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CHRONOPOTENTIOMETRIC AND CHRONOAMPEROMETRIC ELECTROCOAGULATION OF WASTEWATER IN A STATIC SYSTEM

STATYCZNA ELEKTROKOAGULACJA ŚCIEKÓW MODELOWYCH

Abstract: This study presents the results of electrochemical treatment of model wastewater. It compares the parameters and the results of wastewater electrolysis performed by chronopotentiometric electrocoagulation (CHRP) at constant current intensity ($I = \text{const}$) and chronoamperometric electrocoagulation (CHRA) at constant voltage ($U = \text{const}$). Electrolysis was carried out in a static system with the use of an electrolyzer with aluminum electrodes. A six-electrode electrolyzer (three cathodes and three anodes) was applied. The chemical oxygen demand (COD), turbidity, color intensity, suspended solids and total phosphorus concentration of the solution were determined after electrocoagulation and sludge sedimentation.

Keywords: electrocoagulation, chronopotentiometry, chronoamperometry, static system, model wastewater

Waste treatment is one of the numerous environmental protection measures implemented to preserve the purity of surface and underground water resources. The main objective of waste treatment practices should be to modify the composition and properties of wastewater to ensure that when evacuated, it does not pose a threat to life forms residing in receiving water bodies or to the continued use of wastewater receivers [1, 2].

More stringent water protection requirements stimulate research efforts to improve the effectiveness of industrial and municipal wastewater treatment methods [3]. From among the available physical and chemical treatment methods, special emphasis should be placed on coagulation, electroflotation and electrocoagulation [4, 5]. In theory and practice, electrochemical coagulation could pose a specific alternative to wastewater treatment by coagulation. The reported attempts at electrolytic treatment of textile [6, 7], dye [8], pulp-and-paper wastewater [9], as well as the use of electrocoagulation in

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theoretical models [10, 11] indicate that this method could offer a viable alternative to chemical coagulation [12, 13].

This study presents the results of chronoamperometric and chronopotentiometric [14, 15] electrocoagulation with the use of aluminum electrodes as a method of model wastewater treatment [16].

Materials and methods

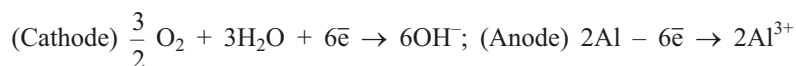
An analysis of model wastewater, with composition similar to that of dairy plant effluents, was carried out under laboratory conditions. Model wastewater was prepared for the experiment in accordance with the procedure described in previous chronopotentiometric and chronoamperometric studies [15, 16]. Electrochemical coagulation was performed in a static system with the use of an electrolyzer comprising six aluminum electrodes. To avoid excessive polarization of electrodes, the direction of current was changed every 256 s, and an environment supporting the self-cleaning of electrodes was established.

The chronopotentiometric electrolysis of wastewater (CHRP) was conducted at current intensity of 1.0, 0.5, 0.3, 0.1, 0.05, 0.03 and 0.01 A, respectively. Thousands of intensity readouts were registered each time, and the calculated average was applied in an equivalent chronoamperometric process (CHRA) at $U = \text{const}$. The treatment process was completed in 512, 1024 and 1536 s. The pH of wastewater was adjusted to 5.5–6.0 with the application of 2 M HCl. After 0.5 h of sedimentation, samples were collected from the above-sludge layer for the determination of wastewater parameters. Chemical oxygen demand (COD), total phosphorus concentrations [17], turbidity and suspended solids were determined by standard spectrophotometry with the use of a HACH DR 2000 spectrophotometer [1, 18], pH and temperature were measured with a HANNA HI 9025 pH-meter.

Results and discussion

As anticipated, the initial measurements of the relationship between pH, the time of electrocoagulation and the applied method (CHRP and CHRA) showed that the longer the electrocoagulation time, the higher the pH of treated wastewater. It was found that the pH of wastewater electrocoagulated at the highest current intensity (for CHRP) or voltage (for CHRA) reached up to > 11 regardless of electrolysis time.

The following diagram was proposed for the processes taking place in the solution during wastewater treatment by electrocoagulation with the use of aluminum electrodes:



where $x < 3$.

