

Lech SMOCZYŃSKI<sup>1</sup>, Kamilla T. DŁUŻYŃSKA<sup>1</sup>,  
Bogusław PIEROŻYŃSKI<sup>1</sup>, Regina WARDZYŃSKA<sup>1</sup>,  
Beata ZAŁĘSKA-CHRÓST<sup>1</sup>  
and Anna A. ZABOROWSKA-PIWOROWICZ<sup>1</sup>

## MECHANISM OF P-PO<sub>4</sub> REMOVAL FROM CHEMICALLY TREATED WASTEWATER

### MECHANIZM USUWANIA P-PO<sub>4</sub> ZE ŚCIEKÓW OCZYSZCZANYCH CHEMICZNIE

**Abstract:** The coagulation-flocculation of model wastewater was studied to compare the coagulation performance of PAC, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and PIX. The proposed hypothesis that the amount of a coagulant has to be precisely determined based on the condition of the minimum of the parabola  $dx = 0$  was confirmed for aluminium coagulants. It was found that the dose of PIX should be calculated using the coordinates of the point of intersection of appropriate straight lines. Then the mechanism of phosphorus removal from model wastewater was examined under conditions of the optimum (constant) coagulant dose. The Al:P molar ratio obtained in the study enabled to exclude the possibility of chemical precipitation of any aluminium orthophosphate. The determination coefficient  $R^2$  for a converted equation of the Langmuir adsorption isotherm indicated chemical nature of orthophosphate (adsorbate) binding by colloidal micelles of Al{OH}<sub>3</sub> and Fe{OH}<sub>3</sub> (adsorbent). Finally, the adsorption equilibrium constant and maximum adsorption capacity were suggested for the sorption process under consideration.

**Keywords:** wastewater treatment, coagulation, inorganic chemicals, phosphate, COD

The main stages of chemical coagulation are: a) destabilization of the colloidal system, b) aggregation and flocculation. Destabilization is most often caused by ions or colloidal particles, referred to as coagulants [1, 2], whose charge is opposite to the surface charge stabilizing eg a sol. Aggregation-flocculation may be generally described as a process in which particles coagulated during latent coagulation combine to form bigger agglomerates-flocs [3].

In the process of wastewater coagulation-flocculation the key problem is the choice of a coagulant and precise determination of its optimum dose [4]. Coagulant deficiency may significantly impair coagulation [5–7], while an excess of coagulant (overdosing)

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<sup>1</sup> Department of Chemistry, University of Warmia and Mazury in Olsztyn, pl. Łódzki 4, 10–957 Olsztyn, email: lechs@uwm.edu.pl, kamilla.munska@uwm.edu.pl

may lead not only to the loss of coagulating properties, but also to sol overload [8] as well as to the release of pollutants coagulated (absorbed) under conditions of an optimum coagulant dose. Theoretically, under optimal conditions, the zeta potential  $\xi$  of the coagulated system should be equal to 0. However, practice often shows that maximal pollutant removal, eg from chemically coagulated wastewater, is not reached at  $\xi = 0$  [5]. Therefore, the jar-test procedure is still widely applied, since it permits precise determination of the optimal coagulant dose [9, 10].

In wastewater treatment technology much attention is paid to the efficiency of chemical removal (also called precipitation) of eutrophicating phosphorus with the use of iron(III) and aluminum cations contained in the most commonly applied inorganic coagulants, ie PIX and alum [11, 12]. A stoichiometric analysis shows that the molar ratio of Fe(Al) : P (the number of moles Fe or Al per mole P) higher than 3 : 1 [11, 13], at a final pH of the system below 5, practically excludes the possibility of precipitation of  $\text{AlPO}_4$  or  $(\text{AlOH})_3(\text{PO}_4)_2$ . The probability of formation of final form  $[\text{Al}(\text{OH})_2]_3\text{PO}_4$  is very low, during this chemical step. On the other hand, the solubility of  $\text{Al}_2(\text{HPO}_4)_3$ , and especially of  $\text{Al}(\text{H}_2\text{PO}_4)_3$ , is so high that it excludes the possibility of P- $\text{PO}_4$  removal in this form, as a sludge component.

It follows that phosphorus removal from chemically coagulated wastewater may be interpreted in a different way. It seems that this process is a result of sorption of orthophosphate  $\text{PO}_4^{3-}$  anions on positively charged particles of  $\{\text{Fe}(\text{OH})_3\}$  or  $\{\text{Al}(\text{OH})_3\}$ , constituting a colloidal sorbent [14]. Therefore, the main aim of this study, apart from presenting a new concept for determining an optimum coagulant dose, was to explain the mechanism of phosphate phosphorus removal from wastewater coagulated with standard inorganic coagulants, such as PIX, alum and PAC.

## Material and methods

The study was conducted on model wastewater obtained by dissolving a constant, precisely weighed analytical sample of milk powder (NESTLE) in 2000  $\text{cm}^3$  of the solution. Accurately measured 200  $\text{cm}^3$  of newly prepared wastewater was transferred into ten beakers. A very precise method was employed in the study: small amounts of a concentrated solution of inorganic coagulant were added to an adequate volume of model wastewater, using a glass pipette. The coagulant was dosed as follows:

- beaker 1 = 0 drops of a coagulant,
- beaker 2 = 1 drop of a coagulant,
- beaker 3 = 2 drops of a coagulant, etc.

The coagulant and wastewater were mixed rapidly for approx. 30 s. Then, following 15 minute sedimentation, 2  $\text{cm}^3$  samples were taken accurately with a pipette from above the surface of the sludge for analysis and physicochemical measurements. Chemical oxygen demand (COD), total phosphorus, turbidity, suspended solids and pH were determined by standard methods [15, 16].

