Elżbieta BEZAK-MAZUR and Renata STOIŃSKA

SPECIATION OF PHOSPHORUS
IN WASTEWATER SEDIMENTS
FROM SELECTED WASTEWATER TREATMENT PLANT

Abstract: The aim of this work was to characterize wastewater sediments of various types of wastewater treatment plants in terms of the occurrence of forms of phosphorus speciation. The preliminary analysis of speciation using sequential extraction by Golterman was made.

It consists in using chelating reagents (Ca-EDTA and Na-EDTA) as well as NaOH and H2SO4 solutions. The quantitative measurement of phosphorus was carried out using spectrophotometric method according to binding rules. The number of individual fractions of phosphorus in wastewater sediments and the concentration of total phosphorus in treated and raw wastewater were examined. According to Golterman the phosphorus absorbed on the surface of sludge particles, so called mobile phosphorus, is a speciation form that is the most easily accessible for organisms. Preliminary results show that the significant participation of mobile phosphorus in wastewater sediments appeared in these wastewater treatment plants, where integrated methods of the wastewater treatment were applied (wastewater treatment plants mechanical-biological-chemical). The results obtained allow to conclude that, depending on the physico-chemical conditions in the various types of wastewater treatment plants, excess sludge shares have different forms of mobile phosphorus speciation, which may affect the recovery of this element from wastewater sediments.

Keywords: mobile phosphorous, wastewater sediments, speciation

Introduction

The growth of the standards of living, legal requirements posed to water treatment plants and the ecological education of the population cause an increasing amount of treated wastewater and the reduction of the amount of raw wastewater entering the environment [1]. This fact is beneficial in terms of the present water and wastewater management. However, the amount of wastewater sediments increases with the
emergence of modern, high-qualified water treatment technologies. Wastewater sediments need to be well managed, because they are the source of many nutrients [2]. Phosphorus, which is one of them, is a major macro element that is necessary for the proper functioning of every cell. First of all phosphorous is a nucleic acid component and a high-energy bond component contained in the molecule of adenosine triphosphate (ATP), which is the primary source of energy for all biochemical reactions occurring in the living body [3]. The form of its occurrence in wastewater should be paid attention to because of the importance of this element to the environment [4]. Knowledge of the occurrence forms of phosphorus in wastewater sediments is important for understanding the bioavailability and mobility of this element in the soil [5, 6].

Speciation analysis determines the amount of phosphorous available to plants. This analysis is based on the procedures which permit the identification of the root forms and their quantitative determination of the examined object [7, 8]. According to the literature, several methods of speciation of phosphorus are known, where the sequential extraction is used [9]. Golterman method is one of them and originally it was used to analyze the speciation of elements in soils and sediments [9, 10] and also it has been used for the analysis of wastewater sediments in recent years [11]. This method involves the usage of chelating reagents (Na-EDTA and Ca-EDTA) sulfuric acid and sodium hydroxide solutions in the analysis. The use of chelating reagents allowed to shorten the time of the sequential analysis and prevented the change of the pH-value and thus the hydrolysis and dissolution of the phosphate. The extraction solvent combination allowed to isolate the phosphorus inorganic form (extracted using chelating reagents) and organic forms (extracted with solutions of NaOH and H₂SO₄). The author of the presented method has concluded that the greatest speciation bioavailability form is phosphorus adsorbed on the surface of the sediments particles, such as the fraction Ca-EDTA-P and fraction Na-EDTA-P [10, 12].

Table 1

<table>
<thead>
<tr>
<th>Stage</th>
<th>Type of extractant and extraction conditions</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05 M Ca-EDTA, 4 h</td>
<td>Ca-EDTA-P</td>
</tr>
<tr>
<td></td>
<td>Phosphorus – associated with iron, aluminum and manganese oxides and hydroxyoxides</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.1 M Na-EDTA, 18 h</td>
<td>Na-EDTA-P</td>
</tr>
<tr>
<td></td>
<td>Phosphorus – associated with carbonates</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.5 M H₂SO₄, 2 h</td>
<td>H₂SO₄-P</td>
</tr>
<tr>
<td></td>
<td>Phosphorus presented with the soluble organic matter connection</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2 M NaOH, 2 h</td>
<td>NaOH-P</td>
</tr>
<tr>
<td></td>
<td>Remaining phosphorus in the association with aluminosilicates and contained in the form of organic matter undergoing no influence of sulfuric acid in stage 3</td>
<td></td>
</tr>
</tbody>
</table>
The content of inorganic phosphorus in sediments was estimated in range from 15 to 80% of $P_{\text{org}}$ [13]. According to other authors inorganic phosphorus content in wastewater sediments is considerably higher than the content of organic phosphorus [4, 14]. The aim of our work is to determine how the quantity of phosphorus speciation profile forms (in particular the bioavailable form) in wastewater sediments depending on their method of wastewater treatment.