The above mechanism implies that the system's pH increases rapidly when Al^{3+} ions are involved in the process of pollutant coagulation and flocculation, as only some of the formed OH^- ions pass to the sludge. At the completion of this stage, successive Al^{3+} ions formed on the anode effectively capture OH^- ions and precipitate them in the form of sparingly soluble hydroxide sediment $\text{Al}(\text{OH})_3\downarrow$. At this point, the increase in pH is inhibited, and in addition to electrolysis parameters, ie current density in electrodes, current intensity (CHRP), current voltage (CHRA) and process time, the final pH of treated wastewater is determined by the possible sorption of OH^- ions on sludge flocs. To ensure optimal treatment results, pH was continuously adjusted in the wastewater solution with the use of 2 M HCl.

The results of wastewater treatment by CHRP and CHRA electrocoagulation are presented in graphic form below. Figures 1a and 1b show a decrease in pollution load that affects the color intensity of wastewater.

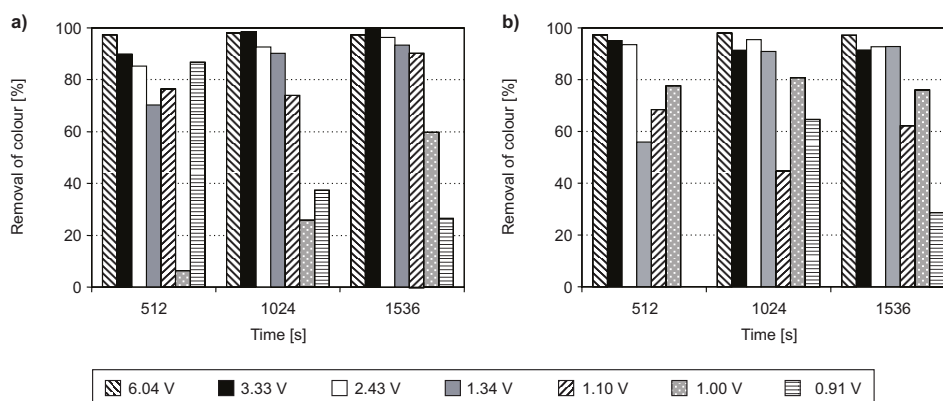


Fig. 1. a) Removal of color (CHRP); b) Removal of color (CHRA)

Figure 1a presents a decrease in pollution load affecting the color intensity of wastewater treated by CHRP electrocoagulation at different current intensity levels. Satisfactory color removal results (80–100 %) were achieved at current intensity of $I \geq 0.3\text{A}$ already at $t = 512\text{s}$. At the longest electrolysis time, similar results were reported at $I \geq 0.5\text{A}$. Minimal color removal was noted at low intensity levels for all three applied time parameters.

The application of constant voltage during electrocoagulation (CHRA) also produced highly satisfactory color removal results. Similarly to CHRP, the reported efficiency was determined by the time of electrolysis. Color removal was least efficient during CHRA electrocoagulation at $U = 0.91\text{V}$ and $t = 512\text{s}$. In the remaining cases, color removal values reached 60 % to 100 %, and the most satisfactory results were observed at the voltage of $\geq 1.31\text{V}$ (Fig. 1b).

As regards the turbidity of the treated model wastewater, the highest removal efficiency was reported at the highest current intensity levels (CHRP), as shown in Figure 2a. Turbidity removal was least efficient at $I = 0.01\text{--}0.03\text{ A}$, reaching only 8 %

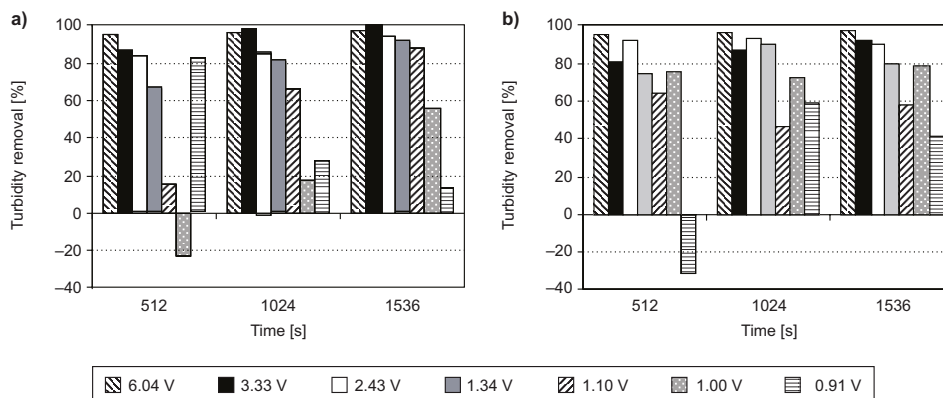


Fig. 2. a) Turbidity removal (CHRP); b) Turbidity removal (CHRA)

after electrolysis time of 1536 s with aluminum electrodes. In general, the effectiveness of turbidity removal reached 100 % at electrolysis time of 1024 s and current intensity of 0.5 A (Fig. 2a).