The measurement of the volume of 100 drops of a given coagulant as well as all coagulation-flocculation tests for each coagulant were performed in seven repetitions, disregarding two highest and two lowest values. Arithmetic means and standard

deviations, calculated based on three remaining values, are presented in tables and figures. Such a procedure permitted accurate determination of the volume of a single drop of a given coagulant as well as of the cation dose used in the experiment.

Values of 100 drops volume and COD, total phosphorus, suspended solids and turbidity of crude wastewater, with standard deviations, are given in Table 1.

Table 1

Characteristics of coagulants and raw wastewater

Coagulant Parameter	PAC	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	PIX	Mean standard deviation
Coagulant amount [mg Al/Fe dm <sup>3</sup> ] in 1 drop	30.70 ± 0	8.66 ± 0	37.68 ± 0	0
mg · dm <sup>-3</sup>				
COD	12450 ± 1278	13912 ± 85.4	12780 ± 503	767
Phosphorus	82 ± 10.4	76 ± 10.8	53 ± 10.4	15.2
Turbidity	96 ± 2.61	98 ± 3.16	119 ± 4.5	12.8
Suspended Solids	85 ± 3.46	93 ± 6.8	85 ± 3.9	4.48
100 drops	4.1 cm <sup>-3</sup> ± 0.0	4.33 cm <sup>-3</sup> ± 0.0	3.68 cm <sup>-3</sup> ± 0.0	0.0

The following inorganic coagulants were used:

a) PAC – produced by DEMPOL-ECO in the form of an aqueous light-gray solution, density: 1.28 g · cm<sup>-3</sup> at 293 K, chemical composition: 20.68 % of Al<sub>2</sub>O<sub>3</sub>, 6.5 % of Cl<sup>-</sup> and 0.02 % of Fe,

b) Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> – obtained at the laboratory by dissolving 61.70 g of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 18H<sub>2</sub>O in 250 cm<sup>3</sup> of the solution,

c) PIX 113 – produced by KEMIPOL in the form of a dark-brown 41 % solution, chemical formula: ≈ Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, density: 1.55 g · cm<sup>-3</sup> in 293 K, chemical composition: 11.8 % of Fe<sup>3+</sup> and 0.45 % of Fe<sup>2+</sup>.

At the next stage of the experiment, a KH<sub>2</sub>PO<sub>4</sub> solution obtained by dissolving 21.95 g of this salt in 250 cm<sup>3</sup> of the solution was added to ten beakers containing 200 cm<sup>3</sup> of model wastewater, in the following amount:

- beaker 1–0.5 cm<sup>3</sup> of a working solution of KH<sub>2</sub>PO<sub>4</sub>, ie 10 mg of P,
- beaker 2–1.0 cm<sup>3</sup> of KH<sub>2</sub>PO<sub>4</sub> = 20 mg of P,
- beaker 3–1.5 cm<sup>3</sup> of KH<sub>2</sub>PO<sub>4</sub> = 30 mg of P, etc.

Then the constant optimum dose of a given coagulant was added to each beaker, ie a) PAC – 150.0 mg Al · dm<sup>-3</sup>, b) Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> – 56.3 mg Al · dm<sup>-3</sup>, c) PIX – 75.4 mg Fe · dm<sup>-3</sup>. Next wastewater samples were mixed rapidly with KH<sub>2</sub>PO<sub>4</sub> and a coagulant, and after 15 minute sedimentation the above sampling procedure was repeated. The phosphorus test was conducted in seven replications for each coagulant, again disregarding two highest and lowest values.

Regression of the ratio between adsorbed phosphorus and equilibrium amount of phosphorus, Pa = f(Pe), was analyzed for the converted Langmuir and Freundlich isotherm models. The transformed dependences had the following mathematical form:

$$\text{a) Langmuir isotherm: } \frac{[P_e]}{[P_a]} = \frac{1}{a_m \cdot K} + \frac{1}{a_m} \cdot [P_e] \quad (1)$$

where:  $[P_e]$  = concentration of equilibrium phosphorus;  $[P_a]$  = concentration of adsorbed phosphorus;  $a_m$  = maximum adsorption capacity;  $K$  = adsorption equilibrium constant.

$$\text{b) Freundlich isotherm: } \lg [P_a] = \lg K + n \cdot \lg [P_e] \quad (2)$$

where:  $[P_e]$  = concentration of equilibrium phosphorus;  $[P_a]$  = concentration of adsorbed phosphorus;  $K$ ,  $n$  = the constants of the Freundlich equation.

An equation of a straight line (the upper right corner in figures) and the value of the determination coefficient  $R^2$  were determined for each of the tested isotherms.

## Results and discussion

Figure 1 presents changes in the pH of model wastewater coagulated with PAC,  $\text{Al}_2(\text{SO}_4)_3$  and PIX.

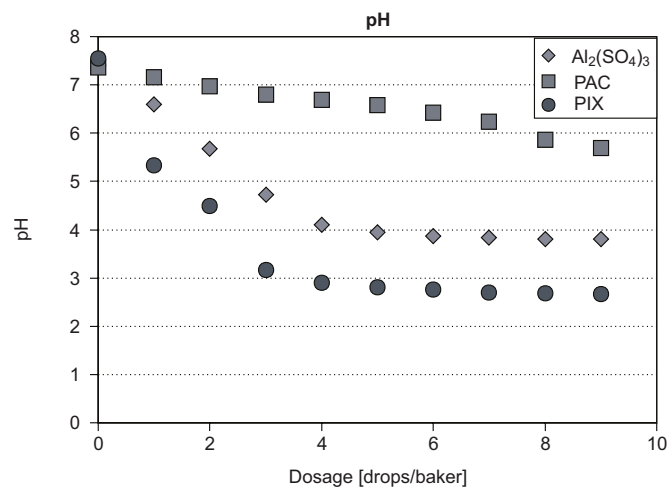


Fig. 1. Changes in the pH of model wastewater coagulated with PAC,  $\text{Al}_2(\text{SO}_4)_3$  and PIX

