Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2023.29654

301 (2023) 209–215
July

Comparative efficiency of phosphorus removal from supernatants by coagulation process

Bartłomiej Macherzyński[a,*], Małgorzata Wszelaka-Rylik[a], Maria Włodarczyk-Makuła[b], Małgorzata Osiak[a], Adam Pietrzak[a], Beata Bień[b], Agnieszka Poniatowska[a]

[a]*Faculty of Biology and Environmental Science, Cardinal Stefan Wyszynski University in Warsaw, Wóycickiego 1/3 Str., 01-938 Warsaw, Poland, emails: b.macherzynski@uksw.edu.pl (B. Macherzyński), m.wszelaka-rylik@uksw.edu.pl (M. Wszelaka-Rylik), maria.wlodarczyk-makula@pcz.pl (M. Osiak), adam.pietrzak141@gmail.com (A. Pietrzak), a.poniatowska@uksw.edu.pl (A. Poniatowska)*

[b]*Faculty of Infrastructure and Environment, Częstochowa University of Technology, J.H. Dąbrowskiego 73 Str., 42-200 Częstochowa, Poland, emails: g.wiacek1997@gmail.com (M. Włodarczyk-Makuła), beata.bien@pcz.pl (B. Bień)*

Received 4 April 2023; Accepted 4 June 2023

ABSTRACT

This paper presents the results of a study on the comparative efficiency of phosphorus precipitation using iron(II) sulfate(VI) and pre-hydrolyzed coagulants. Among the hydrolyzed iron coagulants were selected such as: PIX-113, PIX-110 and PIX-111 and among the aluminous ones: PAX XL60, PAX XL10 and PAX XL19H. Tests were conducted for four different doses of iron(II) sulfate(VI) and three different doses for each of the pre-hydrolyzed coagulants iron polychloride (PIX) and aluminum polychloride (PAX). The raw supernatant were characterized by high phosphate concentrations (227–242 mg·PO_4^{3-}·L^{-1}), and the content of organic compounds expressed by the chemical oxygen demand index was in the range of 130–190 mg·O_2·L^{-1}. The study showed that the precipitation of phosphorus from supernatant is effective with both iron(II) sulfate(VI) and pre-hydrolyzed coagulants of the PIX (iron) and PAX (aluminum) groups. The highest efficiency of phosphorus removal (99.5%) and removal of organic compounds (71%) was achieved using the iron coagulant PIX-110. However, taking into account the other liquid quality indicators from the studied wastewater treatment plant, it is economically reasonable to carry out the coagulation process using iron(II) sulfate(VI).

Keywords: Phosphorus; Precipitation; Coagulants; Iron polychloride (PIX); Aluminum polychloride (PAX) Iron(II); Sulfate(VI)

1. Introduction

Phosphorus is a building material essential for the proper functioning of all organisms. Its recovery from wastewater and sewage sludge is of both ecological and economic importance. It is predicted that the world's reserves of phosphate deposits may run out within 50–100 y. Most of the extracted phosphorus is processed into fertilizers, detergents, animal feed and other products [1,2]. This element is also one of the most important indicators of water pollution. Phosphorus content in surface waters contributes to the intensification of the eutrophication process, as it accelerates the growth of algae and seaweed, which die over time. As they settle in the aquatic environment, they undergo processes of biological degradation. The phenomenon of a deficit of dissolved oxygen in the water then occurs, resulting in the death of aquatic fauna [3–6].

One of the primary sources of phosphorus in water is municipal as well as industrial wastewater. During wastewater treatment using physical-chemical [7,8] and biological [9] processes carried out at wastewater treatment plants, sludge is separated. These are highly hydrated waste materials that are processed through biochemical processes. Stabilized sludge is dewatered using organic polymers. The

* Corresponding author.

Presented at the 15th Scientific Conference on Micropollutants in the Human Environment, 14–16 September 2022, Częstochowa, Poland

1944-3994/1944-3986

supernatant thus separated, are characterized by the presence of biogenic compounds, mainly nitrogen and phosphorus. The current method of managing these liquids at the treatment plant is to direct them to the beginning of technological system for wastewater treatment. Although the amount of formed supernatant is not large compared to the amount of raw sewage, this way of proceeding contributes to an increase in the load of nitrogen and phosphorus compounds in the mainstream of treated wastewater. Too high load of pollutants can pose a threat to the proper functioning of the activated sludge microorganisms of the biological part of treatment plants. Recirculation of supernatant has an adverse effect on the biological efficiency of wastewater treatment and can increase the concentration of phosphorus and nitrogen in the treated wastewater. In addition, the increased pollutant load generates additional costs related to the need to install additional equipment. Taking into account the composition of the resulting supernatant and their adverse impact on the operation of treatment plant, before entering the main wastewater treatment system, they should undergo prior pretreatment to eliminate phosphorus and nitrogen compounds [10–12]. Phosphate removal from the supernatant can be carried out using a number of technologies. Due to the scarcity of phosphorus and the introduction of circular economy principles into water and wastewater management, phosphorus recovery technologies have recently been developed. The most important recovered phosphate salts include calcium phosphates (mainly hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, HAp and brushite $CaHPO_4{\cdot}2H_2O$, DCPD) and magnesium and ammonium (struvite $MgNH_4PO_4{\cdot}6H_2O$ – magnesium ammonium phosphate). Struvite precipitates according to Eq. (1):