Physical, biological or chemical methods are used for the phosphorus removal in wastewater treatment plants. The integrated wastewater treatment methods are used in modern wastewater treatment plants [15]. The biological method relies largely on the use of the ability of certain bacteria (for example of the genus Acinetobacter, Pseudomonas) to the enhanced retrieval of phosphate in the biochemical processes [16, 17]. Anaerobic or aerobic conditions are alternately applied to select and enable the development of specific cultures of bacteria [13, 18]. Chemical methods rely on precipitation of phosphates while using reagents such as precipitating ions of iron, aluminum or calcium [19]. The dephosphatation process causes the transition of the phosphorus in the form of intracellular polyphosphate (biological treatment) or in the form of sparingly soluble salts (chemical treatment) to the wastewater sediments [12].

The removal of biogenes in the process of biological wastewater treatment is strictly correlated with the amount and the metabolic activity of the microorganisms as well as with other factors like temperature [20], pH-value and the age of the sediment, the content of the nutritive substances and the oxygen [21]. The temperature of the surroundings is a significant parameter which influences the biological wastewater treatment because the bacteria involved in the reduction of the contamination develop only in an accurate range of temperature [22]. A substantial part of the population of the bacteria which appear in the wastewater sediments is constituted by the mesophiles, which develop in medium temperatures, that is in such a range of temperatures where the minimal temperature amounts to about 10 °C and the maximum temperature amounts to 45 °C. Parasitic microorganisms and a substantial part of saprophytes belong to this group of bacteria. The optimum of the growth ranges, according to the kind of bacteria, from 20 to 40 °C. Łomotowski and Szpindor [14, 22] present the influence of the temperature on the intensity of the biochemical processes in the wastewaters in the form of the exponential function equation:

$$k(t) = k_{20} \exp[K(t - 20)]$$

where: $k(t)$ – the constant of the biochemical processes speed in temperature $t$, °C;
$k_{20}$ – the constant of the speed in temperature 20 °C;
$K$ – temperature constant, °C$^{-1}$.

The biological processes connected with the phosphorus removal are considered to be less sensitive to temperature changes. It is associated with the metabolism of the psychrophilic bacteria (which are responsible for the reduction of phosphorus in the wastewaters) developing in the lower temperatures that other organisms. The optimal temperature in the dephosphatation processes is included within the range from 10 to 15 °C. However, literature signals that during winter the temperature of the sediments in
the open containers may amount to 5 °C. The metabolic activity of the phosphoric bacteria slows down which results in decrease of the intensity of the enzymatic hydrolysis process. Then, together with the decrease of the sediment temperature, the speed of the endogenous decomposition of organic compounds is reduced which causes the increase of organic substance in the activated sludge [23].

**Material and methods**

The study was performed on the wastewater (raw and treated) and the excess sediment derived from the three wastewater treatment plant such as:

– Radoszyce – which applies mechanical and biological treatment; biological treatment is based on a three-phase activated sludge method (with separate zones: anaerobic and aerobic oxygenated).

– Barcza – where a mechanical-biological and chemical treatment is used. The technology is a combination of the three-phase method of activated sludge and revolved biological field methods. Biological phosphorus removal process is aided by chemical precipitation process coagulant PIX.

– Bartkow – where a mechanical-biological and chemical treatment is used. The biological treatment of sewage sludge phase method and the chemical treatment is carried out by means of the precipitating agent which is calcium.

The content of phosphorous fraction in collected excess sludge samples was specified by means of the fractionation scheme proposed by Golterman [12, 24]. The first stage constituted extraction with solution of Ca-EDTA for a period of 4 hours. In the second stage, the samples were extracted for 18 hours with a solution Na-EDTA. The next stage was the extraction of the sample for the period of 2 hours with a solution of H2SO4. The final stage also lasted 2 hours and NaOH solution was used for the extraction. Every sample was filtered after each extraction stage and the precipitate remaining after filtration was treated with the following reagents in the order of extraction. The concentration of orthophosphate and total phosphorus was measured in obtained filtrate. Spectrophotometric method was used to determine the concentration of phosphorous in wastewater and in sediments extractions. Marcel Media UV/VIS Spectrophotometer was employed. These measurements were repeated in three series and held in accordance to the determination of orthophosphate with blue phosphate – molybdenum and with the determination of total phosphorous after oxidation of the sample with potassium persulphate(VI) solution [25]. The research was repeated in three series in one-year cycle, where average temperatures during the sample collection in spring, summer, autumn and winter amounted to respectively 16 °C, 25 °C, 8 °C, –2 °C.