An increase in the coagulant dose caused a decrease in the pH of model wastewater having lower buffering capacity compare with sewage for instance. The decrease in pH resulted from the hydrolysis of aluminium salts or iron(III) salts. Primary hydrolyzed PAC, with a  $[\text{OH}]/[\text{Al}]$  ratio  $> 2$ , except for two extremely high doses, ensured a pH close to neutral in the coagulated system. Under conditions considered optimal at the subsequent stages of the study, pH was  $\approx 3.0$ – $4.5$  for PIX, whereas for both the optimal and extreme doses of  $\text{Al}_2(\text{SO}_4)_3$  the reaction remained at a relatively stable level, ie  $\text{pH} \approx 4.0$ . Higher doses of PIX reduced the reaction to  $\text{pH} < 3$ . Changes in pH levels

may be related to higher efficiency of condensation, polycondensation and polymerization of hydroxy aluminium cations, compared with hydroxy iron cations [17], resulting from an increase in coagulant concentration. The possibility of forming polycations of the following types:  $[Al_2(OH)_2]^{4+}$ ,  $[Al_3(OH)_4]^{5+}$ ,  $[Al_6(OH)_{12}]^{6+}$  or “ $\{Al_{13...}\}^{7+}$ ” [18, 19] reduces the proton-forming capacity of hydrolysis of aluminium coagulants, in comparison with the proton-forming capacity of hydrolysis of  $Fe^{3+}$  cations. The fact that the so-called zero-point-of-charge of  $Fe(OH)_3$  and  $Al(OH)_3$  occurs at  $pH \approx 8.5$  and  $pH \approx 5.0$ , respectively [20], may confirm the greater ability of aluminum coagulants to produce various polymeric forms within the  $pH \approx 4.0$ – $4.5$  range, compared with iron coagulants. Low pH values of the coagulated system usually contribute to the neutralization of the negatively charged surfaces of wastewater colloids, leading to their destabilization. However, the significance of this phenomenon should not be overestimated, since not all wastewater pollutants have the colloidal form, and their removal is often related to other processes accompanying coagulation-flocculation, such as precipitation, sorption, etc. It follows that acidification of coagulated wastewater may disturb sorption or increase the solubility of newly-formed sludge.

### A. Modeling in wastewater coagulation

Figures 2–4 show turbidity, suspended solids, total phosphorus and COD removal from model wastewater, coagulated with PAC,  $Al_2(SO_4)_3$  and PIX. In the case of PIX, turbidity decreased substantially following the application of the first two doses. This was not a typical parabolic distribution, as confirmed by the low value of the calculated coefficient  $R^2 = 0.6132$  for a quadratic regression equation. Therefore, the results obtained with PIX (Fig. 4) are presented in the form of two intersecting straight lines. The x coordinate of the intersection point of these two straight lines represents the optimal dose of PIX.

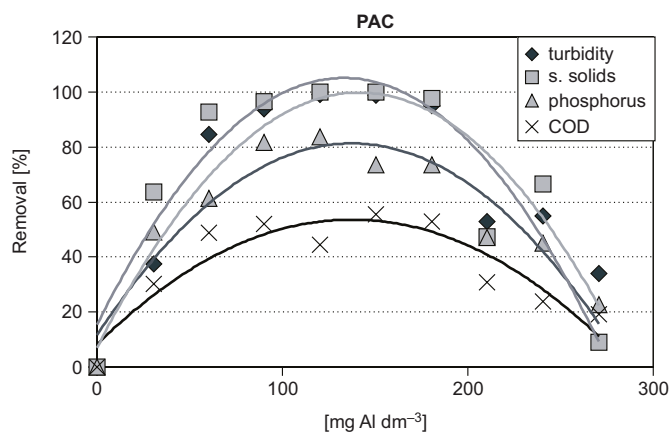


Fig. 2. Turbidity, suspended solids, phosphorus, COD removal from model wastewater coagulated with PAC

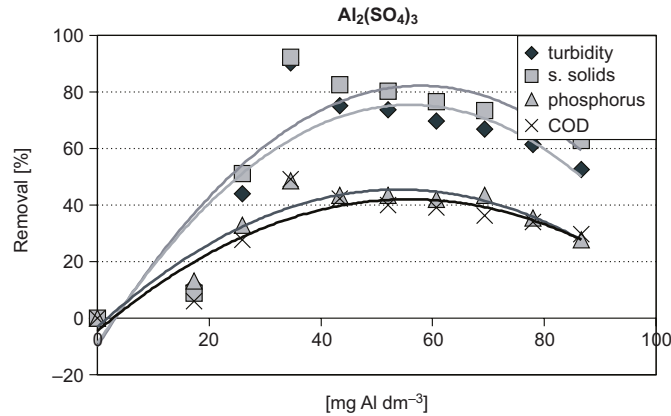


Fig. 3. Turbidity, suspended solids, phosphorus, COD removal from model wastewater coagulated with  $\text{Al}_2(\text{SO}_4)_3$

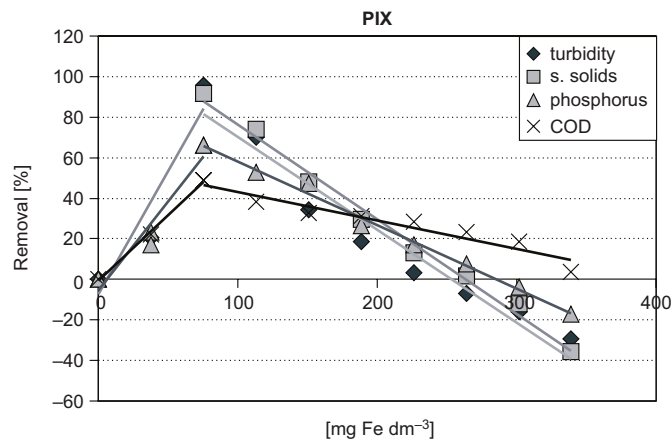


Fig. 4. Turbidity, suspended solids, phosphorus, COD removal from model wastewater coagulated with PIX