Figure 2b presents the relationship (CHRP-equivalent) between turbidity removal in CHRA electrocoagulated wastewater and electrolysis time at different voltage levels. Electrocoagulation time of 1536 s supported the achievement of the desired end result, ie 100 % turbidity removal. The application of low voltage levels at $U = 1.1$ V, 1 V and 0.91 V did not stimulate rapid electrolysis, and coagulation, aggregation and sedimentation processes were not visibly observed. The formation and destabilization of colloidal $Al(OH)_3$ were not highly effective under the applied conditions. The process of anodic dissolution of aluminum and cathodic oxygen polarization led to the formation of non-destabilizing sol, increasing the analyzed system's turbidity even by 40 %.

Similar results were observed in respect of suspended solids (Fig. 3a and 3b). Suspended solid concentrations increased during CHRA electrocoagulation at low

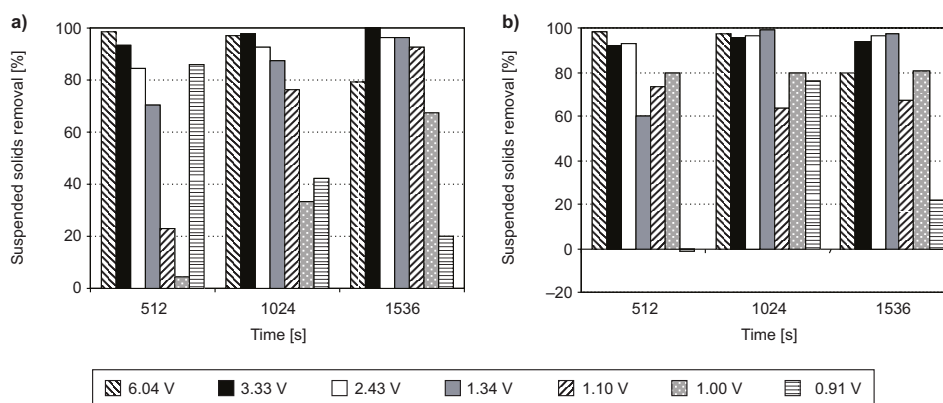


Fig. 3. a) Suspended solids removal (CHRP); b) Suspended solids removal (CHRA)

voltage parameters. The efficiency of suspended solids removal ultimately reached 80–100 % as a result of both CHRA and CHRP electrocoagulation.

COD removal in the treated model wastewater reached 60–65 % following CHRP electrocoagulation at $I \geq 0.3A$. Low current intensity parameters did not enhance removal efficiency, and much better results were noted in chronoamperometric electrocoagulation. Aluminum electrodes supported around 60 % COD removal from the investigated model wastewater already at $t \geq 1024s$.

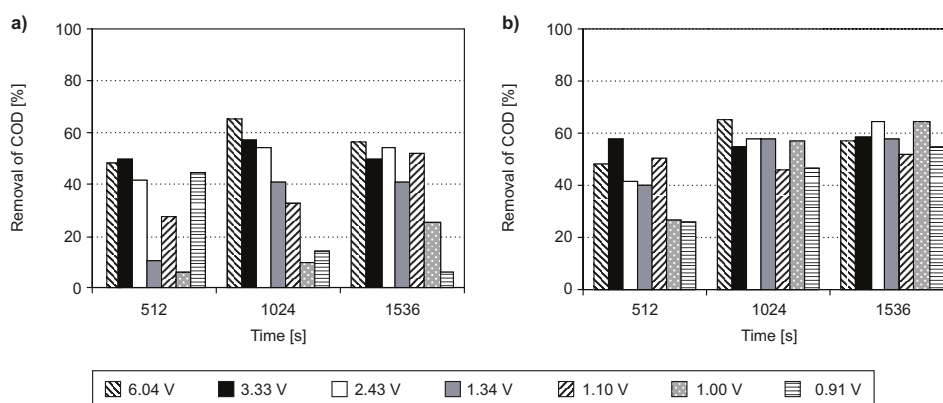


Fig. 4. a) Removal of COD (CHRP); b) Removal of COD (CHRA)

The results of phosphorus removal from wastewater are presented in Tables 1 and 2. For enhanced visualization of the process, the phosphorus removal index (PRI) was calculated each time as mg P removed from the system by 1 C moving charge.

