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PHOSPHORUS SPECIATION IN SEWAGE SLUDGE

Excessive sewage sludge in terms of contained phosphorus speciation forms has been characterized. The analysis allowed identification of mobile forms of phosphorus in sewage sludge. Quantification of mobile forms of phosphorus is very important for its recovery directly from sewage sludge or for its application for natural purposes. Various phosphorus speciation methods have been presented. The results of the sewage sludge speciation conducted by means of two types of wastewater treatment (EvU-Perl technology and activated sludge) have been compared. The analysis covered the effect of such physiochemical factors as oxygenation, use of ultrasound and precipitation with iron chloride(III). It was concluded that changes in physiochemical conditions lead to alterations in the content of phosphorus speciation forms in sewage sludge.

1. INTRODUCTION

Demographic development, urbanization and the excessive use of phosphorus fertilizers in agriculture have all led to adverse changes in the quality of surface waters. The problem of eutrophication, called overnutrition of water with biogenic compounds, is a threat to ecological homeostasis. The excessive growth of phytoplankton in inland waters is already observed at concentrations of phosphorus of above 0.03 mg/dm^3 [1]. Therefore, in recent years, new strategies for environmental protection have been developed, [2] aiming at the pro-ecological education of the society through spreading the awareness of the dangers posed by the uncontrolled discharge of waste or the excessive fertilization of fields. The Ministry of the Environment have dealt with the emerging threats in water management by imposing stricter legal regulations on the wastewater treatment plants discharging treated effluent to the environment [3]. The legal requirements together with the increased percentage of the popula-

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tion served by wastewater treatment facilities have contributed to high-performance integrated sewage treatment technology based on chemical, biological and physical processes. Biological methods mainly consist in taking advantage of the capability demonstrated by certain bacteria of increased phosphorus absorption in biochemical processes[4, 5]. Chemical methods are based on phosphate precipitation by means of such precipitating reagents as the ions of iron, aluminium or calcium [6, 7]. Combined treatment methods produce tangible results, as shown by e.g. a percentage of phosphate reduction in different wastewater treatment plants [8]. Unfortunately, the intensification of the treatment process is closely related to the generation of large amounts of sewage sludge – a waste, which needs to be appropriately managed. So far, the storage of municipal sewage sludge has been the main solution applied in Poland with regard to managing the sediments [6]. However, the aim is to minimize the storage of this type of waste in favour of other disposal methods. Wastewater sediments from small sewage treatment plants can be successfully applied in agriculture, provided they meet the requirements of the Ministry of the Environment [6] and, in the case of sediments from large sewage treatment plants, their incineration is preferable. The use of wastewater for natural purposes recirculates important biogenes into the environment [9]. It is estimated that the total phosphorus content in sewage sludge in terms of the general phosphorus is from 1 to 2.5% d.m. [10]. However, in order to be able to practically assess the role of sediments as a secondary source of biogenes [11], one should estimate the content of the biologically available phosphorus in the sludge, defined as the sum of the phosphorus available immediately, and the one which can be transformed into the available form as a result of the natural processes occurring in the sludge [12, 13]. The content of mobile bioavailable phosphorus can be determined by means of speciation, i.e. such an analytical procedure that allows one to define quantitatively the chemical form in which a given analyte is present [14].

2. METHODS OF PHOSPORUS SPECIATION

The content of phosphorus available to plants can be determined by a speciation analysis. This type of analysis is based on the procedures which permit the identification of particular element forms and on their quantification in the examined object. Several methods of phosphorus speciation have been developed based on sequential extraction.

Originally, the sequential extraction was used to analyse the speciation of elements in soils and sediments, and in recent years, it has also been applied to analyse wastewater sediments. The sequence analysis is based on the isolation of particular phosphorus fractions by a successive application of solvents with an increasing extraction strength [14]. The fractionation scheme was presented for the first time by Chang and Jackson [15] (Table 1).