In every cases PAC was found to be the most effective. PAC was followed by PIX. Exceeding the optimum dose of all coagulants caused a gradual increase in all parameters. The effect of coagulant overdosing on parameters removal was particularly noticeable in the case of PIX, whose maximum dose resulted in the exceeding of the initial value of turbidity, suspended solids, phosphorus. This could be caused eg by colloid overload, leading to: a) undesirable hydrosol restabilization, which in the case of PIX probably increases sol concentration by incorporating a part of colloiddally dispersed  $\{\text{Fe}(\text{OH})_3\}$ , b) partial peptization of the already formed gel/sludge. The lowest increase in parameters was recorded for wastewater coagulated with an excess of  $\text{Al}_2(\text{SO}_4)_3$ . Taking into account a constant level of  $\text{pH} \approx 4.0$  (Fig. 1) in this group of coagulated wastewater samples, the above processes a) and b) for the products of  $\text{Al}_2(\text{SO}_4)_3$  hydrolysis may be disregarded, and a slight increase in parameters may be a

consequence of a certain increase in the concentration of dispersed phase coming from not completely destabilized {Al(OH)<sub>3</sub>}. At pH ≈ 2.7–3.0 and pH ≈ 5.8–7.0 the products of hydrolysis of PIX and PAC, respectively (Fig. 1), are destabilized less effectively and considerably increase the concentration of dispersed phase as well as the all parameters of coagulated wastewater. Overdosing of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> decreased COD removal efficiency by about 13 % only and turbidity, suspended solids, phosphorus removal was still from about 20 % to 60 %, even when the maximum dose of this coagulant was applied. Phosphorus removal by Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was at a comparable level within a relatively wide range of coagulant concentrations (43 to 69 mg of Al · dm<sup>-3</sup>). Such a wide range of effective coagulation could be related to pH ≈ 4.0, which was rather stable for these amounts of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. All of the above relationships indicate that an increase in coagulant dose was more less accompanied by an increase in the phosphorus content of wastewater. Except for PAC, an increase in coagulant dose > “4 drops” led to the activation of phosphate ions in coagulated wastewater, despite the stabilization of the system pH (Fig. 1). This increase may be explained in terms of increasing mobility of protonated orthophosphates or other species undergoing transformation of the following types:

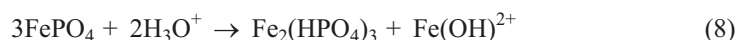
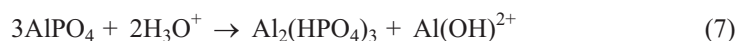


Taking into consideration some changes among the above forms enables to propose the following equations of reactions occurring in the analyzed wastewater and in sludge treated with excess Al<sup>3+</sup> or Fe<sup>3+</sup> ions:



where AlPO<sub>4</sub> or FePO<sub>4</sub> is much less soluble than Al<sub>2</sub>(HPO<sub>4</sub>)<sub>3</sub> or Fe<sub>2</sub>(HPO<sub>4</sub>)<sub>3</sub>.

Simultaneously, hydrogen ions formed during these reactions and hydrogen ions introduced with excess acid coagulant may cause the following changes:



The above diagrams showing the direction of changes explain the experimentally confirmed fact that an overdose of inorganic coagulant has a negative effect on phosphate removal from chemically coagulated wastewater.

The easily noticeable correlation between the pattern of changes in turbidity and suspended solids and the dependence of chemical oxygen demand on inorganic coagulant dose, presented above, suggests that organic substances constituted colloidal dispersed phase in the analyzed wastewater. The mechanism of destabilization of this sol/suspension was most probably based primarily on the neutralization of the negative surface charge by: a) iron or aluminum hydroxy cations or polycations as well as

positively charged micelles of  $\{\text{Fe}(\text{OH})_3\}$  or  $\{\text{Al}(\text{OH})_3\}$ , respectively; b)  $\text{H}^+$  ions formed during hydrolysis of the inorganic coagulants used in the study. Processes a) led to aggregation, agglomeration, flocculation and sedimentation of sludge. At the stage of aggregation the mixture of positively charged hydroxy cations, polycations and micelles constituted a colloidal sorbent that permitted effective “trapping” of phosphates as well as  $\text{P-PO}_4$  removal from the liquid phase of the treated wastewater. If such a mechanism of the observed changes is assumed, both the behavior of PIX, in relation to PAC and  $\text{Al}_2(\text{SO}_4)_3$ , and the differences in the optimal dose of aluminium coagulants, seem to be easy to explain. Under conditions of the optimal dose of PIX,  $\text{pH} = 3.0\text{--}4.5$  (Fig. 1) ensured over ten-fold and over hundred-fold higher  $[\text{H}^+]$  than with the use of  $\text{Al}_2(\text{SO}_4)_3$  and PAC, respectively. The fact that the so-called zero-point-of-charge [26] of  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$  occurs at  $\text{pH} \approx 8.5$  and  $\text{pH} \approx 5.0$ , respectively, indicates that  $\text{pH}=3.0\text{--}4.5$  (PIX) provides a much higher positive surface charge to the  $\{\text{Fe}(\text{OH})_3\}$  micelle than  $\text{pH} = 4.0\text{--}7.0$  to  $\{\text{Al}(\text{OH})_3\}$  micelles. It follows that already the “second drop” of PIX constituted the optimal dose of this coagulant, while in the case of PAC and  $\text{Al}_2(\text{SO}_4)_3$  four or five drops were needed.