$$Mg^{2+} + NH_4^+ + PO_4^{3-} \rightarrow MgNH_4PO_4 \cdot 6H_2O \tag{1}$$

Phosphorus can be recovered in the form of struvite using, among others, fluidized beds (DHV Crystalactor process [13], CSIR [14], Unitika Phoenix, Japan [15]), fixed-fill beds (Kurita process [16]), ion-exchange (REM NUT process [17]), fermentation process (OFMSW and BNR process (organic fraction municipal solid waste and biological nutrient removal) [18].

Chemical removal of phosphorus compounds from wastewater is based on the precipitation processes of mainly orthophosphates and their transformation into insoluble suspensions. These compounds are then removed from wastewater by sedimentation. Elimination of pollutants by chemical precipitation also has the effect of reducing suspended solids by about 70%, reducing the content of organic compounds expressed by the chemical oxygen demand (COD) index by about 70%, and biological oxygen demand (BOD_5) by about 70%–80%. During the precipitation process, the precipitating agent is mixed with either wastewater or sludge liquids. iron(II) sulfate(VI), aluminum sulfate(VI) and pre-hydrolyzed coagulants such as iron polychloride (PIX) and aluminum polychloride (PAX) are typically used as the chemical agent. Calcium hydroxide $Ca(OH)_2$ can also be used. Chemical precipitation can be divided into four basic stages: specific precipitation, coagulation, flocculation and separation. The latter stage is usually carried out by sedimentation. The first stage, specific precipitation, involves mixing the wastewater with a precipitating agent. In this process, dissolved orthophosphates present in the wastewater are converted to metal phosphates. Rapid coagulant mixing with wastewater enables high efficiency of the precipitation process. Coagulation, the second stage of chemical phosphorus precipitation, is a mechanism for neutralizing the surface load of particles contained in the wastewater, as well as forming hydroxides. Metal ions contribute to the formation of flocs, or larger hydroxide complexes, which are responsible for binding the precipitated phosphates. Flocs can also bind other suspended substances present in the wastewater and reduce chemical and biological oxygen demand indicators. The third stage is flocculation, during which flocs are combined into agglomerates of larger size. The final stage is particle separation. It involves the removal of sludge from the system, after prior sedimentation. The formation of insoluble or sparingly soluble salts by chemical binding of phosphorus can be written according to reactions (2)–(5) [19–22]:

$$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4 \downarrow \tag{2}$$

$$3Fe^{2+} + 2PO_4^{3-} \rightarrow Fe_3\left(PO_4\right)_2 \downarrow \tag{3}$$

$$Al^{3+} + PO_4^{3-} \rightarrow AlPO_4 \downarrow \tag{4}$$

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow Ca_{10}\left(PO_4\right)_6\left(OH\right)_2 \downarrow \tag{5}$$

The aim of this study was to determine the efficiency of phosphorus removal from the supernatant in the process of chemical precipitation using different precipitants, taking into account the process economics.

2. Materials and methods

2.1. Materials

Supernatant obtained during sludge dewatering on presses at the Municipal Wastewater Treatment Plant in Łomianki were used for the study. The municipal wastewater treatment plant carries out biological treatment of wastewater in Carrousel-type bioreactors, where oxidation of organic compounds, phosphorus removal, denitrification and nitrification take place. Sewage sludge is stabilized under aerobic conditions in open reactors. Stabilized sludge is directed to mechanical presses, where it is dewatered. Supernatant from the presses are returned to the main line of the treatment plant.

2.2. Phosphorus precipitation

Test stand consisted of reactors placed in a set for conducting the chemical precipitation process. The reactors were provided with mechanical stirrers. Tests were conducted using chemical reagents from the PIX group and PAX. In the first series, iron preparations were used: iron(II) sulfate(VI) and PIXs: 113, 110, 111. In the second, aluminous preparations were used: PAX XL60, PAX XL10 and PAX XL19H. For the study, 5%–10% solutions of coagulants were prepared. The characteristics of coagulants used are shown in Tables 1 and 2.

Based on the phosphorus concentration in the supernatant, the dose of iron(II) sulfate(VI) heptahydrate was calculated.