Table 1

Sequential extraction scheme of phosphorus according to Chang and Jackson [15]

Stage	Extraction conditions	Fraction
1	2 M NH_4Cl, 0.3 h	easily soluble phosphorus
2	0.5 M NH_4F, 1 h	phosphorus associated with iron oxides
3	0.1 M NaOH, 17 h	phosphorus associated with aluminium oxides
4	0.5 M HCl	phosphorus associated with calcium
5	CDB	reduced soluble P
6	NaOH	remaining P

The Chang and Jackson procedure was modified by Williams [16], e.g. by digestion with Na_2CO_3 at high temperature, resulting in formation of an additional fraction of inorganic phosphorus (Table 2).

Table 2

Seven-step sequential extraction scheme of phosphorus according to Williams [16]

Stage	Extraction conditions	Fraction
1	0.5 M NH_4Cl, 30 min	easily soluble phosphorus
2	0.5 M NH_4F, pH = 8.2, 24 h	phosphorus associated with NH_4F
3	0.1 M NaOH + 1 M NaCl, 17 h	first NaOH-P
4	0.3 M sodium citrate + 1 g of sodium dithionate + 1 M $NaHCO_3$, 10 h	reductively soluble phosphorus
5	1 M NaOH, 17 h	second NaOH-P
6	0.5 M HCl, 1 h, 1 M HCl, 4 h	organic phosphorus extracted with acid
7	1 M Na_2CO_3, digestion at high temperature	remaining inorganic phosphorus

In 1972, the method of Williams was modified by Kurmies [17, 18] by replacing steps 3–6 with a 17 h extraction with 0.1 M NaOH. A similar procedure was proposed in 1980 by Hieltjes and Lijklema [18] (Table 3).

Table 3

Phosphorus extraction scheme by the Hieltjes, Lijklema [18] and Kurmies [17] methods

Stage	Hieltjesa and Lijklema	Kurmies	Fraction
1	1 M NH_4Cl, two extractions, 2 h each	1 M NH_4Cl + ethanol, two extractions, 2h each	unbound
2	0.1 M NaOH, 17 h	0.1 M NaOH, 17 h	Fe + Al-P
3	0.5 M HCl, 24 h	0.5 M HCl, 24 h	Ca + Mg-P

In the same year, Williams [19] introduced a new, five-step extraction of phosphorus in soils (Table 4).

Table 4

Five-step sequential phosphorus extraction scheme according to Williams [19]

Stage	Extraction conditions	Fraction
1	1 M NaOH, 4 h	extractable phosphorus (removable)
2	1 M HCl, 4 h	phosphorus associated with carbonates and with apatite
3	residue after 1M NaOH, extracted with 3.5 M HCl, 4 h	phosphorus associated with oxides and iron hydroxyoxides, aluminium and manganese
4	1 M HCl, 2 h, residue incinerated at 550 °C, 1 h, re-extraction 1 M HCl, 2 h	phosphorus associated with organic matter
5	incinerated at 550 °C, 1 h, extraction 3.5 M HCl, 2 h	total phosphorus

An innovative speciation method was proposed by Golterman in 1977 [19, 20] (Table 5). It was based on the use of chelate reagents (Na-EDTA and Ca-EDTA), as well as H_2SO_4 and NaOH solutions. The application of the chelate reagents allowed the fractionation time to be shortened and prevented the pH changes and thus stopped the hydrolysis and dissolution of the phosphate. Such a combination of extraction agents made it possible to distinguish inorganic forms of phosphorus (extracted by Na-EDTA and Ca-EDTA) and the organic forms (extracted using NaOH and H_2SO_4 solutions). Golterman [19, 20] also found that phosphorus adsorbed on the surface of sediment particles, i.e. the Na-EDTA and Ca-EDTA fractions, is the speciation form with the highest bioavailability.

Table 5

Phosphorus sequential extraction scheme according to Golterman [19, 20]

Stage	Extraction conditions	Fraction
1	0.05 M Ca-EDTA (extracted twice), 2 h	phosphorus associated with oxides and hydroxyoxides of iron, aluminium and manganese
2	0.1 M Na-EDTA, 18 h	phosphorus associated with carbonates
3	0.5 M H_2SO_4, 2 h	phosphorus present in soluble combinations with organic matter
4	2 M NaOH, 2 h	the remaining phosphorus, including the one bonded with aluminosilicates and present in organic matter in the form of complexes unaffected by sulphuric acid in stage 3

The phosphorus speciation analysis makes also use of the sequential extraction developed by Ure [21] (the BCR procedure) (Table 6), or the Psenner [22] extraction procedure (Table 7).

