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PRELIMINARY REMOVAL OF PHOSPHORUS FROM MUNICIPAL WASTEWATER

WSTĘPNE USUWANIE FOSFORU ZE ŚCIEKÓW MIEJSKICH

Abstract: The results of municipal wastewater treatment by chemical coagulation with PIX and electrocoagulation in a recirculation system with aluminum electrodes were discussed and interpreted. Those processes were analyzed as: a) preliminary processing before biological treatment, or b) the only treatment procedure. The results of chemical coagulation and electrocoagulation indicate that both methods guarantee the required level of phosphorus and suspended solids removal from wastewater. Despite the above, the COD of treated wastewater decreased to only 200 mg·dm⁻³ which exceeds the norm for effluents discharged from treatment plants (125 mg·dm⁻³). Our results indicate that municipal wastewater treatment cannot rely solely on chemical coagulation and/or electrocoagulation. In successive parts of the study, wastewater was treated with significantly smaller doses of a ferric coagulant (PIX) and an aluminum electrocoagulant (Al electrodes). The above treatments lowered the phosphorus load of wastewater to a level ensuring its nearly complete removal in successive stages of biological treatment. The practical application of the resulting database was evaluated in view of the existing regulations as well as more stringent requirements which could be introduced in the future, in particular with regard to total phosphorus loads.

Keywords: municipal wastewater, chemical treatment, electrocoagulation

Introduction

Global phosphorite and apatite resources will be depleted by around 2050 [1]. This fact and the introduction of increasingly stringent wastewater treatment standards will necessitate the recovery of potential fertilizer nitrogen from treated wastewater. Phosphorus recirculation in the <wastewater sludge - fertilizer - food - phosphorus in wastewater> system can become an important, if not the only source of phosphorus fertilizers.

In Poland, selected municipal wastewater treatment plants are not under obligation to control phosphorus concentrations in processed effluents. The above applies to effluents discharged to a body of flowing water, such as a river, which does not intersect stagnant water bodies, including lakes and ponds [2]. Polish regulations continue to raise many objections in the Baltic states, in particular in Scandinavian countries. Wastewater treatment standards determine research trends, including on the industrial and semi-technical scale. The majority of laboratory research focuses on the development of new methods for preliminary chemical coagulation [3-5] and electrocoagulation [6-8] of wastewater are becoming more and more interesting even for these WWTPs. In view of searching for more efficient and more economical methods for phosphate removals, a comparison of the effectiveness of chemical coagulation and electrocoagulation is interesting. This study discusses the preliminary research on such a comparison with

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a wastewater which is not required to remove phosphorous today, but which might get such a requirement in the future.

Materials and methods

Reszel WWTP in Poland serves an estimated population of 5000 and is not required to control phosphates in its effluents today. The WWTP has mechanical and biological (SBR) unit process. Wastewater samples were collected after the sand trap one day before the experiments and refrigerated until the following morning. The effluent discharges meets the COD and suspended solids (SS) discharge norms, while the effluent phosphorous concentrations, which is not subject to a control, remains around $3.5 \text{ mg}\cdot\text{dm}^{-3}$.

Wastewater samples were brought to the temperature of 21°C . Several cm^3 of saturated NaCl solution was added to 1 dm^3 of wastewater to increase its specific conductance to $0.004 \Omega^{-1}\cdot\text{cm}^{-1}$. In the jar test procedure, the sample and the coagulant were mixed rapidly for 2 minutes (at approximately 400 rpm) and slowly for 15 minutes (at approximately 20 rpm). The mixture was left to stand for 30 minutes. Analytical samples were collected after sedimentation from the liquid above the sludge layer. The applied coagulant was PIX-113 [www.kemipol.com.pl] was used as the coagulant and the experiments were conducted at this time without any pH adjustments.

A diagram of the electrocoagulation reactor with a recirculation system is presented in Figure 1.