The doses of PIX and PAX were calculated according to Eq. (6). Tests were carried out for three different doses of each of the coagulants PIX and PAX, in the calculation of iron(III) and aluminum doses, a multiplication factor of β = 0.7; β = 1.0; β = 1.5 was adopted. The β factor represents the stoichiometric dose multiplication factor. This means that coagulants were used in the study at a dose lower (by 30%), equal to and higher (by 50%) than the calculated dose. In fact, in addition to the doses traditionally applied, resulting from the course of reaction, a dose correction factor is used, the so-called β-factor. It determines the molar ratio of metal cations used during precipitation to the amount of phosphorus precipitated in the process. In order to economically manage the precipitant and reduce the formation of a large amount of precipitate through precipitate formation, it is recommended to keep β values between 1.0–1.5.

$$d = \frac{\beta \cdot c \cdot M_{\mathrm{Fe(Al)}}}{M_P} g\mathrm{PIX} \cdot \mathrm{m}^{-3} \quad (6)$$

where β – precipitant consumption factor (mol·Fe/mol·P); c – concentration of phosphorus P in sludge liquids (g·P/m)^3; M_{Fe} – molar mass of iron (55.85 g·mol^{-1}); M_{Al} – molar mass of aluminum (27.0 g·mol^{-1}); M_P – molar mass of phosphorus (30.97 g·mol^{-1}).

The doses of coagulants used are shown in Table 3.

2.3. Course of study

For coagulants of the PIX and PAX groups, beakers were filled with 1 L each of raw supernatant, and then the calculated dose of coagulant was added (β = 1.0), as well as less (β = 0.7) and more (β = 1.5) than the calculated dose, respectively. Tests using each of the above-mentioned coagulants were carried out in three parallel replicates. After introducing the reagents at predetermined doses, the reactors were placed in a flocculator and agitators were turned on. Two minutes were followed by high-speed stirring – 200 rpm, followed by slow stirring at 20 rpm, for 30 min. After the mixing process was finished, the samples were left for 60 min to sediment the precipitates. After the precipitation process, 400 mL each of the test liquids were decanted from the samples. The following parameters were determined in the collected supernatant before and after the precipitation process:

- phosphates – with the molybdenum method using a DR6000 spectrophotometer,
- pH – with the potentiometric method,
- alkalinity – by the titration method in the presence of indicators (phenolphthalein, methylene orange),
- COD – with the American abbreviated method.

3. Results and discussion

3.1. Characteristics of supernatant

The characteristics of supernatant taken are shown in Table 4. In the first stage, in the supernatant taken after the presses, the pH was 7.5, and the alkalinity was 610 mg·$CaCO_3$·L^{-1}. phosphate concentration was 227.0 mg·PO_4^{3-}·L^{-1} (74.2 mg·P·L^{-1}). The content of organic compounds expressed by the COD index remained at 190 mg·O_2·L^{-1}.

In the second series, pH was 6.93 and alkalinity was 441 mg·$CaCO_3$·L^{-1}. Phosphate concentration was 242.0 mg·PO_4^{3-}·L^{-1} (79.0 mg·P·L^{-1}), and COD was 130 mg·O_2·L^{-1}. Supernatant isolated from sludge after presses are characterized by a high pollutant load, mainly high concentrations of phosphorus and organic compounds.

3.2. Precipitation with iron coagulants

The values of supernatant quality indicators depending on the dose and type of iron coagulants are shown in Table 5.

Table 1
Characteristics of the iron-based coagulants used

Coagulant	Iron, %	Density, g·mL^{-1}	pH
PIX-113	11.8 ± 0.4	1.52 ± 0.06	<1
PIX-110	12.5 ± 0.5	1.46 ± 0.08	<1
PIX-111	13.4 ± 0.6	1.44 ± 0.06	<1

Table 2
Characteristics of the aluminum-based coagulants used

Coagulant	Al^{3+}, %	Density, g·mL^{-1}	pH
PAX XL60	7.5 ± 0.3	1.31 ± 0.02	1.5 ± 0.5
PAX XL10	5.0 ± 0.2	1.22 ± 0.02	2.5 ± 0.5
PAX XL19H	12.5 ± 0.3	1.35 ± 0.04	3.5 ± 0.4

Table 3
Coagulant doses used in the study

	Concentration, g·Fe·m^{-3}			
	d_1 = 94	d_2 = 133	d_3 = 200	d_4 = 300
Multiplicity of the dose $FeSO_4 \cdot 7H_2O$	0.5	0.7	1.0	1.5
Wear factor (β) PIX	0.7	1.0	1.5	–
	Concentration, g·Al·m^{-3}			
	d_1 = 114	d_2 = 163	d_3 = 245	–
Wear factor (β) PAX	0.7	1.0	1.5	–

Table 4
Characteristics of supernatant after filter presses

Indicator	I stage	II stage
pH	7.5	6.93
Alkalinity, mg·$CaCO_3$·L^{-1}	610	441
Chemical oxygen demand, mg·O_2·L^{-1}	190	130
Phosphates, mg·PO_4^{3-}·L^{-1}	227.0	242.0
Phosphorus, mg·P^-·L^{-1}	74.2	79.0