Table 2

Regression equations and determination coefficients  $R^2$ 

Parameter	PAC	$\text{Al}_2(\text{SO}_4)_3$	PIX
Suspended solids	$y = 0.0043x^2 - 1.1465x + 71.935$ $R^2 = 0.8624$	$y = 0.0258x^2 - 2.9787x + 102.7$ $R^2 = 0.8145$	1) $y_1 = -1.0377x + 91.567$ $R_1^2 = 0.9263$ 2) $y_2 = 0.3977 - 19.671$ $R_2^2 = 0.9894$
Turbidity	$y = 0.0045x^2 - 1.2641x + 89.546$ $R^2 = 0.8951$	$y = 0.0269x^2 - 2.9784x + 106.06$ $R^2 = 0.8039$	1) $y_1 = -1.5127x + 130.2$ $R_1^2 = 0.9028$ 2) $y_2 = 0.5451x - 18.86$ $R_2^2 = 0.944$
Phosphorus	$y = 0.003x^2 - 0.8277 + 2.175$ $R^2 = 0.9002$	$y = 0.0127x^2 - 1.3704x + 78.421$ $R^2 = 0.8039$	1) $y_1 = -0.4644x + 55.833$ $R_1^2 = 0.9271$ 2) $y_2 = 0.1662x + 5.5595$ $R_2^2 = 0.9921$
COD	$y = 0.2984x^2 - 82.063x + 11420$ $R^2 = 0.8413$	$y = 2.0868x^2 - 232.55x + 14544$ $R^2 = 0.805$	1) $y_1 = -82.803x + 12880$ $R_1^2 = 0.9968$ 2) $y_2 = 17.917x + 5470.6$ $R_2^2 = 0.9232$

Table 2 presents second degree regression equations (parabolas) and determination coefficients  $R^2$  for changes in turbidity, suspended solids, total phosphorus and COD. The optimum doses of PAC,  $\text{Al}_2(\text{SO}_4)_3$  were determined based on the condition of the minimum of the parabola  $df(x) = 0$ , while the optimum dose of PIX was determined using the x coordinate of the point of intersection of appropriate straight lines, since this



procedure provided the maximum value of the determination coefficient  $R^2$ . Then a mean value was calculated from the above four optimum doses (for turbidity, suspended solids, total phosphorus and COD). This mean value was considered to be the optimum dose of a given coagulant. The optimum doses ( $\pm$  standard deviations) as well as the coefficients of correlation between turbidity and suspended solids, COD and total phosphorus, are given in Table 3. Tables 4 to 7 show the values  $f(x)$ , calculated based on respective regression equations. In order to better illustrate the coagulation-flocculation process, removal efficiency is given in  $[\text{mg dm}^{-3}]$  and in  $[\%]$ , whereas coagulant efficiency is expressed as mg of removed quantity of removed parameter per mg of coagulant.

Table 3

Mean optimum coagulant doses

Coagulant	COD	Turbidity	Suspended solids	Phosphorus	Mean	SD	Correlation	
							T:S	C:P
$\text{mg} \cdot \text{dm}^{-3}$								
PAC	138	140	133	138	137	2.97	0.940	0.945
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	55.7	55.4	57.5	53.9	55.6	1.48	0.994	0.979
PIX	73.6	77.5	72.43	79.7	75.8	3.38	0.986	0.904

The data in Table 3 show that there are certain differences between the optimum coagulant doses for particular parameters. The greatest differences were recorded for PIX, whose doses ranged from 72.43 to 79.7  $\text{mg} \cdot \text{dm}^{-3}$ , while the smallest differences were noted for Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> whose doses varied from 54 to 57.5  $\text{mg} \cdot \text{dm}^{-3}$ . Table 3 presents also the correlations between mean values of turbidity and suspended solids as well as between COD and phosphorus for particular coagulants. The coefficient of correlation between turbidity and suspended solids was the highest for PIX (0.986) and the lowest for PAC (0.940). The correlation between COD and phosphorus was comparable for all coagulants (0.945). The high coefficients of correlation, higher than 0.940, confirm the correctness of the new concept/method for determining the optimum coagulant dose based on parabolic equations, proposed in this study.

Table 4

Turbidity at the optimum coagulant dose

Coagulant	Optimum coagulant dose [ $\text{mg Al}^{3+}$ or $\text{Fe}^{3+} \cdot \text{dm}^{-3}$ ]	Turbidity at the mean coagulant dose [ $\text{mg} \cdot \text{dm}^{-3}$ ]	Turbidity removal [ $\text{mg} \cdot \text{dm}^{-3}$ ]	Turbidity removal [%]	Coagulant efficiency [ $\text{mg turbidity per mg Al or mg Fe}$ ]
PAC	150	1.21	95.2	98.8	0.63
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	56.3	23.6	74.4	75.9	1.32
PIX	75.4	19.21	100.2	83.9	1.33

Table 5

Suspended solids at the optimum coagulant dose

Coagulant	Optimum coagulant dose [mg Al <sup>3+</sup> or Fe <sup>3+</sup> · dm <sup>-3</sup> ]	Suspended solids at the mean coagulant dose [mg · dm <sup>-3</sup> ]	Suspended solids removal [mg · dm <sup>-3</sup> ]	Suspended solids removal [%]	Coagulant efficiency [mg suspended solids per mg Al or mg Fe]
PAC	150	-3.24	88.2	103.8	0.58
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	56.3	16.8	76.6	82	1.36
PIX	75.4	11.8	73.4	86	0.97