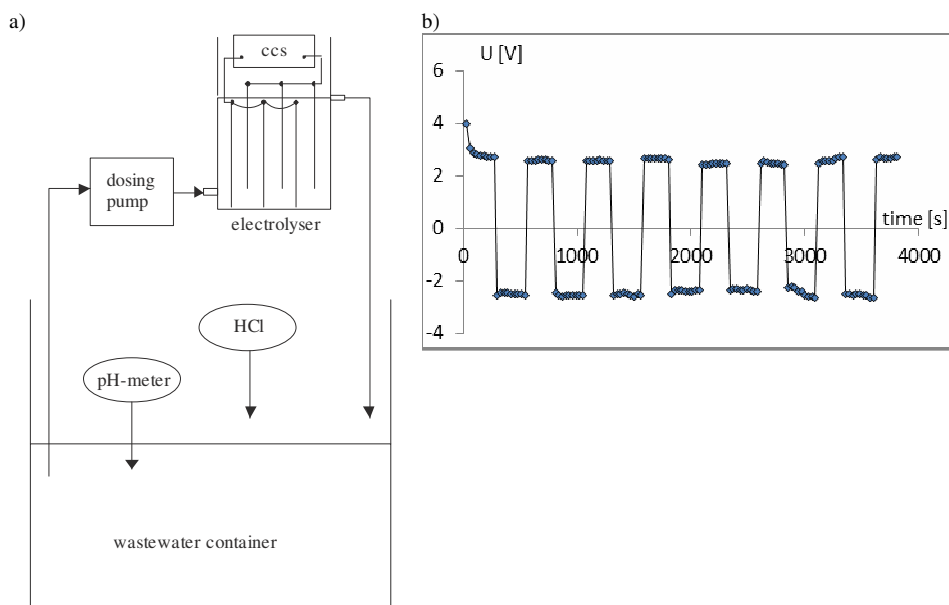


Fig. 1. Diagram of the electrocoagulation reactor (a) and change in applied voltage (b)

Electrocoagulated wastewater was recirculated between the electrolyzer and the reservoir. The process was performed chronopotentiometrically at constant current intensity of 0.3 or 0.15 A, and changes in voltage were registered (Fig. 1b). The direction of the current was reversed automatically every 256 s [9] to clean the electrodes. Wastewater samples of 1 or 2 dm³ were recirculated within 22 minutes to 1 hour. The pH of wastewater samples was maintained at 6.0 through the addition of 2M HCl. Analytical specimens were collected every 5-15 minutes. Their colour, suspended solid concentrations and turbidity were determined, and the specimens were fed back into the recirculated wastewater reservoir to minimize changes in system volume.

The pH, specific conductance, colour, turbidity, suspended solid concentrations, total phosphorus and total nitrogen concentrations, and COD were determined in raw and processed wastewater samples. Specific conductance was measured in the Delta OHM HD 2156.2 conductometer, pH was determined with the Hanna Instruments HI 8242 pH meter, and the remaining measurements were performed with the use of the Hach Lange DR 2800 spectrophotometer [10].

Results and discussion

The results of chemical coagulation of wastewater, applied as the only treatment method, are presented in Figure 2.

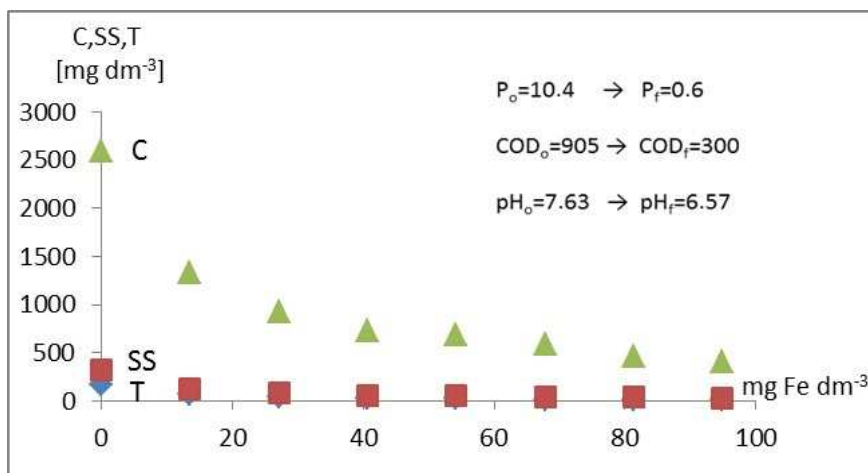


Fig. 2. PIX coagulation of municipal wastewater as the only treatment method; (C - Colour, SS - Suspended Solids, T - Turbidity)

The chemical coagulation process with PIX is presented in Figure 2. Changes in the colour, suspended solid concentrations and turbidity of wastewater samples at increasing coagulant doses are shown here. The first PIX dose of 13.55 mg Fe·dm⁻³ (0.24 mmol·dm⁻³) removed 49% colour, 60% suspended solids and 61% turbidity from coagulated wastewater. The highest PIX dose of 95 mg Fe·dm⁻³ (1.7 mmol·dm⁻³) reduced colour in 85% (from approximately 2600 mg·dm⁻³ in raw wastewater to 403 mg·dm⁻³ in

treated wastewater), suspended solids - in 95% (from approximately 320 to 31 $\text{mg}\cdot\text{dm}^{-3}$) and turbidity in 93% (from 173 to 12 $\text{mg}\cdot\text{dm}^{-3}$). The highest PIX dose lowered the pH of wastewater from $\text{pH}_0 = 7.63$ to $\text{pH}_f = 6.57$. Total phosphorus concentrations decreased by 94% from $P_o = 10.4$ to $P_f = 0.6 \text{ mg}\cdot\text{dm}^{-3}$, and COD decreased by 67% from $\text{COD}_o = 905$ to $\text{COD}_f = 300 \text{ mg}\cdot\text{dm}^{-3}$. The effluent wastewater satisfied Polish discharge regulations [2] with regards to total phosphorus and suspended solid concentrations, but the COD of the analyzed effluent insignificantly exceeded the statutory threshold of $125 \text{ mg}\cdot\text{dm}^{-3}$.

