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PHOSPHORUS AND COD REMOVAL FROM CHEMICALLY AND ELECTROCHEMICALLY COAGULATED WASTEWATER

Wastewater coagulation and electrocoagulation were investigated as sorption processes involving colloidal sorbents such as $(Al(OH)_3)_n$, $(Fe(OH)_3)_m$ and $(Fe(OH)_2)_p$. An attempt was made to fit experimental data to two popular sorption models. Based on a statistical and mathematical analysis of the obtained results, the Langmuir model of chemical adsorption was regarded more probable than the Freundlich model. The highest maximum adsorption of phosphorus in the analyzed wastewater was achieved with the use of PIX, and the lowest adsorption maxima were reported for an iron electrocoagulant. PAC was most effective in reducing COD of wastewater. PAC and PIX delivered higher adsorption maxima for compounds responsible for COD than aluminum and iron electrocoagulants.

1. INTRODUCTION

Chemical coagulation is a preliminary process in wastewater treatment [1, 2]. Electrocoagulation of wastewater poses an alternative to chemical treatment [3–5]. Successive stages of coagulation, aggregation and flocculation support partial removal of phosphorus and compounds responsible for COD from wastewater [6, 7]. In the coagulation process, aluminum cations and polycations [8, 9] from PAC and iron cations [10] from PIX are hydrolyzed in wastewater to form positively charged colloidal sols [11, 12]. The above leads to a decrease in the pH of the system. During electrocoagulation, aluminum and iron anodes are dissolved [13, 14], and cations produced in wastewater are hydrolyzed. Unlike coagulation, this process leads to an increase in the pH of the system.

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Various interpretations of the mechanisms of the pollutant removal from chemically and electrochemically coagulated wastewater are subject to controversy and debate. A popular view that phosphates are precipitated or co-precipitated as $AlPO_4\downarrow$, or $FePO_4\downarrow$ should be verified to account for the competitive precipitation of aluminum and iron(III) hydroxides. The coagulation-flocculation [15] of compounds responsible for COD in wastewater is regarded the product of two different processes:

• neutralization of negatively charged wastewater colloids with the use of, for example, positively charged polycations [11, 12] which, from the fundamental point of view, can be described as latent and slow coagulation [16],

• sweep flocculation [17] where excess micelles and sludge flocs sweep wastewater pollutants.

The latter process appears to be a simple surface phenomenon where wastewater pollutants are adsorbed on the surface of colloidal micelles such as $(Al(OH)_3)_n$, $(Fe(OH)_3)_m$ or $(Fe(OH)_2)_p$, leading to their destabilization during sorption, coagulation and flocculation. This is a basic process in the treatment of electrocoagulated wastewater because at pH of 8–9, negatively charged colloids are unlikely to be neutralized (process 1).

The discussed controversies prompted the authors to verify the hypothesis that the removal of phosphorus and compounds responsible for COD from wastewater takes place through sorption with colloidal sorbents such as $(Al(OH)_3)_n$, $(Fe(OH)_3)_m$ or $(Fe(OH)_2)_p$.

2. MATERIALS AND METHODS

The analyzed material was synthetic wastewater produced by dissolving various doses of Nestle milk powder and KH_2PO_4 in water. Wastewater was subjected to chemical coagulation with the use of:

• PAC – manufactured by DEMPOL-ECO, supplied in the form of a light grey aqueous solution with the density of $1.28 \text{ g} \cdot \text{dm}^{-3}$ and the following composition: 20.68% Al_2O_3, 6.5% Cl^- and 0.02% Fe,

• PIX – manufactured by KEMIPOL, with the chemical formula $+/- Fe_2(SO_4)_3$, supplied in the form of a dark brown 40–42% solution with the density of $1.5–1.6 \text{ g} \cdot \text{dm}^{-3}$ and the following composition: 11–12.6% of Fe^{3+} and 0.2–0.75% of Fe^{2+}.

