following parameters: COD_o = 731 mg O_2/dm^3, turbidity – 1240 mg/dm^3, color – 240 mg/dm^3, suspended solids – 75 mg/dm^3.

The static system for wastewater electrocoagulation comprised a pair of aluminum electrodes measuring 16 × 1 × 0.1 cm, separated by a distance of 1 cm and immersed in a sewage tank. A self-designed control and supply system stabilized current intensity required for the analyzed process at I_1 = 50 mA and I_2 = 100 mA. In this experiment, the density of current flowing through the electrodes was ρ_1 = 3.125 mA/cm^2 and ρ_2 = 6.25 mA/cm^2. A pH-meter and a burette for dosing 1 M HCl were installed in the sewage tank to maintain wastewater pH at 5.5–6.0 [18]. Samples were collected at equal time intervals, and after sedimentation, COD, turbidity, color and suspended solids were determined by spectrophotometry using a HACH DR 2000 spectrophotometer [19, 20]. Temperature and pH were measured with a HANNA HI 9025 pH meter.

The fractal dimension D of sludge aggregates produced in the treatment process was also determined during electrocoagulation. Fractal dimension values of the studied aggregates were measured 1 h after sedimentation. Fractal dimension was determined by the photographic method. The sedimentation path of aggregates formed by electrocoagulation was photographed. The resulting images were used to determine the actual size (diameter) of flocs and their settling velocity, and to calculate the density "d", of the examined aggregates. Fractal dimension was measured using Stokes' law and the resulting correlation between an object's density and its dimensions:

$$d \sim v / r^2 \tag{1}$$

where: d – density,
r – the object's dimension,
v – settling velocity.

Because:

$$M(r) \sim r^D \tag{2}$$

if D is the fractal dimension, M(r) – mass, then the following dependency can be obtained after a number of transformations:

$$\log d = (D - 3) \log r \tag{3}$$

A comparison between formula (3) and the general power law $y = ax^{\alpha}$ (a – amplitude, α – exponent) indicates that exponent α, ie the expression (D – 3) for formula 3, is equal to the logarithmic slope:

$$\log d \sim f(\log r) \tag{4}$$

The properties of 110 to 160 aggregates were measured for each process type. The collected data were used to map a logarithmic correlation (4) (Fig. 6 and 8) whose slope produced the value of D.

Results

The results of electrocoagulation treatment of wastewater with initial COD_o of 731 mg O_2/dm^3 in a static system are presented below. The process was conducted at two current density values of ρ_1 = 3.125 mA/cm^2 and ρ_2 = 6.25 mA/cm^2 and at different time intervals.

Figures 1 and 2 illustrate changes in the quantity of pollutants removed during electrocoagulation over time t = 3600 s. Analytical samples were collected at equal time intervals of 900 s. The effects of wastewater treatment, both at ρ_1 = 3.125 mA/cm^2 and ρ_2 = 6.25 mA/cm^2, were visible already after 900 s of electrolysis, and they were magnified in the course of the process. A similar drop in COD values reaching a maximum of around 65 % was noted at both current density levels. At higher current density applied to the electrodes (ρ_2), the pollutants responsible for color and suspended solids were removed at a faster rate. Turbidity decreased at a slower rate, and its removal was maintained at a relatively low level of approximately 62 % throughout the process. Various forms of waste purified by electrocoagulation probably remained in the solution, contributing to an increase in turbidity values.