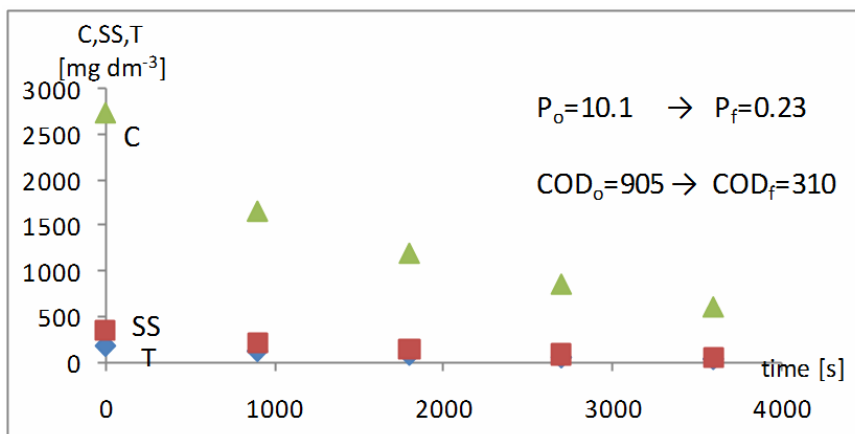


Fig. 3. Electrocoagulation of municipal wastewater in a recirculation system as the only treatment method (C - Colour, SS - Suspended Solids, T - Turbidity)

The results of electrocoagulation of wastewater in a recirculation system, applied as the second treatment method, are presented in Figure 3. Changes in the colour, suspended solids concentrations and turbidity of wastewater samples at increasing doses of the aluminum are shown here. A dosage of electrocoagulant was proportional to the time of electrolysis according to Faraday's law, $m = k \cdot i \cdot t$, where the chemical equivalent of aluminum is:

$$k = 27 / (96500 \cdot 3) = 9.3 \cdot 10^{-5} \text{ g}\cdot\text{A}^{-1}\cdot\text{s}^{-1}$$

The intensity of the electrical current was kept constant at 0.3 A. The degree of wastewater purification was checked every 15 minutes (900 s). The first (minimal) dose of the aluminum electrocoagulant (approximately $25 \text{ mg Al}\cdot\text{dm}^{-3} = 0.92 \text{ mmol of Al}\cdot\text{dm}^{-3}$) removed colour and suspended solids in 40% and turbidity in 33%. The highest Al dose of approximately $100 \text{ mg Al}\cdot\text{dm}^{-3}$ ($3.7 \text{ mmol}\cdot\text{dm}^{-3}$) removed 78% colour, 83% suspended solids and 88% turbidity. Total phosphorus concentrations decreased by 98% from $P_o = 10.1$ to $P_f = 0.23 \text{ mg}\cdot\text{dm}^{-3}$, and COD decreased by 65% from $\text{COD}_o = 905$ to $\text{COD}_f = 310 \text{ mg}\cdot\text{dm}^{-3}$. The system's pH increases during electrolysis [11], and approximately 5 cm^3 of 2M HCl was added per 1 dm^3 of the sample to maintain a constant pH of 6.0 during one hour of electrocoagulation. Treated wastewater met the prescribed values for total phosphorus concentrations, whereas suspended solid concentrations and COD of the analyzed effluents insignificantly exceeded the statutory thresholds.

The biological treatment normally removes 50-60% of the total phosphorus in the WWTP studied. We wanted to study the requirement of coagulation processes to supplement this removal to achieve the discharge standards. For the comparison purposes we have thus studied the coagulation requirements to remove about 50% of the total phosphates.

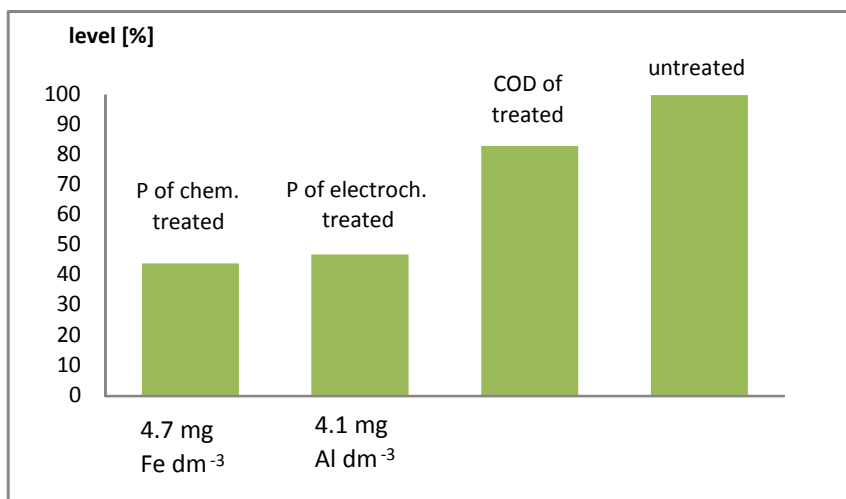


Fig. 4. Preliminary PIX chemical coagulation and preliminary electrocoagulation of municipal wastewater in a recirculation system