Table 5
Change in physical and chemical properties during precipitation of phosphorus from supernatant using iron-based coagulants

	$FeSO_4·7H_2O$				PIX-113			PIX-110			PIX-111		
Dose	d_1	d_2	d_3	d_4	d_1	d_2	d_3	d_1	d_2	d_3	d_1	d_2	d_3
pH	7.04	6.96	6.87	6.83	7.12	7.01	6.89	7.04	7.01	6.98	7.16	6.98	6.81
Alkalinity, $mg·CaCO_3·L^{-1}$	505	470	445	410	395	315	300	375	310	260	345	260	140
Chemical oxygen demand, $mg·O_2·L^{-1}$	123	98	59	51	99	94	83	78	71	55	148	143	130
Phosphates, $mg·PO_4^{3-}·L^{-1}$	97.0	76.9	55.6	44.8	54.5	16.2	2.5	55.6	19.3	1.2	51.1	19.6	4.3
Phosphorus, $mg·P^{-}·L^{-1}$	32.1	25.1	18.2	14.6	17.8	5.3	0.8	18.2	6.3	0.4	16.7	6.4	1.4

With the use of $FeSO_4·7H_2O$, the phosphorus concentration in the tested supernatant decreased from 74.2 to 32.1, 25.1, 18.2 and 14.6 $mg·P·L^{-1}$ for the doses d_1, d_2, d_3 and d_4, respectively. In the supernatant after the precipitation process, the content of organic compounds, determined as COD, ranged from 123 to 51 $mg·O_2·L^{-1}$. Phosphorus concentrations decreased to 0.8, 0.4 and 1.4 $mg·P·L^{-1}$, respectively, when PIX-113, 110 and 111 were applied at the highest coagulant dose. The organic compound content after precipitation for d_1 doses ranged from 78 to 148 $mg·O_2·L^{-1}$, for d_2 doses from 71 to 143 $mg·O_2·L^{-1}$, and for d_3 from 55 to 130 $mg·O_2·L^{-1}$.

The efficiency of phosphorus removal in all samples increased as the dose of a given precipitant increased (Fig. 1). Phosphorus removal efficiency using different iron coagulants in supernatant ranged from 56.7 (iron(II) sulfate(VI), dose 0.5) to 99.5% (PIX-110, dose 1.5).

The highest phosphorus removal efficiency for a dose of d_1 was obtained using PIX-111, for which the decrease in phosphorus concentration was 77.5%, and the lowest – for iron(II) sulfate(VI), for which the value of phosphorus removal was 66.1%. The highest phosphorus removal efficiency for a dose of d_2 was obtained using PIX-113, for which the phosphorus removal value was 92.9%. However, the lowest was observed for iron(II) sulfate(VI), for which the phosphorus removal value was 75.5%. The highest phosphorus removal efficiency for a dose of d_3 was obtained using PIX-110, for which the phosphorus removal value was 99.4%, and the lowest for iron(II) sulfate(VI), for which the phosphorus removal value was 80.3%.

An increase in coagulant dose had the most effective effect on phosphorus reduction for PIX-110, the difference in phosphorus removal efficiency between the lowest and highest dose for this precipitant was 24%. The least effect of precipitant dose on phosphorus removal efficiency was observed for PIX-111, for which the difference in efficiency between the lowest and highest dose was 20.6%.

The content of organic compounds determined as COD in the tested supernatant also decreased during the chemical precipitation process. The efficiency of organic compound removal depending on the dose and type of coagulant is shown in Fig. 2. The COD removal efficiency increased as the applied dose of each precipitant increased. The efficiency did not exceed 72%. The best effect for COD removal was reported with PIX-110 coagulant, using the maximum dose. While the least contribution to the reduction of COD in the studied liquids was made by PIX-111, the highest dose of which resulted in a reduction of COD by only 31.6%. The effect of dose on COD reduction in the group of PIX pre-hydrolyzed coagulants is most noticeable with PIX-110 – increasing the stoichiometric dose from 0.7 to 1.5 allowed to increase the efficiency by 12.2%. The smallest difference in efficiency depending on the dose was recorded for PIX-113, it was 6.1%. With 98.8% phosphate elimination, COD organic compound removal was 53.4% (PIX-113; 1.5 dose). On the other hand, with the

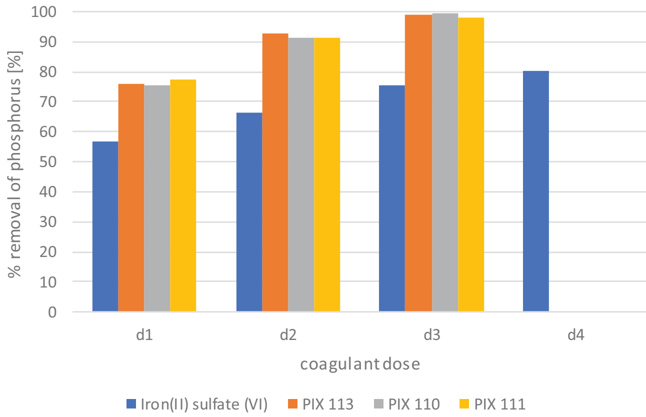

Fig. 1. Efficiency of phosphorus removal depending on iron coagulant type and dose.