Table 1

Phosphorus removal efficiency (ChRP)

Current [A]	Time [s]	Removal of P [%]	Q [$C \cdot dm^{-3}$]	PRI mg P _{og} /1 C
1.0	512	78.3	512	0.069
	1024	82.6	1024	0.036
	1536	78.3	1536	0.023
0.5	512	73.9	256	0.13
	1024	65.2	512	0.058
	1536	82.6	768	0.049
0.3	512	65.2	154	0.2
	1024	73.9	307	0.11
	1536	82.6	461	0.082
0.1	512	47.8	51	0.43
	1024	65.2	102	0.29
	1536	73.9	154	0.22

Table 1 contd.

Current [A]	Time [s]	Removal of P [%]	Q [C·dm ⁻³]	PRI mg P _{og} /1 C
0.05	512	56.5	26	1.0
	1024	56.5	51	0.51
	1536	65.2	77	0.39
0.03	512	52.2	15	1.56
	1024	47.8	37	0.88
	1536	73.9	46	0.72

Table 2

Phosphorus removal efficiency (ChRA)

Voltage [V]	Average current [A]	Time [s]	Removal of P [%]	Q [C·dm ⁻³]	PRI mg P _{og} /1 C
3.22	0.405	512	69.6	207	0.15
3.38	0.488	1024	65.2	500	0.062
3.39	0.452	1536	86.9	694	0.053
2.35	0.241	512	82.6	123	0.30
2.47	0.244	1024	91.3	250	0.17
2.38	0.249	1536	73.9	382	0.089
1.39	0.078	512	52.2	40	0.6
1.32	0.093	1024	65.2	95	0.31
1.31	0.092	1536	73.9	141	0.24
1.12	0.058	512	69.6	30	1.055
1.09	0.052	1024	73.9	53	0.63
1.07	0.022	1536	86.9	34	1.13
1.04	0.025	512	31.8	13	1.22
0.99	0.022	1024	65.2	22	1.33
0.98	0.022	1536	73.9	34	1
0.907	0.014	512	34.8	7	2.2
0.909	0.003	1024	30.4	3	5.1
0.911	0.003	1536	8.7	5	0.8

CHRP electrocoagulation involving aluminum electrodes resulted in 47–82 % total phosphorus removal from the treated wastewater at $I = 0.1$ – 1.0 A, with minimum phosphorus removal efficiency of 65 %. As expected, similarly to COD removal, the efficiency of total phosphorus removal increased with an extension of electrolysis time. Up to 91 % of total phosphorus was removed from wastewater during CHRA electrocoagulation. Removal efficiency at voltage levels higher than 0.98V reached 60–91 %.

PRI values support an evaluation of the analyzed process with regard to its energy efficiency and economic feasibility. Higher PRI values are indicative of increased

phosphorus removal efficiency of 1 C and, consequently, lower energy consumption of the process. The relationship between PRI, current intensity and electrolysis time is reversely proportional. In CHRA electrocoagulation with aluminum electrodes, PRI values are even 2–3 times higher than in the CHRP method. The reported results could suggest that CHRA is superior to CHRP. The highest RPI and phosphorus removal efficiency values for this method were reported already at the voltage range of 0.98–1.12V.

Conclusions

1. Static electrocoagulation of wastewater, carried out with the application of aluminum electrodes and pH adjustment, facilitated more than 50 % COD removal, more than 70 % total phosphorus removal, and nearly 100 % color, turbidity and suspended solids removal from the treated model wastewater.

2. With the application of optimal process parameters, chronoamperometric and chronopotentiometric electrocoagulation proved to be highly efficient methods for the treatment of model wastewater.