Table 6

Scheme of phosphorus sequential extraction according to BCR method [21]

Stage	Extraction conditions	Fraction
1	0.1 M CH_3COOH, 4 h	phosphorus associated with carbonates
2	0.1 M $NH_2OH \cdot HCl$, pH = 2, 4 h	phosphorus associated with oxides and hydroxy-oxides of iron, aluminium and manganese
3	digestion at high temperature at the presence of 30% H_2O_2, 1 h, followed by the extraction of 1 M CH_3COONH_4, pH = 2, 12 h	phosphorus in combination with organic matter

Table 7

Sequential extraction scheme of phosphorus according to Psenner [22]

Stage	Extraction conditions	Fraction
1	0.1 M NH_4Cl, 2 h	loosely bound phosphorus
2	0.1 M $NaHCO_3$ + 0.1 M $Na_2S_2O_4$, 2 h	phosphorus found in combinations with iron
3	1 M NaOH, 18 h	phosphorus associated with aluminium and organic matter
4	0.5 M HCl, 18 h	phosphorus in combination with lime

The presented extraction methods differ from each other not only by the kind of the applied extraction agents, their concentration, the handling of the samples, the extraction conditions but also, partly, by the derived fractions. According to the Psenner method, phosphorus loosely adsorbed on the surface of the sludge particles, called loosely bound phosphorus (the NH_4Cl-P fraction), is the form with the highest availability. Phosphorus in combination with iron (the $NaHCO_3$ + 0.1 M $Na_2S_2O_4$-P fraction) also manifests high mobility. According to Welch [23], phosphorus combined with aluminium or contained in the organic matter is less bioavailable, whereas the availability of phosphorus in combination with calcium is practically negligible. The Psenner method was used by Gil [24] in her study. She identified qualitative changes of phosphorus in wastewater sediments during their methane fermentation. The speciation analysis results depend on the original structure of the sediment and on its processing in different stages of the treatment. Proceeding with different dynamics, these stages involve physical, chemical and biological factors, and the changes of the sediment properties both in the solid and in the liquid phase affect the mobility of the individual phosphorus fractions in the sediment. The study was conducted in order to examine phosphorus speciation forms in excess sludge.

3. METHODS OF INVESTIGATION

The excessive sediment from two mechanical-biological sewage treatment plants was the subject of the investigation. In one of them, apart from the activated sludge, the fluidized biological bed was additionally applied (EvU-Perl technology). According to the data presented in Table 8, the excess sludge contained an average of 1.61% phosphorus with respect to the dry matter, whereas the sludge obtained using EvU-Perl technology – 1.70%. The excess sludge was examined by the speciation analysis according to Williams and Golterman and then the investigation focused on the effect that the selected physiochemical factors such as oxygenation, the use of ultrasound and the precipitation of iron chloride (III) have on the phosphorus speciation conducted by the Golterman method.

Table 8

Physicochemical characteristics of the examined wastewater sludge

Parameter	Excessive sludge			Evu-Perl technology		
	Minimum value	Maximum value	Mean value[a]	Minimum value	Maximum value	Mean value[a]
Dry mass, %	16.60	211.50	18.96	17.50	22.30	19.20
General phosphorus, % d.m.	1.17	2.23	1.61	1.22	2.20	1.70
Organic substance, % d.m.	48.96	67.36	61.94	47.15	68.20	60.15
General nitrogen, % d.m.	0.96	2.24	1.91	1.05	2.80	1.85
pH	8.21	8.83	8.46	8.15	8.80	8.40

[a]Calculated from ten repetitions.

Measurements were performed under the following conditions:

Presence of oxygen. The oxygenation of the sludge samples (5 g) was conducted using the Drechsler laboratory gas washer. Mixing the sample with 30 cm^3 of distilled water was followed by bubbling with air with the flow intensity of 50 dm^3/h. The oxygenation lasted for 5, 10, 20, 30, 40, 50 and 60 min.