The following optimal coagulant doses were used: PAC – 235 mg $Al \cdot \text{dm}^{-3}$ and PIX – 452 mg $Fe \cdot \text{dm}^{-3}$. After coagulation, pH of the wastewater decreased from 7.5 to 6.0 for PAC and to 5.5 for PIX. In the phosphorus test, seven beakers containing 100 cm^3 of wastewater each with constant COD = 10 000 $\text{mg} \cdot \text{dm}^{-3}$ were enriched with P from the K_2HPO_4 bulk solution to produce: 120, 170, 220, 270, 320, 370, 420 mg $P \cdot \text{dm}^{-3}$, and a constant, optimal dose of the coagulant was added. Wastewater was stirred for

15 s, and after 30 min of sedimentation, samples for the determination of total phosphorus concentrations were collected above the sediment layer.

The COD coagulation test was performed in line with the above method on wastewater samples with constant phosphorus concentrations of 120 mg·dm^{-3} mixed with milk powder doses to produce COD values of 10 000, 11 000, 12 000, 13 000, 14 000, 15 000, and 16000 mg·dm^{-3} with a constant coagulant dose. Samples for COD determination were collected above the sediment layer.
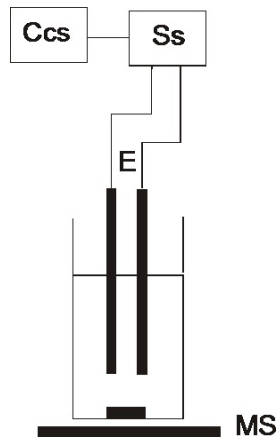

Fig. 1. Apparatus for static electrocoagulation of wastewater

Electrocoagulation was performed using a simple system which is shown in Fig. 1. A pair of Fe-Fe or Al-Al electrodes measuring 5×1×0.1 cm was connected to a computer-controlled power source. Dedicated hardware and software were used for chronopotentiometric electrolysis at a constant current I of 0.3 A to guarantee constant current density at approximately 30 mA/cm^2. In order to maintain $I = 0.3$ At, the required voltage values were selected and recorded by the system. Current direction was changed every 256 s to support electrode (cathode) self-cleaning and minimize polarization losses [5].

This simple method of electrocoagulation supported gravimetric determination of the actual and optimal electrocoagulant doses. After electrolysis, the electrodes were washed with distilled water and dried for 10 min at 120 °C. They were cooled in an exicator for 10 min, weighed on laboratory scales, and the results were rounded off to the fourth decimal place. The above procedure supported the determination of the actual quantity of Al or Fe dissolved by anodes which constituted the respective electrocoagulant dose. Prior to repeated use, the electrodes were cleaned by wet sanding, rinsed in distilled water, dried by the described method and weighed. The optimal electrocoagulant doses were set at 600 mg Al^{3+}·dm^{-3} and 550 mg Fe·dm^{-3}. pH of the electrocoagulated wastewater increased to 9.0 for both electrocoagulants. The parame-

ters of wastewater samples analyzed in phosphorus and COD tests were identical to those in the coagulation test. Every test was performed in three replications. The results were expressed as means ±SD.

3. RESULTS AND DISCUSSION

The results of the phosphorus tests were subjected to a regression analysis to examine the correlations between adsorbed phosphorus and phosphorus at equilibrium $P_{\text{adsorbed}} = f(P_{\text{equilibrium}})$ levels for converted Langmuir and Freundlich models. Adjusted models may be described by the following equations :
- Langmuir isotherm:

$$\frac{P_e}{P_a} = \frac{1}{a_m K} + \frac{P_e}{a_m}$$

where: P_e is the concentration of phosphorus at the equilibrium state, P_a – concentration of adsorbed phosphorus, a_m – maximum adsorption, K – adsorption equilibrium constant.
- Freundlich isotherm:

$$\log P_a = \log K + n \log P_e$$

where: P_e is the concentration of phosphorus at the equilibrium state, P_a – concentrations of adsorbed phosphorus, K, n – Freundlich equation constants.