Table 6

Phosphates at the optimum coagulant dose

Coagulant	Optimum coagulant dose [mg Al <sup>3+</sup> or Fe <sup>3+</sup> · dm <sup>-3</sup> ]	Phosphorus at the mean coagulant dose [mg · dm <sup>-3</sup> ]	Phosphorus removal [mg · dm <sup>-3</sup> ]	Phosphorus removal [%]	Coagulant efficiency [mg P per mg Al or mg Fe]
PAC	150	15.5	66.2	80.1	0.44
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	56.3	41.5	34.5	45.4	0.61
PIX	75.4	19.5	34	63.5	0.45

Table 7

COD at the optimum coagulant dose

Coagulant	Optimum coagulant dose [mg Al <sup>3+</sup> or Fe <sup>3+</sup> · dm <sup>-3</sup> ]	COD at the mean coagulant dose [mg · dm <sup>-3</sup> ]	COD removal [mg · dm <sup>-3</sup> ]	COD removal [%]	Coagulant efficiency [mg COD per mg Al or mg Fe]
PAC	150	5827	6623	53.2	44
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	56.3	8066	5847	42	104
PIX	75.4	6730	6050	47.3	80

PAC was found to be the most effective but also the most consumed coagulant. Its efficiency could result from possibility {Al<sub>13</sub>}<sup>+7</sup> [21] polycations forming, whose coagulating capacity, calculated from extrapolation of the classical Schultz-Hardy rule [22, 23] may be even 12 000-fold higher than that of simple cations Al<sup>3+</sup>. In most cases the level of pollutant load removal with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and PIX was comparable. However Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was characterized by the highest efficiency in mg/mg Al. PIX was less effective than PAC, but its consumption in mg Fe dm<sup>-3</sup> was smaller than PAC in mg Al dm<sup>-3</sup>.

## B. P-PO<sub>4</sub> removal

The widely used Langmuir and Freundlich isotherm models, explaining the sorption mechanism, differ from each other. Therefore, the values of the determination

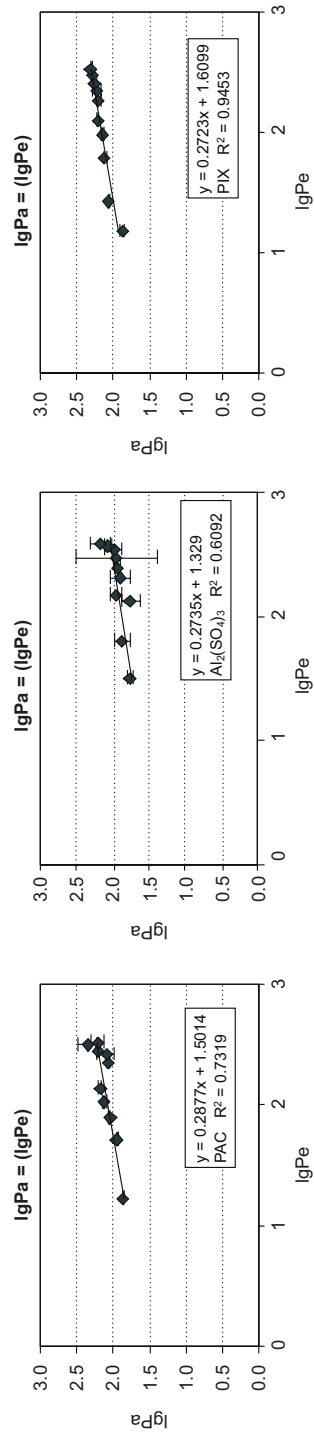


Fig. 5. Freundlich isotherms for PAC, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and PIX, respectively

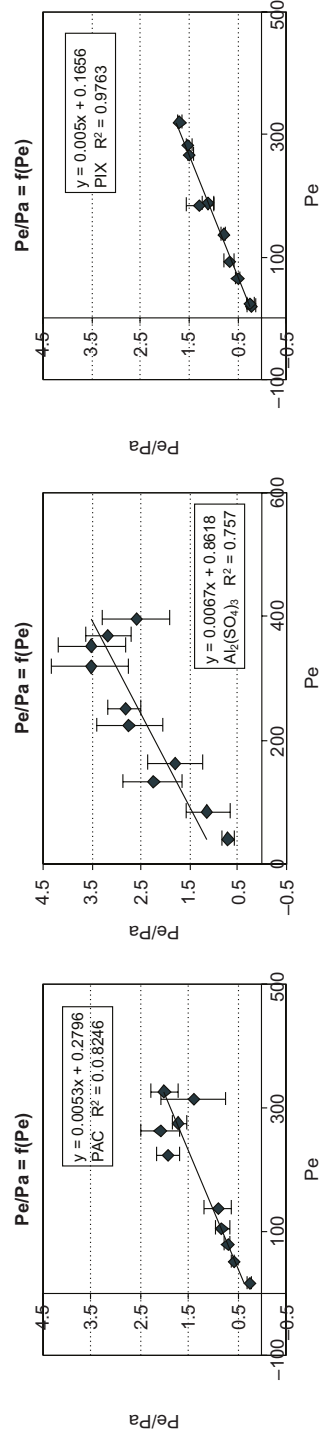


Fig. 6. Langmuir isotherms for PAC, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and PIX, respectively

coefficients for converted equations of straight lines, derived based on the experimental database, will not have to but may enable to choose one of these models. The results of testing the dependence  $P_a = f(P_e)$ , for PAC,  $Al_2(SO_4)_3$  and PIX, are shown in Figures 5, 6 and in Tables 8, 9.