Concentration of the precipitant. The samples of an excess sludge (as in point 1) were treated with the precipitating agent, i.e. Fe^{3+} ions with the concentration of 0.3 mol/dm^3 for 5–80 min.

Ultrasounds. Ultrasonic irradiation was performed with an ultrasonic cleaner Merck Eurolab using ultrasounds of 35 kHz frequency for the duration of 3, 6, 9, 12, 15 min.

In such modified sediments, phosphorus speciation was performed with the Golterman and Williams methods. After each extraction stage, the samples were permeated, and the sediment remaining after the permeation was treated with the next extraction reagent listed in Tables 4 and 5. In the resulting permeate, the general phosphorus concentration was determined using a UV-VIS PERKIN ELMER spectrophotometer. These measurements were conducted in accordance with the procedure of general phosphorus determination after the prior oxygenation of the sample with potassium persulfate(VI) [26].

4. RESULTS AND DISCUSSION

4.1. THE INVESTIGATION OF PHOSPHORUS SPECIATION IN THE EXCESSIVE SEDIMENT BY THE WILLIAMS METHOD

The analysis of speciation results for general phosphorus, obtained by the Williams method in excess sludge (Fig. 1), coming from the sewage treatment plant operated with the use of activated sludge, indicates the dominance of the NaOH-P and $HCl_{(1M)}$-P and $HCl_{(3.5M)}$-P fractions.

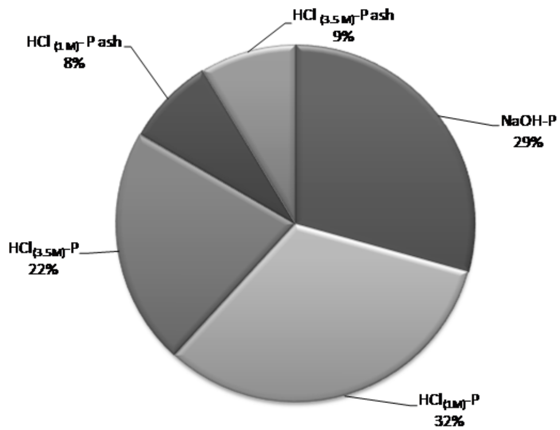

Fig. 1. The percentage of general phosphorus divided into fractions obtained by the Williams method in excess sediment originating from a wastewater treatment plant operated with the use of activated sludge

These fractions correspond to the form of exchangeable phosphorus associated with carbonates and apatites and the one associated with iron, aluminium and manganese hydroxyoxides, respectively. These forms are recognized as mobile and bioavailable which confirms the role of excess sludge in the process of depositing and removing phosphorus from wastewater.

4.2. THE PHOSPHORUS SPECIATION INVESTIGATION IN THE EXCESS SLUDGE BY THE GOLTERMAN METHOD

The results of the speciation performed on the excess sludge samples from two wastewater treatment plants (Figs. 2, 3) indicate a dominance of the fraction containing a mobile and a biologically available phosphorus, i.e. the fraction obtained as a result of the extraction with the chelate reagents (Ca-EDTA-P and Na-EDTA-P fractions). The content of the general phosphorus Ca-EDTA-P fraction is the highest in comparison with the other phosphorus fractions for both investigated plants.

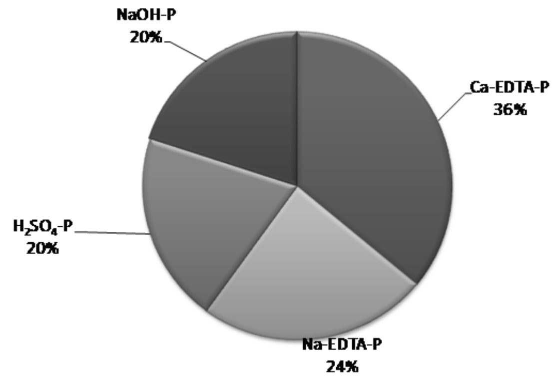

Fig. 2. The percentages of general phosphorus divided into fractions obtained by the Golterman method in the excess sludge coming from a wastewater treatment plant operated with the use of activated sludge