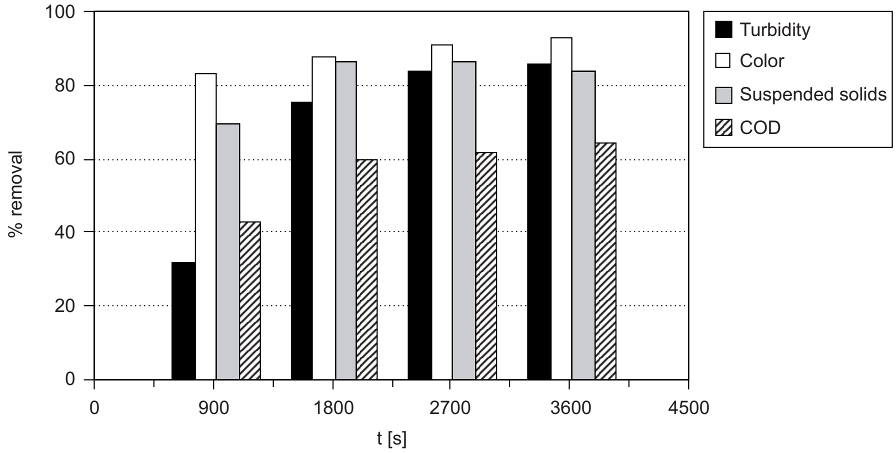

Fig. 1. Percentage removal of pollutants, described by selected parameters, during electrocoagulation performed at ρ_1 = 3.125 mA/cm^2 and t_{max}= 3600 s

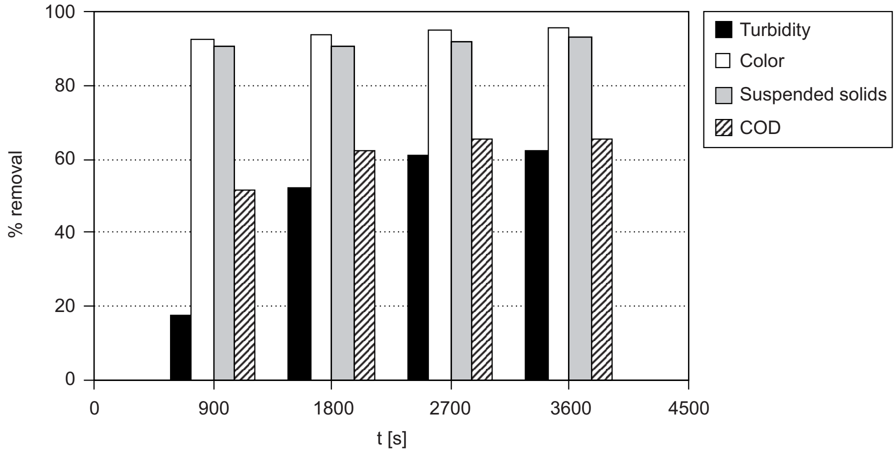

Fig. 2. Percentage removal of pollutants, described by selected parameters, during electrocoagulation performed ρ_2 = 6.25 mA/cm^2 and t_{max}= 3600 s

In view of prior research and the results of the referenced studies, the following diagram was proposed for processes taking place in the solution during electrocoagulation treatment involving aluminum electrodes [6, 9, 11]:

in cathode (–) — in anode (+)

$$3\ H_2O + 3e \rightarrow 3/2H_2\uparrow + 3OH^- \quad (5) \qquad Al \rightarrow Al^{3+} + 3e \quad (6)$$

When Al^{3+} ions become "engaged" in the coagulation-flocculation process during wastewater treatment with the use of aluminum electrodes, the pH of the system increases rapidly because only a part of the formed OH^- ions are transferred to the sludge:

For $x < 3$

$$Al^{3+} + nOH^- + pollutants^{(-)} \rightarrow \{Al(OH)_x\ pollutants\}\downarrow + (n - x)OH^- \qquad (7)$$

After this stage, Al^{3+} ions formed on the anode effectively capture OH^- ions and precipitate them in the form of hardly soluble hydroxide sludge $Al(OH)_3\downarrow$. When the charge threshold is exceeded, the system is quickly destabilized, and an increase in Al^{3+} concentrations leads to the aggregation and flocculation of waste colloids, followed by sedimentation of the resulting sludge.

It cannot be ruled out that the time of sedimentation before sample collection was too short to support the separation of the resulting sludge, therefore turbidity removal values remained low. The increase in the degree of wastewater purification after the approximate time of t = 1800 s was insignificant enough for this value of t to be regarded as sufficient for the process, in particular at higher current density of $\rho_2 = 6.25$ mA/cm^2. The above findings were taken into account in the next series of experiments whose results are presented below.