Regression equations of the converted Langmuir isotherm model were characterized by significantly higher values of the determination coefficient (Figs. 5, 6). The values of the determination coefficient  $R^2$  for the Langmuir isotherm and for the Freundlich isotherm ranged from 0.757 to 0.9763 and from 0.6092 to 0.9453, respectively. This may suggest that orthophosphates are adsorbed on colloidal sorbents,  $\{Al(OH)_3\}$  and  $\{Fe(OH)_3\}$ , fundamentally and statistically in accordance with the Langmuir sorption model [24, 25]. According to this model, the adsorbate forms a monolayer of molecules on the adsorbent surface, which interact “vertically” with adsorption centers, but generally do not interact with one another (such interactions, if present, are weak). In addition, adsorption is limited and there is no possibility of forming a multilayer. The energy of adsorption is constant, and the adsorbent surface is homogenous in terms of energy distribution. It follows that orthophosphate sorption is of chemical nature and can be referred to as chemisorption. In this process the adsorbate particles are attached to the adsorbent surface mostly through covalent bonds, filling active centers. In this kind of sorption the chemical properties of the adsorbent and adsorbate may change at the adsorbent-adsorbate phase boundary. These properties can be also modified as a result of irreversible reactions, which means that sorption and desorption processes are not always reversible.

Table 8

Parameters and converted equations of the Langmuir isotherm model

	Equation of a straight-line Langmuir isotherm	Maximum adsorption capacity $a_m$ [mg P per g Al or g Fe]	Adsorption equilibrium constant $K$
PAC	$y = 0.0053x + 0.2796$	188	0.019
$Al_2(SO_4)_3$	$y = 0.0067x + 0.8618$	149	0.0078
PIX	$y = 0.005x + 0.1656$	200	0.03

Maximum adsorption capacity and the adsorption equilibrium constant, being a measure of the binding energy of the sorbent-sorbate system, were determined based on the converted Langmuir isotherm equation (Table 8). PIX had the highest maximum adsorption capacity, which indicates that this coagulant was able to “trap”, ie permanently adsorb, the largest amounts of orthophosphates. It does not mean, however, that PIX guarantees the highest effectiveness of phosphorus removal, since PAC was characterized by the highest degree of phosphorus removal. The lowest maximum adsorption capacity,  $a_m = 149$  mg P per g Al, was recorded for aluminium sulfate. It should be noted that PIX had higher sorption capacity than aluminium coagulants,  $a_m\{Fe(OH)_3\} > a_m\{Al(OH)_3\}$ . As for the adsorption equilibrium constant, it was the highest ( $K = 0.03$ ) for PIX, and the lowest ( $K = 0.0078$ ) for  $Al_2(SO_4)_3$ . When the constant  $K$  increases, the equilibrium of the adsorption  $\rightleftharpoons$  desorption process shifts to the right. Low values of the constant  $K$  indicate high quality of a coagulant, able to

permanently adsorb orthophosphates. In such a situation small amounts of orthophosphate ions are present in treated effluents, because they undergo only slight desorption on the sludge surface. Among the tested coagulants, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> provided the highest level of phosphorus retention, despite the lowest maximum adsorption capacity.

Table 9

P:Al and P:Fe ratio

Ratio Coagulant	Moles P per moles Fe or moles Al	mg P per mg Al or mg Fe
PAC	1 : 6.2	1 : 5.3
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	1 : 7.7	1 : 6.7
PIX	1 : 2.8	1 : 4.5

Phosphorus sorption by {Al(OH)<sub>3</sub>} and {Fe(OH)<sub>3</sub>} depended on the coagulant used. Table 9 presents the molar ratios of P : Al and P : Fe, ie the number of moles Al or Fe required to adsorb one mole P, as well as the corresponding weight ratios [mg]. Maximum adsorption values and the optimum coagulant dose, expressed in moles and mg, were used to calculate these ratios. The molar ratios show that there were fewer moles Fe from PIX than moles Al from aluminium coagulants per mole P. The molar ratio of Fe : P around 3 : 1 does not exclude the possibility of FePO<sub>4</sub> precipitation as a process of phosphorus removal from wastewater coagulated with PIX, whereas the molar ratio of Al : P varying from 6 : 1 to 8 : 1 excludes the possibility of precipitation of any aluminium phosphate as a process of phosphorus removal from wastewater coagulated with aluminium coagulants. From the commercial perspective, the amount of a coagulant required to remove phosphorus from wastewater is also important. In the present study this amount remained within a relatively narrow range, ie from 4.5 mg Fe from PIX to 6.7 mg Al from Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> per mg P.

## Conclusions

The model wastewater used in the study is readily treatable by chemical coagulation, which permits experimental reproducibility as well as a reliable statistical analysis of the database. The results obtained for aluminium coagulants were found to be correlated, which confirmed that the optimum dose of such coagulants can be successfully determined based on a second degree regression equation (parabola). However, the optimum dose of iron coagulants (PIX) should not be determined by this method, although it is perfectly suited for calculating the optimum dose of aluminium coagulants. PAC was the most effective of all tested coagulants, and ensured the highest level of pollutant load removal. However, this result was achieved at the highest optimum dose of this coagulant. Exceeding the optimum doses (overdosing) of all coagulants resulted in a decrease in coagulation efficiency. The negative consequences of overdosing were the least serious in the case of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and the most serious in that of PIX. The mechanism of phosphate removal may follow the Langmuir isotherm pattern, indicating a limited range of adsorption. PIX was characterized by the highest

maximum adsorption capability, and adsorbed the greatest quantities of phosphates.  $\text{Al}_2(\text{SO}_4)_3$  ensured the highest phosphorus retention levels.