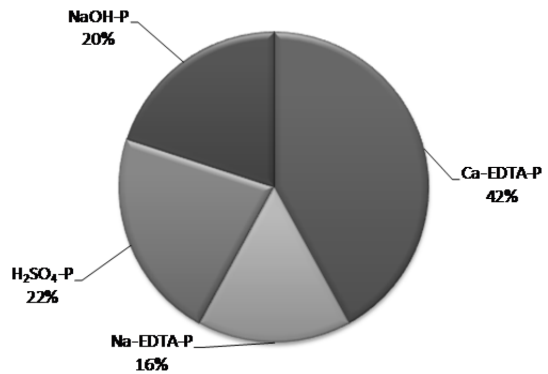

Fig. 3. The percentage of general phosphorus divided into fractions obtained by the Golterman method in the excess sludge coming from a wastewater treatment operated with the use of the EvU-Perl technology

The comparison of the phosphorus speciation by the two methods shows that in the case of the Williams method the content of mobile and bioavailable fractions is higher (70%) than in the Golterman method (ca. 60%). This fact can be explained by the changes in the solubility of phosphates after the introduction of the next extraction reagent in the Williams method, which changes the reaction. Therefore the Golterman method, in which the application of the extraction reagent does not change the reaction and the solubility of the phosphorus compounds, was chosen for further investigation.

4.3 THE EFFECT OF PHYSICOCHEMICAL FACTORS ON THE SPECIATION OF PHOSPHORUS IN THE EXCESS SLUDGE

The influence of oxygenation. The results of analysis of the oxygenation effect on the speciation of phosphorus marked as general phosphorus obtained by the Golterman method in the excess sludge (Fig. 4), coming from the wastewater treatment plant operated with the use of activated sludge, shows that as the agent's operating time increases, the content of the Ca-EDTA-P fraction also increases, however, the equilibrium is not established in the considered investigation time. The oxygenation of the excess sludge derived from the wastewater treatment plant causes also the decrease in the content of the Na-EDTA-P and H_2SO_4-P fractions. In the case of the NaOH-P fraction, the oxygenation does not result in significant changes in the content of phosphorus, defined as the general phosphorus.

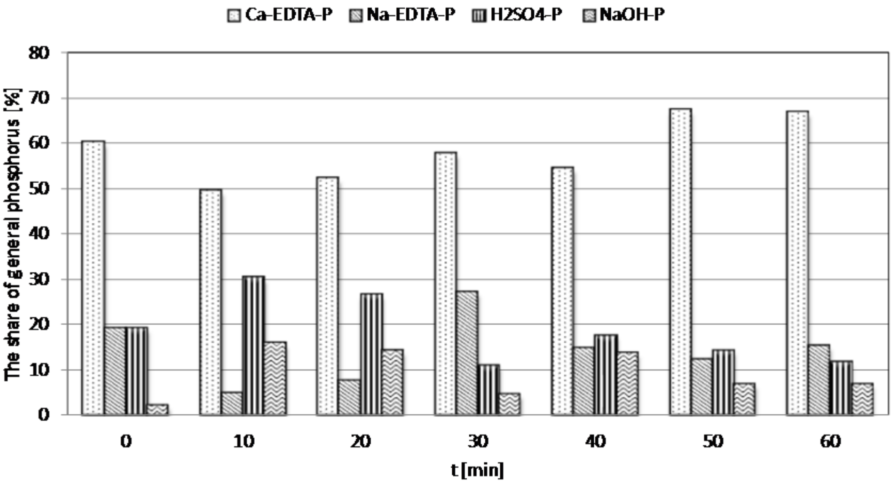

Fig. 4. The effect of oxygenation time on the content of phosphorus speciation forms marked as general phosphorus obtained by the Golterman method in excess sludge, coming from the wastewater treatment plant operated with the use of activated sludge

The results of the oxygenation effect on the speciation of general phosphorus obtained by the Golterman method in the excess sludge (Fig. 5), coming from wastewater treatment plant operated with the EvU-Perl technology indicate that as the oxygenation time increases, the content of phosphorus dominant fraction i.e. (Ca-EDTA-P) increases.