3. Satisfactory treatment results were reported when chronopotentiometric electrocoagulation was performed at electrolysis time of $t = 1024\text{s}$ and current intensity of $I \geq 0.3\text{A}$.

4. Optimal conditions for chronoamperometric electrocoagulation were determined at $U = 0.98\text{--}1.39\text{V}$ and $t \geq 1024\text{s}$.

References

- [1] Hermanowicz W., Dojlido J. Dożańska W., Kozirowski E. and Zerbe J.: *Fizykochemiczne badanie wody i ścieków*. Arkady, Warszawa 1999.
- [2] Roman M.: *Standardy jakości i ochrony śródlądowych wód powierzchniowych w przepisach UE i w przepisach polskich*. Monografie PZITS, Serie Wodociągi i Kanalizacja, 1998, 1.
- [3] Smoczyński L. and Wardzyńska R.: *Study on macroscopic aggregation of silica suspensions and sewage*, *J. Colloid Interf. Sci.* 1996, **183**, 309–314.
- [4] Vik E.A., Carlson D.A., Eikun A.S. and Gjessing E.T.: *Electrocoagulation of potable water*. *Water Res.*, 1984, **18**(11), 1355–1360.
- [5] Rajesh R.S.: *Electrochemical treatment of cigarette industry wastewater: feasibility study*. *Water Res.*, 2002, **36**(17), 4386–4390.
- [6] 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.
- [7] 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.
- [8] Jia J., Yang J., Liao J., Wang W. and Wang Z.: *Treatment of dyeing wastewater with ACF electrodes*. *Water Res.* 1999, **33**, 881–884.
- [9] Smoczyński L. and Załęska-Chróst B.: *Electrocoagulation of pulp and paper wastewater in a recirculation system*. *Polish J. Natur. Sci.* 2002, **12**(3), 293–301.
- [10] Chen X., Chen G. and Yue P.L.: *Investigation on the electrolysis voltage of electrocoagulation*. *Chem. Eng. Sci.*, 2002, **57**, 2449–2455.
- [11] 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, **B114**, 199–210.
- [12] Chen X., Chen G. and Yue P.L.: *Separation of pollutants from restaurant wastewater by electrocoagulation*. *Sep. Purif. Technol.*, 2000, **19**, 65–76.

- [13] Holt P., Barton G., Wark M. and Mitchell A.: *A quantitative comparison between chemical dosing and electrocoagulation*. Colloids Surf., 2002, **211**, 233–248.
- [14] Smoczyński L., Kalinowski S. and Zaborowska A.: *Electrochemical treatment of model wastewater*. Ecol. Chem. Eng., 2004, **11**, 1345–1354.
- [15] Smoczyński L., Kalinowski S., Zaborowska A. and Smoczyńska A.: *Chronoamperometry in wastewater electrocoagulation*. Ecol. Chem. Eng., 2004, **11**, 1355–1362.
- [16] Jiang J.-Q., Graham N., Andre C., Kelsall G.H. and Brandon N.: *Laboratory study of electro-coagulation flotation for water treatment*. Water Res., 2002, **36**(16), 4064–4078.
- [17] Groterud O. and Smoczyński L.: *Phosphorus removal from water by electrolysis*. Water Res., 1986, **20**(5), 667–669.
- [18] HACH DR /2000 Spectrophotometr Handbook, Procedure Manual, 1993.

STATYCZNA ELEKTROKOAGULACJA ŚCIEKÓW MODELOWYCH

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Abstrakt: Przedstawiono wyniki elektrochemicznego oczyszczania ścieków modelowych. Porównano parametry oraz efekty elektrolitycznego oczyszczania ścieków w warunkach chronopotencjometrycznych (CHRP), tj. przy stałym natężeniu prądu ($I = \text{const}$) oraz chronoamperometrycznych (CHRA), tj. przy stałym napięciu ($U = \text{const}$). Elektrolizę prowadzono w układzie statycznym z użyciem elektrolizera z elektrodami glinowymi. Zastosowano 6-elektrodowy (3 katody i 3 anody) elektrolizer. Po elektrokoagulacji i sedymentacji osadu w roztworze oznaczano chemiczne zapotrzebowanie na tlen ChZT, mętność, barwę, zawiesiny oraz stężenie fosforu ogólnego.

Słowa kluczowe: elektrokoagulacja, system statyczny, ścieki modelowe