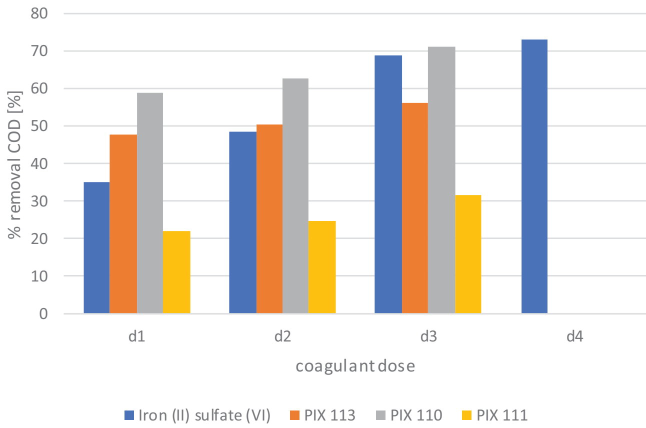

Fig. 2. Chemical oxygen demand removal depending on iron coagulant type and dose.

highest COD removal of 71.1%, the phosphate reduction was 99.1% (PIX-110; 1.5 doses).

Alkalinity consumption was also observed after the precipitation process. In the raw supernatant, the alkalinity value remained at 610 mg·$CaCO_3$·L^{-1}. The greatest level of alkalinity consumption was caused by the PIX-111. The post-process alkalinity was 140 mg·$CaCO_3$·L^{-1} for the maximum dose. The smallest reduction in this value was reported for iron(II) sulfate(VI), where the alkalinity was 410 mg·$CaCO_3$·L^{-1}, using the highest dose.

3.3. Precipitation with aluminum coagulants

The change in supernatant liquid parameters depending on the dose and type of aluminum coagulants is shown in Table 6.

The highest phosphorus removal efficiency for a dose of 0.7 was obtained with PAX XL19H (from 79.0 to 33.0 mg·P·L^{-1}), the lowest removal value was obtained with PAX XL19H coagulant (39.5 mg·P·L^{-1}). Phosphorus concentration with PAX XL60 decreased to 4.6 mg·P·L^{-1}, PAX XL10 to 15.5, PAX XL19H to 24.8 at 1.5 times the dose.

After the precipitation process, the content of organic compounds expressed by the COD index in the supernatant ranged from 39 to 102 mg·O_2·L^{-1}. The lowest value was obtained for PAX XL10 and dose d_3.

The efficiency of phosphorus removal is shown in Fig. 3. The highest phosphorus removal efficiency for a dose of d_1 was obtained with PAX XL60 (the percentage of phosphorus removal was 58.2%), the lowest removal value was obtained with PAX XL19H coagulant where it was 50%. The highest phosphorus removal efficiency for d_2 was obtained using PAX XL60 (74.2%), the lowest removal value was obtained using PAX XL19H coagulant where it was 59%. The highest phosphorus removal efficiency for a dose of 1.5 times was obtained using PAX XL60 (94.2%), the lowest removal value was obtained using PAX XL19H coagulant, which was 68.6%.

The removal efficiency of organic compounds depending on the dose and type of aluminum coagulant is shown in Fig. 4. The COD removal efficiency when using aluminum coagulants did not exceed 70%. The best COD removal effect was reported with PAX XL10 coagulant, using a dose of d_3. The least effective removal of organic compounds determined as COD PAX XL60 at a dose of d_1 (22%). The effect of dose on the reduction of COD content in the group of PAX pre-hydrolyzed coagulants is most noticeable with PAX XL10 – increasing the stoichiometric dose from 0.7 to 1.5 allowed to increase the efficiency by 47%. The smallest dose-dependent difference in efficiency was noted for PAX XL19H, it was 5%.