Figures 3 and 4 illustrate the results of electrocoagulation performed in the successive phase of parameter optimization, within a shorter time interval of 1620 s and at identical current density applied to electrodes ρ_1 and ρ_2. In this group of experiments, two samples were collected for analysis during each process. In the first sample, the rate of COD removal exceeded 55 % already at half the time planned for the process. The application of higher current density ρ_2 (Fig. 4) resulted in high efficiency of turbidity removal and the complete elimination of suspended solids and color from the system. At the lower value of ρ_1 (Fig. 3), suspended solids were completely eliminated, turbidity removal reached 80 % and color removal – 90 %. The noted results indicate

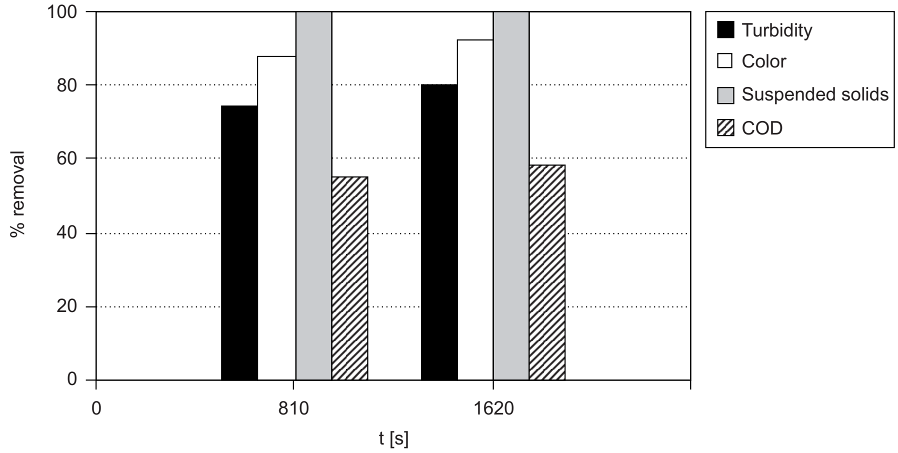

Fig. 3. Percentage removal of pollutants, described by selected parameters, during electrocoagulation performed at $\rho_1 = 3.125$ mA/cm^2 and t_{max}= 1620 s

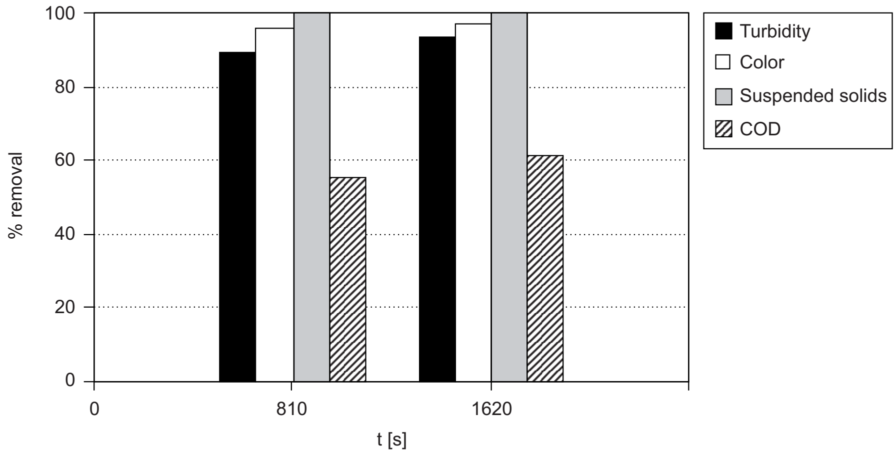

Fig. 4. Percentage removal of pollutants, described by selected parameters, during electrocoagulation performed at ρ_2 = 6.25 mA/cm^2 and t_{max}= 1620 s

that the studied process was more effective at a higher value of ρ_2 and that 1620 s was the optimal time for wastewater treatment.

The correlation between the value of electric charge Q supplied to the solution and purification effectiveness, measured in terms of COD removal, was also determined (Fig. 5). The value of Q was calculated using formula $Q = I \cdot t$ (Q – charge, I – current intensity) in terms of 1 dm^3 of wastewater. The above correlation indicates that an increase in electrical charge from 0 to around 650 C/dm^3 led to the continuous removal of more than 60 % COD from the treated wastewater. In excess of the above value, no further progress was observed in COD removal.