## References

- [1] Cheng W.P., Chi F.H. and Yu R.: *Effect of phosphate on removal of humic substances by aluminum sulfate coagulant*. J. Colloid Int. Sci., 2004, **272**, 153–157.
- [2] Jiang J.-Q. and Lloyd B.: *Progress in the development and use of ferrate(VI) salts as an oxidant and coagulant for water and wastewater treatment*. Water Res., 2002, **36**(6), 1397–1408.
- [3] Smoczynski L. and Wardzynska R.: *Study on macroscopic aggregation of silica suspension and sewage*. J. Colloid Int. Sci., 1996, **183**, 309–314.
- [4] Edzwald J.K. and Tobiason J.E.: *Enhanced coagulation: US requirements and broader view*. Water Sci. Technol., 1999, **40**(9), 63–70.
- [5] Han M., Kim W. and Dockko S.: *Collision efficiency factor of bubble and particle in DAF: theory and experimental verification*. Water Sci. Technol., 2001, **43**(8), 139–144.
- [6] Jewwel L.L., Fasemore O.A., Glasser D., Hildebrandt D., Heron L., van Wyk N. and Coorey B.: *Toward zero waste production in the paint industry*. Water SA, 2004, **30**(5), 95.
- [7] Lyklema J.: *Overcharging, Charge Reversal: Chemistry or physics?* Colloids Surf. A, 2006, **291**, 3–12.
- [8] Jiang J.-Q. and Lloyd B.: *Progress in the development and use of ferrate(VI) salts as an oxidant and coagulant for water and wastewater treatment*. Water Res., 2002, **36**(6), 1397–1408.
- [9] Bouyer D., Escudé R. and Liné A.: *Experimental analysis of hydrodynamics in a jar-test process*. Saf. Environ. Protect., 2005, **83**(B1), 22–30.
- [10] Sheng Chang; Waite D.T., Ong P.E.A., Shafer A.I. and Fane A.G.: *Assessment of trace estrogenic contaminants removal by coagulant addition, powered activated carbon adsorption and powered activated carbon/microfiltration processes*. J. Environ. Eng., 2004, **130**(7), 736–742.
- [11] Oguz E.: *Sorption of phosphate from solid/liquid interface by fly ash*. Colloids Surf. A, 2005, **262**, 113–117.
- [12] Rossini M., Garcia Garrido J. and Galluzzo M.: *Optimization of the coagulation-flocculation treatment: influence of rapid mix parameters*. Water Res., 1999, **33**(8), 1817–1826.
- [13] Tanada S., Kabayama M., Kawasaki N., Sakiyamam T., Nakamura T., Araki M. and Tamura T.: *Removal of phosphate by aluminum oxide hydroxide*. J. Colloid Int. Sci., 2003, **257**, 135–140.
- [14] Aguilar M.I., Llor M., Soler O. and Ortu J.F.: *Nutrient removal and sludge production in the coagulation flocculation process*. Water Res., 2002, **36**(11), 2910–2919.
- [15] APHA, AWWA and WEF.: *Standards methods for examination of water and wastewater*, 19<sup>th</sup> Ed., DC: APHA, AWWA and WEF, Washington 1995.
- [16] HACH DR/2000: *Spectrophotometer Handbook*, Procedure Manual, 1993
- [17] Bottero J.Y. and Bersillion J.L.: *Aluminum and Iron Chemistry*. Adv. Chem. Ser., 1989, **219**, 425–442.
- [18] Exall K.N. and Loon van G.W.: *Effects of raw water conditions on solution-state aluminum speciation during coagulant dilution*. Water Res., 2003, **37**, 3341–3350.
- [19] Houndt T.R. and O'Melia C.R.: *Aluminum-fluvic acid interactions: Mechanism and applications*. J. Amer. Water Works Assoc., 1988, **80**(4), 176–186.
- [20] Stumm W. and Morgan J.J.: *Aquatic chemistry*, Wiley, New York 1996.
- [21] Bottero J.Y., Tchoubar D., Axelos M.A.V. and Quienne P.: *Flocculation of silica colloids with hydroxy aluminum polycations, relation between floc structure and aggregation mechanisms*. Langmuir, 1988, **6**(3), 596–601.
- [22] Hsu J.P. and Kuo J.H.: *Critical coagulation concentration of cations for negatively charged particles with an ion-penetrable surface layer*. J. Colloid Int. Sci., 1995, **174**, 250–257.
- [23] Weiser H.B.: *A textbook of colloid chemistry*, 2nd Ed. J. Wiley & Sons, Ltd., London 1950.
- [24] Deyi W., Baohua Z., Chunjie L., Zhenjiao Z. and Hainan K.: *Simultaneous removal of ammonium and phosphate by zeolite synthesized from fly ash as influenced by salt treatment*. J. Colloid Int. Sci., 2006, **304**, 300–306.
- [25] Srivastava V.C., Mall I.D. and Mishra I.M.: *Treatment of pulp and paper mill wastewater with polyaluminium chloride and bagasse fly ash*. Colloids Surf. A, 2005, **260**, 17–28.

**MECHANIZM USUWANIA P-PO<sub>4</sub> ZE ŚCIEKÓW OCZYSZCZANYCH CHEMICZNIE**

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

**Abstrakt:** Porównano zdolność koagulacyjną PAC-u, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> i PIX-u w ściekach modelowych. Dla koagulantów glinowych potwierdzono słuszność nowej koncepcji dokładnego obliczania ilości koagulantu z warunku minimum paraboli  $dx = 0$ . Stwierdzono, że dawkę PIX-u należy obliczać ze współrzędnych przecięcia odpowiednich prostych. W warunkach „dawki optymalnej” koagulantu badano mechanizm usuwania fosforu z koagulowanych ścieków modelowych. Wartości współczynnika determinacji R<sup>2</sup> dla skonwertowanego równania izotermy adsorpcji Langmuira wskazały na chemiczny charakter wiązania fosforanów(V) przez koloidalne micelle {Al(OH)<sub>3</sub>} i {Fe(OH)<sub>3</sub>}. W konsekwencji takiej konkluzji określono stałą równowagi i „adsorpcję maksymalną” dla badanego procesu sorpcji. Ustalona molowa zależność Al:P wykluczyła chemiczne wytrącanie osadu jakiegokolwiek fosforanu(V) glinu.

**Słowa kluczowe:** koagulacja-flokulacja, nieorganiczne sorbenty koloidalne, ścieki modelowe, sorpcja fosforanów