When each of the selected coagulants was applied to the chemical precipitation process, very good phosphorus removal results were obtained. In addition, the added coagulants resulted in a reduction in the concentration of phosphorus and organic compounds in the tested supernatant. A reduction in the content of organic compounds determined as COD was also reported. The results of our

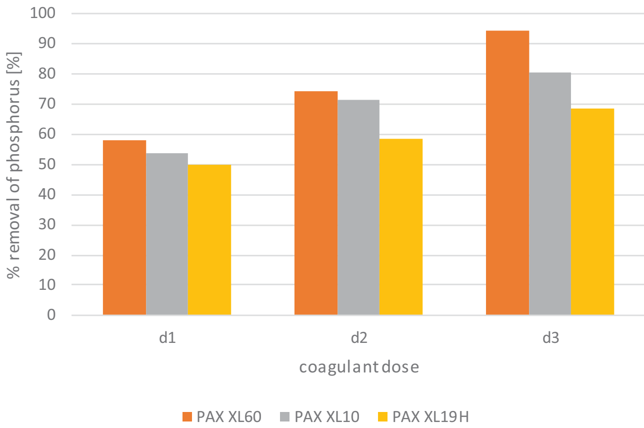

Fig. 3. Efficiency of phosphorus removal depending on aluminum coagulant type and dose.

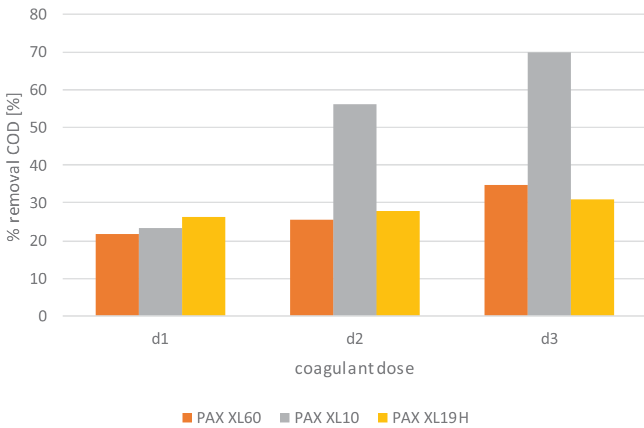

Fig. 4. Chemical oxygen demand removal depending on aluminum coagulant type and dose.

Table 6
Change in physical and chemical properties during precipitation of phosphorus from supernatant using aluminum-based coagulants

	PAX XL60			PAX XL10			PAX XL19H		
Dose	d_1	d_2	d_3	d_1	d_2	d_3	d_1	d_2	d_3
pH	6.63	6.42	6.26	6.76	6.52	6.52	6.92	6.88	6.83
Alkalinity, mg·$CaCO_3$·L^{-1}	324	278	324	355	332	275	390	385	360
Chemical oxygen demand, mg·O_2·L^{-1}	102	97	85	100	57	39	96	94	90
Phosphates, mg·PO_4^{3-}·L^{-1}	99.1	61.3	13.8	109.4	67.9	46.5	118.6	98.1	74.5
Phosphorus, mg·P^-·L^{-1}	33.0	20.4	4.6	36.5	22.6	15.5	39.5	32.7	24.8

own study corresponded with those of other authors. In a study conducted by Sperczyńska [23], four coagulants were used on digestion supernatant: aluminum sulfate(VI), low alkali PAX 18, medium alkali PAX XL10 and high alkali PAX XL1905. Three series were carried out for each of the three stoichiometric doses (0.7; 1; 1.5), and fast stirring for 2 min (200 rpm), slow stirring for 28 min (30 rpm) were used. Sedimentation time was 1 h. The sedimentary liquids tested were characterized by high concentrations of nitrogen (891 mg·NKj·L^{-1}), phosphate (125 mg·PO_4^{3-}·L^{-1}) and COD (592 mg·O_2·L^{-1}). The highest efficiency was observed for the highest coagulant doses, and the highest phosphate removal efficiency was observed for PAX 18 (96%). It was also noted that with the reduction in phosphate concentration there was a simultaneous slight reduction in COD. The maximum reduction in organic content was observed for the highly alkaline PAX XL1905 (47%). The lowest dose of coagulants allowed phosphate removal by a maximum of 83% (PAX 18).

Studies conducted by Bień [24] on the supernatant formed after mechanical dewatering of sewage sludge were carried out using PIX-113 and PIX-113 combined with Zetag 8160 polyelectrolyte. In the raw wastewater, the concentration of phosphorus was 7.94 mg·P·L^{-1}, and organic compounds determined as COD – 784 mg·O_2·L^{-1}. The use of coagulant PIX-113 without the addition of polyelectrolyte proved to be more effective. After the phosphate precipitation process using PIX-113, a decrease in pH values was reported with an increase in the precipitant dose. A pH reduction of 17.6% was reported for the lowest dose. The highest phosphorus removal efficiency was reported for the highest dose of PIX-113 and was 93.8%. In another study [25], in the supernatant separated from digested sludge, the phosphorus concentration was 40 mg·P·L^{-1}, and the content of organic compounds determined as COD was 2,240 mg·O_2·L^{-1}. After the addition of coagulant PIX-113, phosphorus concentration decreased in the range of 75% to 89%, and COD from 66% to 88%.