The regression analysis was also performed to determine the overall correlations between adsorbed COD and COD at equilibrium ($COD_{\text{adsorbed}} = f(COD_{\text{equilibrium}})$) for the converted Langmuir and Freundlich models. Adjusted models in the COD test were as follows:
- Langmuir isotherm:

$$\frac{COD_e}{COD_a} = \frac{1}{a_m K} + \frac{COD_e}{a_m}$$

where: COD_e is the COD at equilibrium, COD_a – adsorbed COD, a_m – maximum adsorption, K – adsorption equilibrium constant,
- Freundlich isotherm:

$$\log COD_a = \log K + n \log COD_e$$

where: COD_e – COD at equilibrium, COD_a – adsorbed COD, K, n – constants in the Freundlich equation.

Corresponding regression equations with the value of coefficient R^2 were obtained for every $P_a = f(P_e)$ and $COD_a = f(COD_e)$ correlation.

3.1. PHOSPHORUS TEST

The correlation $P_e/P_a = f(P_e i)$ representing the converted Langmuir isotherm for removing phosphorus from wastewater electrocoagulated with aluminum electrodes is presented in Fig. 2. The value of the coefficient $R^2 = 0.988$ indicates that a good fit to experimental data was achieved by the Langmuir sorption model. The data relating to phosphate removal from wastewater coagulated or electrocoagulated with PAC, PIX or Al and Fe electrocoagulants was analyzed, and the results are presented in Table 1.
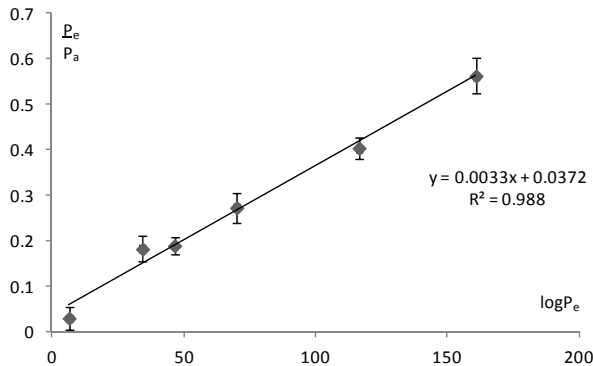

$$y = 0.0033x + 0.0372$$
$$R^2 = 0.988$$

Fig. 2. Langmuir isotherm for phosphorus removal from wastewater
electrocoagulated with aluminum electrodes

Table 1

Parameters of the Langmuir isotherm model for phosphorus adsorption

Coagulant, electrocoagulant	R^2	Maximum adsorption [g P/g Al (Fe)]
PAC (Al)	0.9651	1.038
PIX (Fe)	0.8052	0.962
Al electrodes	0.9880	1.010
Fe electrodes	0.9318	0.200

In general, the values of the coefficient R^2 for Langmuir isotherms were reported in the range of 0.805–0.988, and the values of R^2 for the Freundlich isotherms – in the range of 0.0631–0.9505. The above results could suggest that the sorption of phosphorus compounds on colloidal micelles of aluminum(III), iron(II) and iron(III) hydrox-

ides follows the Langmuir model of chemical adsorption. Similar conclusions were formulated by other authors [18, 19].

The rejected Freundlich model describes physical adsorption. It allows formation of an adsorbate multilayer on the surface of the adsorbent on the assumption that adsorption is unlimited. Under given conditions, adsorbate particles can be physically removed from the area of direct contact with adsorbent surface, and the above process leads to the formation of the adsorbate multilayer. Unlike chemical sorption, physical sorption does not induce changes in the nature or chemical structure of particles.