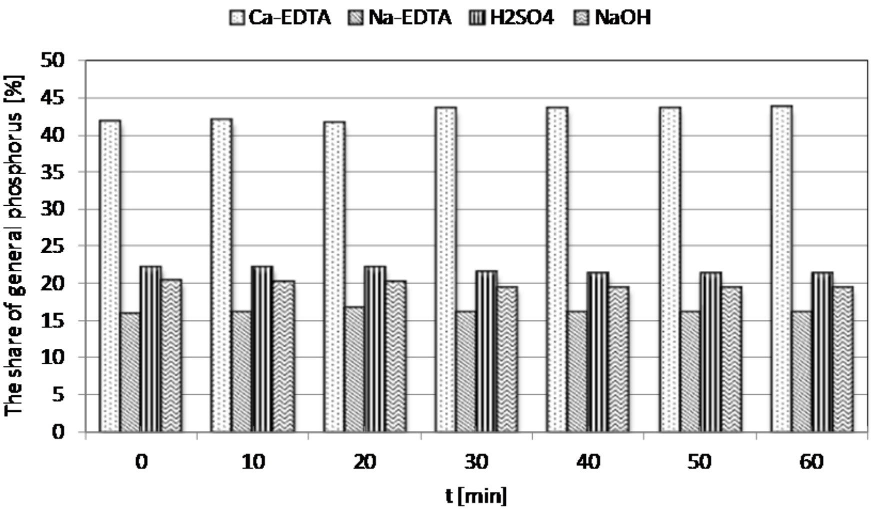

Fig. 5. The effect of oxygenation time on the content of phosphorus speciation forms marked as general phosphorus obtained by the Golterman method in the excess sludge, coming from the wastewater treatment plant operated with the use of the EvU-Perl technology

In the case of this fraction, the equilibrium in the system is established in approximately 30 min. The oxygenation of the excess sludge coming from this sewage treatment plant does not cause significant changes in the content of general phosphorus for the remaining fractions.

Influence of iron chloride as the precipitating agent. The application of the precipitating agent in the form of 0.3 M $FeCl_3$ solution for the duration of 0.5 to 80 minutes resulted in the increase of the Ca-EDTA-P fraction, i.e. a mobile and bioavailable one, in phosphorus defined as general phosphorus in the excess sludge (Fig. 6), coming from a plant operated with the use of activated sludge. As for other phosphorus fractions analyzed in this sludge, the content of phosphorus defined as general phosphorus slightly decreased.

The effect of the precipitating agent on general phosphorus speciation in the excess sludge (Fig. 7), coming from the wastewater treatment plant operated with the EvU-Perl technology indicates that as the contact time of 0.3 M solution of $FeCl_3$ is extended, the content of individual phosphorus fractions remains unchanged.

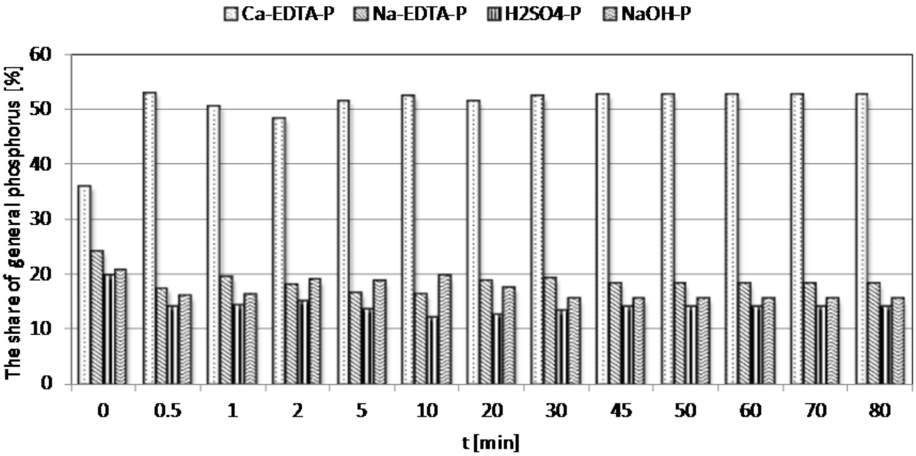

Fig. 6. The effect of contact time with the solution of 0.3 M $FeCl_3$ on the content of phosphorus speciation forms defined as general phosphorus obtained by the Golterman method in the excess sludge coming from the wastewater treatment plant operated with the use of activated sludge