The results of analyses examining the aggregates produced during the electrocoagulation treatment of pulp and paper waste are presented in Tables 1 and 2.

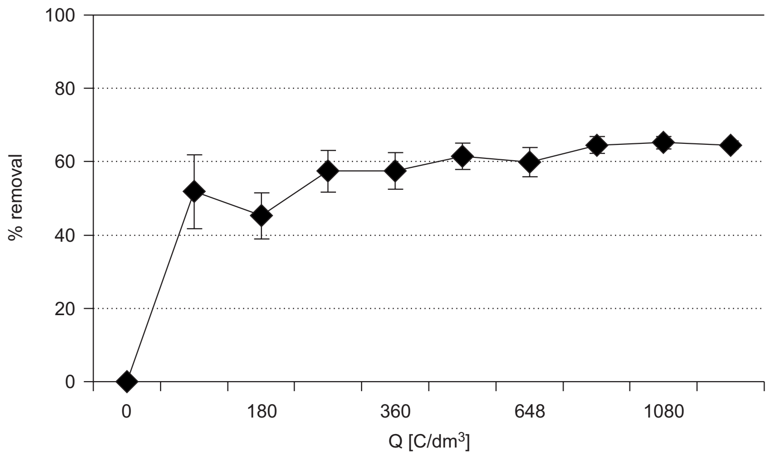

Fig. 5. COD removal subject to the charge flowing through the solution

Treatment effectiveness, expressed by changes in COD removal values, varied during the process. Sludge aggregates were sampled at various stages of treatment to determine their fractal dimension D.

Table 1

Fractal dimension of aggregates produced during the electrocoagulation of pulp and paper wastewater at ρ_1 = 3.125 mA/cm^2

Electric charge flowing through the solution [C/dm^3]	% removal COD	Fractal dimension D
360	30.45	1.55
720	51.72	1.78
810	55.27	1.80
1620	58.14	1.90

Table 2

Fractal dimension of aggregates produced during the electrocoagulation of pulp and paper wastewater at ρ_2 = 6.25 mA/cm^2

Electric charge flowing through the solution [C/dm^3]	% removal COD	Fractal dimension D
360	39.46	1.57
810	55.40	1.60
1620	61.56	1.85
3600	65.86	1.94

The fractal dimension D of the resulting aggregates was determined in the range of 1.55–1.90 for ρ_1 and 1.57–1.94 for ρ_2. A proportional dependency was observed between the degree of wastewater purification and the value of D. The applied current density influenced the effectiveness of treatment (% COD removal) and, consequently, the value of D. The fractal dimension of aggregates in the treated wastewater is, to a varied extent, determined by the degree of sludge hydration. Lower values of D denote sludge characterized by a higher degree of hydration. With an increase in treatment effectiveness, the produced aggregates were marked by growing values of D. The above implies that the degree of sludge hydration decreased with an increase in the treatment effectiveness of liquid-phase waste.

Figures 6 and 8 present logarithmic dependencies lg d = f(lg r) for selected aggregates based on which fractal dimension, D, was determined. The coefficients of determination for successive measurements were marked by symbol R^2. The method of determining the fractal dimension based on dependency lg d = f(lg r) proved to be statistically justified for all aggregates (the coefficient of determination for all processes exceeded 0.9), indicating that the produced aggregates are self-similar objects with fractal characteristics (Fig. 6 and 8).