In the Langmuir model, the surface of the adsorbent contains a fixed number of sites for adsorbed particles, and a single site can be occupied by only one particle. In line with this theory, the adsorbate forms a monolayer of particles on adsorbent surface. Particles interact "vertically" only with adsorption centers, whereas mutual interactions between particles are weak or non-existent. Liquid phase adsorbate particles are adsorbed by colliding with the surface of the adsorbent. In this model, adsorption is limited, and a multilayer cannot be formed. The probability of adsorption increases with the availability of "free" (unoccupied) surface area. Desorption (reverse of adsorption) of adsorbed particles is also possible. Adsorption and desorption are determined by the energy and temperature of adsorption. At higher concentrations, particles are more likely to collide with the surface whose "available" area decreases. The surface of the adsorbent is energetically homogenous, and adsorption energy is constant.

The results of our experiment indicate that phosphorus and phosphate adsorption is a chemical sorption process (chemisorption). During chemisorption, covalent bonds are formed between adsorbate particles and the adsorbent surface where multiple centers exist. Chemical properties of adsorbent and adsorbate may be modified along the adsorbent–adsorbate phase boundary. Those properties may also undergo change as the result of irreversible reactions which implies that sorption and desorption are not always reversible. A highly probable Langmuir model of adsorption for all coagulants/electrocoagulants as colloidal phosphorus sorbents (orthophosphates) was used to calculate the value of maximum adsorption a_m in grams of P and moles of P per g of Al or Fe (Table 1). The above values were determined in view of adsorption maxima and optimal doses expressed in moles and grams, respectively.

The quantity of phosphorus compounds adsorbed on colloidal micelles of Al hydroxide and Fe hydroxides can vary depending on the applied coagulant or electrocoagulant. The data presented in Table 1 suggests that aluminum ions from PAC and the aluminum electrocoagulant are equally effective in absorbing phosphorus compounds. The above applies to adsorption maxima expressed in both mol and mg. In wastewater coagulated with PIX, adsorption maxima can be nearly five-fold higher than during coagulation with iron electrocoagulants. Based on the results (Table 1), Fe electrocoagulant appears to be least effective, while PIX emerged as the most effective coagulant in phosphorus elimination from wastewater.
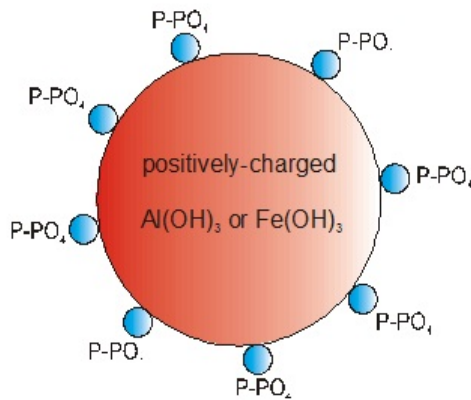
Fig. 3. Diagram of chemical sorption of phosphate with
$(Al(OH)_3)_n$ and $(Fe(OH)_3)_m$ colloidal sorbents

The process of sorption of phosphates with $(Al(OH)_3)_n$ and $(Fe(OH)_3)_m$ colloidal sorbents is illustrated in Fig. 3. A similar mechanism may be involved in sorption of non-phosphate alternatives, such as organic phosphorus.

3.2. COD TEST

The plot $\log COD_a = f(\log COD_e)$ representing the converted Freundlich isotherm for COD adsorption from wastewater electrocoagulated chemically with PIX is shown in Fig. 4. Unlike in Fig. 2, the value of $R^2 = 0.093$ indicates that the Freundlich sorption model does not fit experimental data.
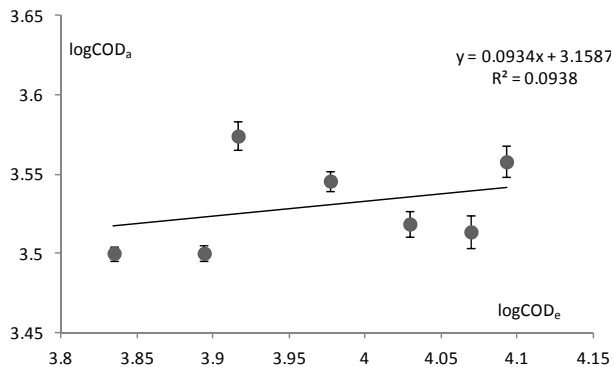