The results of preliminary PIX chemical coagulation and electrocoagulation are presented in Figure 4. Approximately $4.7 \text{ mg Fe}\cdot\text{dm}^{-3}$ ($0.084 \text{ mmol}\cdot\text{dm}^{-3}$) was required to reduce the total phosphorus load by 50%. The above implies that a treatment plant with daily processing capacity of 1000 m^3 wastewater would consume minimum 12 tons of PIX per year.

A 50% reduction in the total phosphorus load of electrocoagulated waste was achieved by applying an electrocoagulant dose of $4.1 \text{ mg Al}\cdot\text{dm}^{-3}$ ($0.15 \text{ mmol}\cdot\text{dm}^{-3}$) and consuming $10^{-5} \text{ kWh}\cdot\text{dm}^{-3}$ of electricity at $I = 0.15 \text{ A}$ and mean $U = 1.5 \text{ V}$. This implies that a treatment plant with daily processing capacity of 1000 m^3 wastewater would consume minimum 1.2 tons of scrap aluminum (electrodes) and 300 kWh energy per year.

A 50% reduction in total phosphorus load (by coagulation and electrocoagulation) decreases COD by approximately 17% on average.

Conclusions

Coagulation experiments documented by using $0.084 \text{ mmol}\cdot\text{Fe}\cdot\text{dm}^{-3}$ of PIX-113 (conventional coagulation) or $0.15 \text{ mmol}\cdot\text{Al}\cdot\text{dm}^{-3}$ (electrocoagulation) it is possible to achieve comparable removals of total phosphorus, which resulted in about 50% reduction. Such a supplementary removal, in addition to the removals by the biological treatment processes, will then satisfy the Polish discharge standards. In practical terms, 12 tons of

PIX or 1.2 tons of scrap aluminum (electrodes) and 3000 kWh of energy will be required to achieve the above targets annually. It will produce about 3 tons of phosphorus annually, which is equivalent to 13 tons of fertilizer with chemical formula CaHPO_4 .

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KAPITAŁ LUDZKI
NARODOWA STRATEGIA SPÓJNOŚĆ



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WSTĘPNE USUWANIE FOSFORU ZE ŚCIEKÓW MIEJSKICH

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Abstrakt: W pracy opisano i zinterpretowano rezultaty procesów oczyszczania ścieków miejskich koagulowanych chemicznie PIX-em oraz elektrokoagulowanych recykulacyjnie na elektrodach glinowych. Procesy te potraktowano jako: a) etap wstępny, przed biologicznym oczyszczaniem badanych ścieków oraz b) jedyne i ostateczne oczyszczanie ścieków. Wyniki badań procesu koagulacji chemicznej oraz elektrokoagulacji badanych

ścieków pokazały, że metody te zapewniają wymagany poziom usunięcia zawiesin i fosforu z oczyszczanych ścieków. Jednakże ChZT tak oczyszczonych ścieków obniżało się tylko do ok. $200 \text{ mg} \cdot \text{dm}^{-3}$ przy wymaganym poziomie $125 \text{ mg} \cdot \text{dm}^{-3}$ w odpływie z oczyszczalni. Fakt ten nie pozwala więc traktować koagulacji chemicznej lub/i elektrokoagulacji jako jedynej i ostatecznego etapu oczyszczania badanych ścieków miejskich. Stąd w dalszej części badań ścieki traktowano znacznie mniejszymi dawkami koagulantu żelazowego (PIX) i elektrokoagulantu glinowego (elektrody Al). Prowadziło to do częściowego usunięcia fosforu, zapewniając takie obniżenie poziomu P, aby kolejny etap biologicznego oczyszczania mógł zapewnić stężenie tego biogenu w odpływie bliskie zeru. Dokonano oceny wartości aplikacyjnej uzyskanej bazy danych w świetle aktualnych norm i uwarunkowań, jak również w szerszej perspektywie zaostrożenia wymagań w zakresie stopnia oczyszczenia ścieków, szczególnie w zakresie usuwania fosforu.

Słowa kluczowe: ścieki miejskie, chemiczne oczyszczanie, elektrokoagulacja