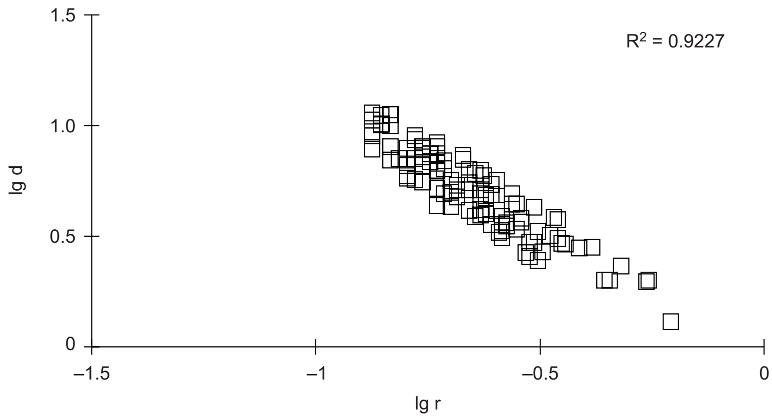

Fig. 6. Dependency lg d = f (lg r) for I = 100 mA, ρ_2 = 6.25 mA/cm^2, COD rem. = 39.46 %, number of analyzed aggregates – 134, D–1.57

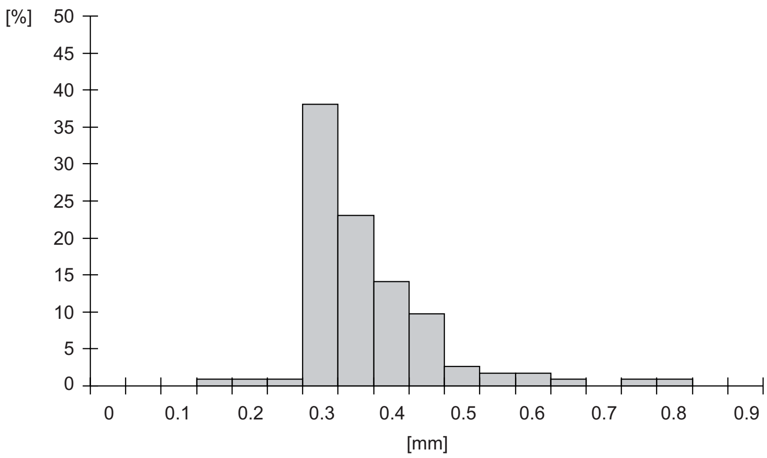

Fig. 7. Percentage share of aggregates in sludge subject to their actual size at ρ_2 = 6.25 mA/cm^2, aggregate size and sedimentation rate: r: 0.09–0.43 mm v: 0.09–0.39 mm/s, respectively

Figures 7 and 9 present the percentage share of aggregates in sludge subject to their actual size. Small-sized flocs with a diameter in the range of 0.06–0.93 mm were found to be the most predominant. A correlation was noted between fractal dimension and the percentage share of flocs of a given size. Sludge that contained a higher percentage of small flocs was characterized by higher values of D. A higher content of small flocs in post-coagulation sludge decreases sludge hydration and promotes the filling of sludge spaces with the solid phase. The resulting sludge comprised small aggregates, and it was also characterized by a low settling velocity, v, of individual flocs in the range of 0.07–0.65 mm/s, already during the sedimentation process.

The noted results once again [13] indicate that the fractal dimension of aggregates is an important tool during the evaluation of post-coagulation sludge. The fractal

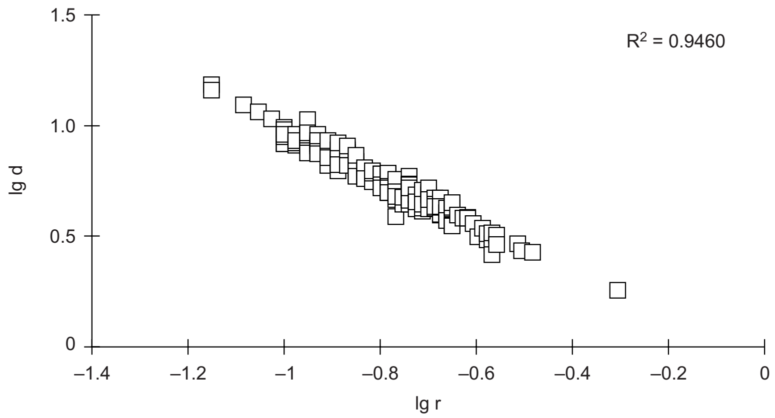

Fig. 8. Dependency lg d = f (lg r) for I = 50 mA, ρ_1 = 3.125 mA/cm^2, COD rem.= 55.27 %, number of analyzed aggregates – 151, D–1.90