Fig. 4. Freundlich isotherm for COD adsorption with PIX

The values of the coefficient R^2 for the Langmuir isotherms (Table 2) were reported in the range of 0.9084–0.9835, and for the Freundlich isotherms – in the range of 0.0938–0.9353. In all tests, regression equations of the converted Langmuir isotherm

were characterized by higher values of R^2 than Freundlich equations. The above re-
sults indicate that similarly to phosphorus adsorption, the adsorption of compounds
responsible for COD on colloidal micelles of aluminum, iron(II) and iron(III) hydrox-
ides follows the Langmuir model. This observation suggests that the adsorption of
compounds responsible for COD is a chemical sorption process. Liquid phase com-
pounds responsible for COD are adsorbed by colliding with the surface of the colloi-
dal adsorbent. Covalent bonds are formed between adsorbate particles and the adsor-
bent surface where multiple centers exist. This type of sorption is limited, and
multilayers are not formed. The chemical properties of adsorbent and adsorbate may
be modified along the adsorbent–adsorbate phase boundary. Those properties may also
undergo change as the result of irreversible reactions, which implies that sorption and
desorption of compounds responsible for COD are not always reversible.

Table 2

Parameters of the Langmuir isotherm model for adsorption
of compounds responsible for COD

Coagulant, Electrocoagulant	Determination coefficient R^2	Maximum adsorption [g COD/g Al or Fe]
PAC (Al)	0.9084	47.2
PIX (Fe)	0.9168	7.37
Al electrodes	0.9662	3.33
Fe electrodes	0.9835	2.02

A highly probable Langmuir model of adsorption for the studied coagulants and
electrocoagulants as colloidal sorbents was used to calculate the value of the coeffi-
cient R^2 and maximum adsorption a_m (Table 2). The quantity of compounds responsi-
ble for COD, neutralized or adsorbed on colloidal micelles of Al hydroxide and Fe
hydroxides varied depending on the applied coagulant or electrocoagulant. To illus-
trate, 1 g of aluminum ions from PAC was capable of absorbing 47.2 g of compounds
responsible for COD. An iron electrocoagulant was 23-times less effective. Significant
differences in COD sorption levels were observed between Al and Fe ions from co-
agulation and electrocoagulation. Distinct variations were also noted with regard to
aluminum ions where the ratio of potential coagulation effectiveness to potential elec-
trocoagulation effectiveness was approximately 14.

In general, PAC emerged as the most effective coagulant. Differences in the effec-
tiveness of PAC and PIX can be attributed to the influence of anions, including chlo-
ride anions from PAC and sulfate(VI) anions from PIX, on coagulation, neutralization
and sorption. The probability that initially hydrolyzed forms of aluminum are present
in PAC is higher than the probability of occurrence of hydrolyzed iron in PIX.

Chloride anions can prove to be more effective than SO_4^{2-} in the flocculation of
wastewater pollutants [11, 12]. This hypothesis could result from an oversimplified

interpretation of the Schultz–Hardy rule. The "self-coagulating" ability of sulfate(VI) anions from PIX is at least 10-fold higher in comparison with that of chloride anions from PAC. Therefore, the solution produced by PAC is more stable than that obtained with PIX. Hence, the destabilization of $(Al(OH)_3)_n$ sol requires a given level of negatively-charged impurities during wastewater coagulation. $(Fe(OH)_3)_m$ sol, which is significantly more susceptible to destabilization, should be less effective in adsorbing wastewater pollutants.