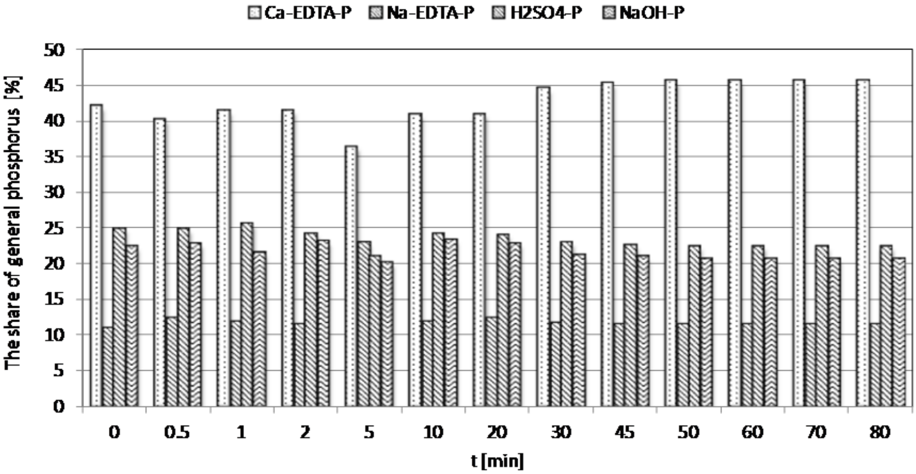

Fig. 7. The effect of the contact time with the solution of 0.3 M $FeCl_3$ on the content of phosphorus speciation forms defined as general phosphorus obtained by the Golterman method in the excess sludge coming from the wastewater treatment plant operated with the EvU-Perl technology

The effect of ultrasound treatment. The results of the sludge treatment by ultrasound on the general phosphorus speciation obtained by the Golterman method in the excess sludge (Fig. 8), coming from the plant operated with the use of activated sludge, indicates that this agent causes an increase in the content of the Ca-EDTA-P phosphorus fraction, with the system equilibrium being established already after

3 min of the agent's operation. The ultrasound treatment of the excess sludge coming from the wastewater treatment plant also causes a significant decrease in the H_2SO_4-P fraction. The increase in the mobile fractions content and the decrease in the content of phosphorus present in the soluble complexes with organic matter, can be explained by the characteristic effects of ultrasounds on living cells.

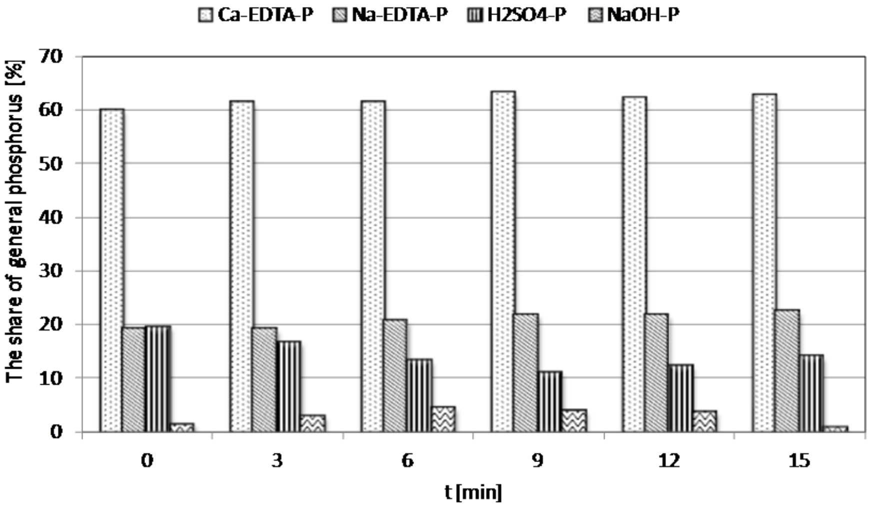

Fig. 8. The effect of the ultrasound treatment time on the content of phosphorus speciation forms defined as general phosphorus obtained by the Golterman method in the excess sludge, coming from the wastewater treatment plant operated with the use of activated sludge