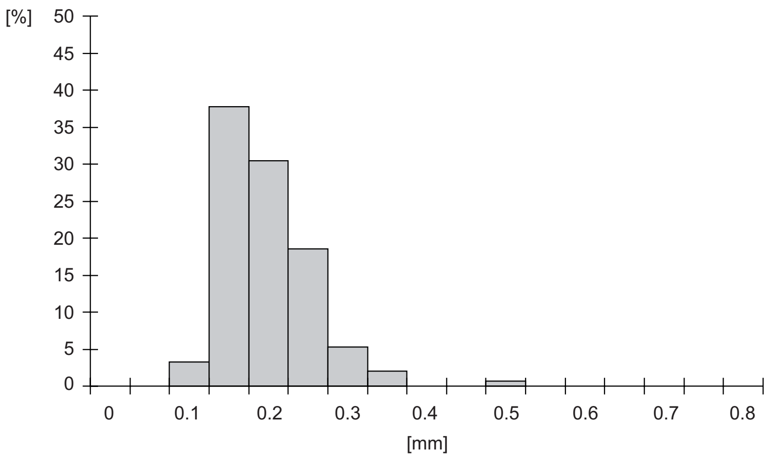

Fig. 9. Percentage share of aggregates in sludge subject to their actual size at ρ_1 = 3.125 mA/cm^2, aggregate size and sedimentation rate: r: 0.06–0.55 mm v: 0.07–0.44 mm/s, respectively

dimension of sludge is practically the only method supporting a quantitative description of irregularities, ie the degree of the studied objects' surface deformations, and the coefficient of determination (R^2) for dependency lg d ~ (lg r) statistically proves the self-similarity of the studied aggregates.

Conclusions

1. The process of static electrocoagulation of pulp and paper wastewater with the involvement of aluminum electrodes was found to be an effective treatment method. It supported the removal of more than 60 % COD and a nearly complete elimination of color, turbidity and suspended solids from the treated wastewater.

2. The optimal results of wastewater treatment by static electrocoagulation were noted at t = 1620 s and current density of ρ_2 = 6.25 mA/cm^2.

3. The actual size of aggregates and their sedimentation rate was r: 0.06–0.93 mm and v: 0.07–0.65 mm/s, respectively, indicating that aggregates maintain the same morphological properties, and that every sub-unit has identical characteristics to the entire aggregate.

4. The parameters that affect waste treatment, ie electrolysis time, current density applied to the electrodes and pH, also determine the aggregation mechanism by influencing the aggregates' structure, size, shape and porosity and, consequently, the fractal dimension D of post-coagulation sludge.

5. Small-sized flocs had the highest share of post-coagulation sludge. This attribute supports the dewatering process because a higher contribution of small aggregates promotes the filling of sludge spaces with the solid phase.

References

[1] Lin S.H. and Peng C.F.: *Continuous treatment of textile wastewater by combined coagulation, electrochemical oxidation and activated sludge.* Water Res. 1996, **30**(2), 587–592.

[2] Ciardelli G. and Ranieri N.: *The treatment and reuse of wastewater in the textile industry by means of ozonation and electrocoagulation.* Water Res. 2001, **35**, 567–572.

[3] Zongo I., Maiga A. H., Wethe J., Valentin G., Leclerc J.-P., Paternotte G. and Lapicque F.: *Electrocoagulation for the treatment of textile wastewaters with Al or Fe electrodes: Compared variations of COD levels, turbidity and absorbance.* J. Hazard. Mater. 2009, **169**, 70–76.

[4] Jia J., Yang J., Liao J., Wang W.: Wang Z.:*Treatment of dyeing wastewater with ACF electrodes*. Water Res. 1999, **33**, 881–884.

[5] Szpyrkowicz L., Naumczyk J. and Zilio Grandi F.: *Application of electrochemical processes for tannery wastewater*. Toxicol. Environ. Chem. 1994, **44**, 189–202.

[6] Smoczyński L. and Załęska-Chróst B.:. *Electrocoagulation of pulp and paper wastewater in a re-circulation system.* Polish J. Natur. Sci. 2002, **12**(3), 293–301.