The results of our own research in terms of the efficiency of phosphorus removal from supernatant corresponded with the results of studies reported in the literature. The results obtained confirm the possibility of obtaining high phosphorus removal efficiency from the supernatant during the precipitation process. It can be noted the similarity of phosphorus removal efficiency for PIX-113, which both in our own studies and those presented by Bień [24] were above 90% at the highest precipitating agent dose.

3.4. Economics of the coagulation process

In order to determine the economic viability of the coagulation process, a cost analysis of the coagulants used was carried out on the basis of phosphorus reduction in the supernatant. The assumed prices of coagulants and the comparison of process costs are shown in Table 7.

In addition to the maximization of phosphorus compound removal, it is undoubtedly necessary to always pay attention to the economic aspect. In case of wastewater treatment plants in the economic context, iron(II) sulfate(VI) should be indicated as the optimal coagulant, but in terms of phosphorus removal efficiency, PIX-110 was a better coagulant.

Table 7
Cost comparison of the precipitation process

Coagulant	Average unit price	Unit price of the precipitation process, EURO·m^{-3}			
		d_1	d_2	d_3	d_4
$FeSO_4·7H_2O$	30 EURO·25 kg^{-1}	0.11	0.16	0.24	0.36
PIX-110	40 EURO·25 L^{-1}	1.27	1.81	2.72	–
PAX XL60	70 EURO·25 L^{-1}	4.27	6.08	9.15	–

4. Conclusion

Based on the study, the following conclusions were drawn:

- supernatant formed during sludge dewatering on presses are characterized by a high phosphorus concentration of 74.2–79.0 mg·P·L^{-1} and a high content of organic compounds designated as COD of 130–190 mg·O_2·L^{-1};
- efficiency of phosphorus removal from supernatant, using iron(II) sulfate(VI) was in the range of 56.7%–80.3%;
- efficiency of phosphorus removal from supernatant, using pre-hydrolyzed iron coagulants was in the range of 75.5% to 99.5%;
- efficiency of phosphorus removal from supernatant, using pre-hydrolyzed aluminum coagulants was in the range of 58.2% to 94.2%;
- among the iron coagulants, PIX-110 was the most effective and its use allowed to achieve an efficiency of up to 99.5%;
- among the aluminum coagulants, PAX XL60 was the most effective, with an efficiency of up to 94.2%;
- efficiency of phosphorus removal was dependent on the dose of coagulant and was highest after the use of PIX-110 for a dose 50% higher than the calculated one;
- the highest removal efficiency of organic compounds determined as COD was obtained for PIX-110 (71%) and iron(II) sulfate(VI) (73%);
- for the supernatant tested, in terms of economics, iron(II) sulfate(VI) is the optimal coagulant.

Acknowledgements

The study was funded by the scientific subvention of Cardinal Stefan Wyszynski University in Warsaw and of Czestochowa University of Technology.

References

[1] O.S. Djandja, A.A. Salami, Z.-C. Wang, J. Duo, L.-X. Yin, P.-G. Duan, Random forest-based modeling for insights on phosphorus content in hydrochar produced from hydrothermal carbonization of sewage sludge, Energy, 245 (2022) 123295, doi: 10.1016/j.energy.2022.123295.
[2] Y. Zhong, G. Liu, X. Yang, Isolating elemental phosphorus from sewage sludge ash by electrochemistry, Resour. Conserv. Recycl., 190 (2023) 106815, doi: 10.1016/j.resconrec.2022.106815.
[3] Y. Ren, W. Zheng, X. Duan, N. Goswami, Y. Liu, Recent advances in electrochemical removal and recovery of phosphorus from water: a review, Adv. Funct. Mater., 1 (2022) 10–20.
[4] X. Chen, Y. Wang, Z. Bai, L. Ma, M. Strokal, C. Kroeze, X. Chen, F. Zhang, X. Shi, Mitigating phosphorus pollution from

detergents in the surface waters of China, Sci. Total Environ., 804 (2022) 150125, doi: 10.1016/j.scitotenv.2021.150125.

[5] W. Feng, T. Wang, Y. Zhu, F. Sun, J.P. Giesy, F. Wu, Chemical composition, sources, and ecological effect of organic phosphorus in water ecosystems: a review, Carbon Res., 2 (2023) 12, doi: 10.1007/s44246-023-00038-4.

[6] Y. Jia, S. Sun, S. Wang, X. Yan, J. Qian, B. Pan, Phosphorus in water: a review on the speciation analysis and species specific removal strategies, Crit. Rev. Env. Sci. Technol., 53 (2023) 435–456.

[7] W. Chu, Y. Shi, L. Zhang, Recovery of phosphorus in wastewater in the form of polyphosphates: a review, Processes, 10 (2022) 144, doi: 10.3390/pr10010144.