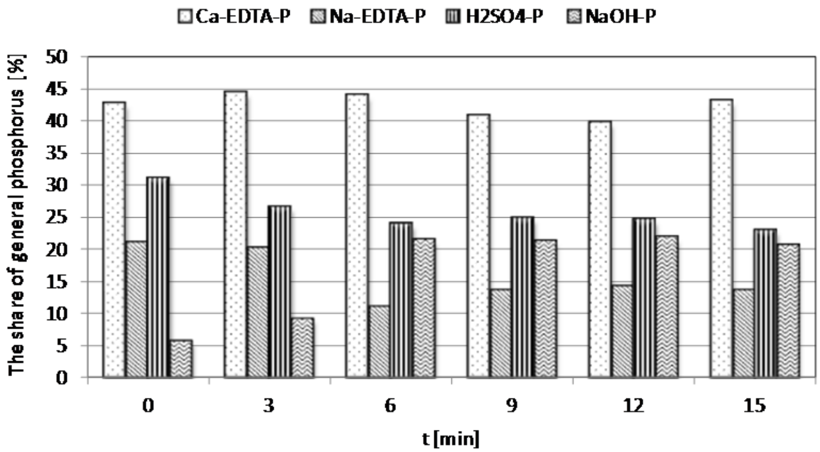

Fig. 9. The effect of the ultrasound treatment time on the content of phosphorus speciation forms defined as general phosphorus obtained by the Golterman method in the excess sludge, coming from the wastewater treatment plant operated with the use of the EvU-Perl technology

The results of the ultrasound treatment effect on the general phosphorus speciation by the Golterman method in the excess sludge (Fig. 9) coming from the wastewater treatment plant operated with the EvU-Perl technology indicate that as the time of the ultrasound treatment increases, the content of individual phosphorus fractions changes only to a small extent. The ultrasound treatment for the excess sludge coming from this wastewater treatment plant also causes a clear decrease in the content of general phosphorus for the Na-EDTA-P and NaOH-P fractions.

4.4. EFFECT OF SELECTED PHYSICOCHEMICAL FACTORS ON PHOSPHORUS SPECIATION

A multiple regression was performed in order to define the dependence between the phosphorus speciation in wastewater sludge (dependent variable) and the effect of such parameters as the presence of oxygen, ultrasound treatment, the presence of a precipitating agent (independent variable). Table 9 shows the values of factor coefficients determining the effect of given parameters on the phosphorus speciation.

Table 9

Factor coefficients determining the effect of a selected parameter on phosphorus speciation in excess sludge

Fraction	Oxygenation		Precipitating agent 0.3 M $FeCl_3$		Sludge ultrasound treatment	
	Activated sludge	EvU-Perl	Activated sludge	EvU-Perl	Activated sludge	EvU-Perl
Ca-EDTA-P	4.459	6.329	0.236	0.291	1.195	0.665
Na-EDTA-P	4.370	6.389	0.247	0.313	1.068	0.642
H_2SO_4-P	4.467	6.372	0.198	0.305	1.023	0.568
NaOH-P	4.452	6.345	0.211	0.274	1.017	0.526

To evaluate the effect of particular factors on the variations in various forms of speciation, certain factor coefficients (Table 9) using multiple regression were specified. The values of these factors indicate a significant impact of analyzed parameters. The data shows that oxygenation and ultrasound treatment have the greatest impact on the phosphorus speciation in the excess sludge, while the precipitating agent has a lesser effect on the phosphorus speciation. In the case of the excess sludge from the plant using the EvU-Perl fluidized biological bed, it is the oxygenation that has the greatest impact on the phosphorus speciation (cf. Table 9, the values of this coefficient).

5. SUMMARY

To sum up, it can be concluded, that depending on the variable parameters applied to excess sludge treatment and depending on the type of the applied wastewater treatment technology, both the forms of phosphorus speciation and their content become changed, which may affect the process of phosphorus recovery from wastewater sediment. According to the experimental results, it can also be stated that the excess sludge coming from the fluidized biological bed (EvU-Perl technology) is less sensitive to the influence of physicochemical factors.

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