The superior coagulation capacity of PAC in comparison with PIX can also be attributed to the presence of ions with the valence higher than 3+, including $Al_8(OH)_{20}^{4+}$, and, in particular, a stable polycation $AlO_4Al_{12}(OH)_2(H_2O)_{12}^{7+}$ [10, 11]. In this context, the Schultze–Hardy rule can be easily extrapolated:

$$Ka^+ : Ka^{2+} : Ka^{3+} : Ka^{4+} : ... \ Ka^{7+} = 1 : (10) \ 20 : 500 : 10\ 000 : ... \ 80\ 000\ 000$$

to demonstrate that the addition of only 0.1% of $Al_{13}{}^{7+}$ polycation can result in a 10-fold increase in the coagulating capacity of PAC even in the presence of seven aluminum ions. Stable Al_{13}^{7+} polycations and other aluminum (poly)ions (4+, 5+, 6+) play a highly significant role during the initial and the most important phase of latent coagulation [11, 20]. They can effectively neutralize negatively charged impurities responsible for COD, turbidity and wastewater suspensions. The last stage of final coagulation of lyophobic sol is often referred to as sweep flocculation [17]. Contrary to the subtle and effective phase of latent coagulation, sweep flocculation is characterized by high coagulant consumption which decreases the effectiveness of wastewater treatment.
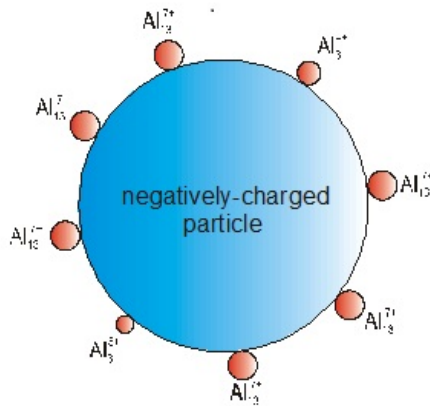

Fig. 5. Neutralization of wastewater charge

The mechanism of charge neutralization and adsorption of $AlO_4Al_{12}(OH)_2(H_2O)_{12}^{7+}$ and other aluminum ions (4+, 5+, 6+) on negatively charged compounds responsible

for COD is presented in Fig. 5. The discussed process leads to the formation of sludge agglomerates, aggregates and flocs of the first type. The second type of sludge may be formed during chemical adsorption of negatively charged impurities responsible for COD on positively charged sols of aluminum, iron(II) and iron(III) hydroxides. This sorption process most closely resembles sweep flocculation.

COD

COD

COD

COD

positively-charged
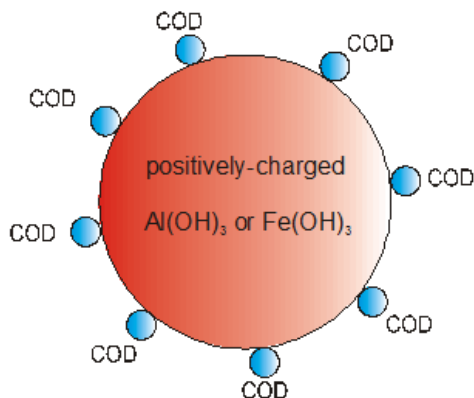
$Al(OH)_3$ or $Fe(OH)_3$

COD

COD

COD

COD

COD

Fig. 6. Mechanism underlying the sorption of wastewater
impurities responsible for COD during sweep flocculation

The adsorption (sweeping) of chemical impurities responsible for COD on colloidal sorbents such as $(Al(OH)_3)_n$ and $(Fe(OH)_3)_m$ is shown in Fig. 6. The above process may contribute to the formation of the second type of sludge flocs.

4. CONCLUSIONS

Coagulation and electrocoagulation of phosphorus compounds and substances responsible for COD of synthetic wastewater may involve chemical adsorption on colloidal sorbents such as $(Al(OH)_3)_n$, $(Fe(OH)_3)_m$ or $(Fe(OH)_2)_p$. The maximum adsorption of phosphates was reported for PIX, and the lowest – for the iron electrocoagulant, whereas PAC and the aluminum electrocoagulant were characterized by similar effectiveness of phosphate adsorption. PAC was most effective in eliminating compounds responsible for COD from wastewater. Coagulants showed higher maximum adsorption of compounds responsible for COD than electrocoagulants. The lowest adsorption maxima for the above compounds were noted for the iron electrocoagulant.

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