[8] S. Dai, Q. Wen, F. Huang, Y. Bao, X. Xi, Z. Liao, J. Shi, C. Ou, J. Qin, Preparation and application of MgO-loaded tobermorite to simultaneously remove nitrogen and phosphorus from wastewater, Chem. Eng. J., 446 (2022) 136809, doi: 10.1016/j.cej.2022.136809.

[9] Q. Zhou, H. Sun, L. Jia, W. Wu, J. Wang, Simultaneous biological removal of nitrogen and phosphorus from secondary effluent of wastewater treatment plants by advanced treatment: a review, Chemosphere, 296 (2022) 134054, doi: 10.1016/j.chemosphere.2022.134054.

[10] C. Zhang, A. Guisasola, J.A. Baeza, A review on the integration of mainstream P-recovery strategies with enhanced biological phosphorus removal, Water Res., 212 (2022) 118102, doi: 10.1016/j.watres.2022.118102.

[11] Z. Fan, W. Zeng, Q. Meng, H. Liu, C. Ma, Y. Peng, Achieving partial nitrification, enhanced biological phosphorus removal and in-situ fermentation (PNPRF) in continuous-flow system and mechanism analysis at transcriptional level, Chem. Eng. J., 428 (2022) 131098, doi: 10.1016/j.cej.2021.131098.

[12] D. Hu, C. Zhang, Y. Zhang, Comparison of different pretreatment methods on phosphorus release and recovery as struvite from excess sludge, Environ. Technol., 44 (2023) 161–169.

[13] A. Grobelak, L. Spinosa, Chapter 12 – Sustainable/Integrated/Sewage Sludge Management, M.N.V. Prasad, M. Smol, Eds., Sustainable and Circular Management of Resources and Waste Towards a Green Deal, Elsevier, 2023, pp. 163–181, doi: 10.1016/B978-0-323-95278-1.00016-4.

[14] A. Mavhungu, V. Masindi, S. Foteinis, R. Mbaya, M. Tekere, I. Kortidis, E. Chatzisymeon, Advocating circular economy in wastewater treatment: struvite formation and drinking water reclamation from real municipal effluents, J. Environ. Chem. Eng., 8 (2020) 103957, doi: 10.1016/j.jece.2020.103957.

[15] N. Park, H. Chang, Y. Jang, H. Lim, J. Jung, W. Kim, Prediction of adequate pH and Mg^{2+} dosage using an empirical MgO solubility model for struvite crystallization, Environ. Technol. Innovation, 21 (2021) 101347, doi: 10.1016/j.eti.2020.101347.

[16] T. Jóźwiak, A. Kowalkowska, U. Filipkowska, J. Struk-Sokołowska, L. Bolozan, L. Gache, M. Ilie, M. Recovery of phosphorus as soluble phosphates from aqueous solutions using chitosan hydrogel sorbents, Sci. Rep., 11 (2021) 16766, doi: 10.1038/s41598-021-96416-2.

[17] E. Wiśniowska, Possibilities of Potassium Recovery From Wastewater, 2nd International Conference Strategies toward Green Deal Implementation – Water, Raw Materials & Energy, Copyright by Mineral and Energy Economy Research Institute PAS – Publishing House, Cracow, Printed in Poland, 8–10 December 2021, 2022, pp. 144–154.

[18] F. Cecchi, C. Cavinato, Smart approaches to food waste final disposal, Int. J. Environ. Res. Public Health, 16 (2019) 2860, doi: 10.3390/ijerph16162860.

[19] T. Park, V. Ampunan, S. Lee, E. Chung, Chemical behavior of different species of phosphorus in coagulation, Chemosphere, 144 (2016) 2264–2269.

[20] J. Ge, X. Meng, Y. Song, A. Terracciano, Effect of phosphate releasing in activated sludge on phosphorus removal from municipal wastewater, J. Environ. Sci., 67 (2018) 216–223.

[21] L.D. Manamperuma, H.C. Ratnaweera, A. Martsul, Mechanisms during suspended solids and phosphate concentration variations in wastewater coagulation process, Environ. Technol., 37 (2016) 2405–2413.

[22] M. Preisner, M. Smol, Investigating phosphorus loads removed by chemical and biological methods in municipal wastewater treatment plants in Poland, J. Environ. Manage., 322 (2022) 116058, doi: 10.1016/j.jenvman.2022.116058.

[23] Sperczyńska E. Usuwanie fosforanów z pofermentacyjnych cieczy nadosadowych (Removal of phosphates from fermentation supernatants), Ecol. Eng., 48 (2016) 196–201.

[24] B. Bień, The influence of condition on the quality of reject water after sewage sludge mechanical dewatering, Proc. ECOpole, 11 (2017) 471–478.

[25] B. Bień, J.D. Bień, Analysis of reject water formed in the mechanical dewatering process of digested sludge conditioned by physical and chemical methods, Energies, 15 (2022) 1678, doi: 10.3390/en15051678.