[7] Chen X., Chen G. and Yue P.L.: *Investigation on the electrolysis voltage of electrocoagulation.* Chem. Eng. Sci. 2002, **57**, 2449–2455.

[8] Mollah M., Morkovsky P., Gomes J.A.G., Kesmez M., Parga J. and Cocke D.: *Fundamentals, present and future perspectives of electrocoagulation.* J. Hazard. Mater. 2004, **B 114**, 199–210.

[9] Kobya M. and Delipinar S.: *Treatment of the baker's yeast wastewater by electrocoagulation*. J. Hazard. Mater. 2008, **154**, 1133–1140.

[10] Chen L. Lai and Sheng H. Lin: *Treatment of chemical mechanical polishing wastewater by electro-coagulation: system performances and sludge settling characteristics.* Chemosphere 2004, **54**, 235–242.

[11] Khemis M., Leclerc J.-P., Tanguy G., Valentin G. and Lapicque F.: *Treatment of industrial liquid wastes by electrocoagulation: Experimental investigations and an overall interpretation model.* Chem. Eng. Sci. 2006, **61**, 3602–3609.

[12] Holt P., Barton G., Wark M. and Mitchell A.: *A quantitative comparison between chemical dosing and electrocoagulation*. Colloids Surf. 2002, **211**, 233–248.

[13] Smoczyński L., Wardzyńska R. and Załęska-Chróst B.: *Elektrokoagulacja a koagulacja chemiczna. Porównanie metod oczyszczania ścieków celulozowo-papierniczych.* Acta Sci. Pol. Form. Circumiectus 2004, **3**(2), 3–14.

[14] Mandelbrot B.B.: The Fractal Geometry of Nature. Freeman, New York 1983.

[15] Da-Hong L. and Ganczarczyk J.: *Stroboscopic determination of settling velocity, size and porosity of activated sludge flocs.* Water Res. 1987, **21**(3), 257–262.

[16] Smoczyński L. and Wardzyńska R.: *Study on macroscopic aggregation of silica suspensions and sewage*. J. Colloid Interf. Sci. 1996, **183**, 309–314.

[17] Harif T. and Adin A.: *Characteristics of aggregates formed by electroflocculation of a colloidal suspension*. Water Res. 2007, **41**, 2951–2961.
[18] Stumm W. and Morgan J.J.: Aquatic Chemistry. Willey Interscience, New York 1970.
[19] Hermanowicz W., Dożańska W., Dojlido J., Koziorowski B. and Zerbe J.: Fizyko-chemiczne badanie wody i ścieków. Arkady, Warszawa 1999.
[20] HACH DR /2000 Spectrophotometer Procedures Manual, Hach Company, Loveland, USA 1993.

OCZYSZCZANIE ŚCIEKÓW CELULOZOWO-PAPIERNICZYCH METODĄ ELEKTROKOAGULACJI W SYSTEMIE STATYCZNYM

Katedra Chemii, Wydział Kształtowania Środowiska i Rolnictwa
Uniwersytet Warmińsko-Mazurski w Olsztynie

Abstrakt: W niniejszej pracy przedstawiono wyniki elektrochemicznego oczyszczania ścieków celulozowo-papierniczych. Elektrolizę prowadzono w układzie statycznym, z użyciem elektrod glinowych. Badania prowadzono przy dwóch wartościach gęstości prądu na elektrodach 3,125 mA/cm^2 i 6,25 mA/cm^2. Po elektrokoagulacji i sedymentacji mierzono w roztworze ChZT, mętność, barwę oraz zawiesiny. Jednocześnie określono właściwości fraktalne otrzymanych agregatów-kłaczków osadu ściekowego i oznaczono ich rozmiary fraktalne. Badany proces elektrokoagulacji okazał się skuteczną metodą oczyszczania ścieków celulozowo-papierniczych. Badane agregaty-kłaczki były obiektami „samopodobnymi”.

Słowa kluczowe: elektrokoagulacja, ścieki celulozowo-papiernicze, rozmiar fraktalny