**Results and discussion**

The obtained results of phosphorus concentration in the treated and raw wastewaters lead to a conclusion that the highest degree of the removal of the element from selected objects was found in wastewater treatment plants Barcza and Bartkow (Fig. 1).
The percentage of total phosphorus in the wastewater in wastewater treatment plant in Barcza in one-year cycle is almost constant and equaled about 90%. In the case of wastewater treatment plant in Bartkow in the period of spring, summer and autumn the percentage of total phosphorus removal in the wastewater was also high and fluctuated around 90%, while in winter it dropped distinctly and amounted to 66%. The lowest percentage of total phosphorus removal was observed in the wastewater treatment plant in Radoszyce. The highest percentage of the removal in this object was observed in autumn and winter and fluctuated around 39%. The above mentioned results which
show the degree of phosphorus reduction in the wastewater can be linked to phosphorus efficiency of the process conditions in the wastewater treatment plant. It can be concluded that the more extensive the combination of wastewater treatment systems is the bigger the percentage of phosphorus reduction in the wastewater is.

The analysis of the results of phosphorus speciation marked as total phosphorus in a one-year cycle in the excess sediment from the wastewater treatment plant in Bartkow shows that in the spring-autumn period dominated the bioavailable fractions (Ca-EDTA and Na-EDTA), while in the autumn-winter period the shares of these fractions were reduced together with the drop of temperature of the surroundings. The dominating total phosphorus fractions in the autumn-winter period were H₂SO₄ and NaOH fractions, that is the organic phosphorus fractions (Fig. 2). Such a reversal of proportions between the shares of easily and not easily bioavailable phosphorus forms may result from the inhibition of biochemical processes of the microorganisms during winter, caused by the drop of temperature of their surroundings. The shares of the organic phosphorus forms are increased.

Similar results of the analysis may be observed in case of the excess sediments from the wastewater treatment plant in Barcza (Fig. 3) and in Radoszyce (Fig. 4) In the spring-summer period the bioavailable fractions (Ca-EDTA and Na-EDTA) were dominating, while in the autumn-winter period the organic phosphorus fractions (H₂SO₄ and NaOH) dominated. Despite the fact that each of the three wastewater treatment plants carries out the clearance of the wastewater on different levels of integrating the methods, the shares of the phosphorus fractions in the excess sediments from these wastewater treatment plants changes by analogy in a one-year cycle.

Then, it can be stated that together with the drop of temperature of the surroundings of the microorganisms, the metabolic activity of the phosphoric bacteria also slows down, which results in the intensity of the enzymatic hydrolysis decreases. In this
connection, the drop of temperature of the sediment causes the reduction of the endogenous decomposition speed of the organic compounds, which causes the increase of the organic substance in the wastewater sediment.

The analysis of the results (Fig. 5) also showed that bigger disproportions between the shares of the bioavailable phosphorus forms in one-years cycle can be notices in the wastewater sediments from the wastewater treatment plants where the integrated methods of the wastewater treatment (mechanical-biological-chemical) are used. In case of the sediment from the wastewater treatment plant in Bartkow the sum of the percent
share of Ca-EDTA and Na-EDTA fractions amounted to in spring and summer 60 % and 79 % respectively, whereas in autumn and winter 12 % and 8 % respectively.

The drastic reduction of shares of the bioavailable forms in one-year cycle could be noticed also in the examined sediments from the wastewater treatment plant in Barcza. In the excess sludge from this wastewater treatment plant in spring and summer the total share of the bioavailable phosphorus forms amounted to 59 % and 78 % respectively, while the shares of these forms in autumn and winter equaled 7 % and 6 % respectively.

In case of the sediment from a mechanical-biological wastewater treatment plant in Radoszyce the sum of the percent share of the Ca-EDTA and Na-EDTA amounted to respectively 58 % and 55 % in spring and summer, while in autumn and winter equaled 29 % and 27 % respectively.

The statistic evaluation of the results of the phosphorus contents marking in the sediments expressed as total phosphorus, divided into fractions, obtained by means of the Goltermann method was based on the linear regression.

\[ y = a \cdot x + b \]

where: \( y \) – dependent variable (the speciation of phosphorus in the wastewater sediments),
\( x \) – independent variable (the influence of the factor – air temperature),
\( a, b \) – parameters of the model,

In order to check the correctness of the model, the determination coefficients \( R^2 \) were determined. They describe what percent of the total data changeability is explained by the admitted model (Table 2). In course of testing the significance of the regression coefficients, the F-Snedecor test was applied. The statistic program R was used for the computations. On the basis of the data the statistically relevant influence of the air temperature on the change of the share of the \( \text{H}_2\text{SO}_4 \) fraction in the sediment from the wastewater treatment plant in Bartkow and Barcza was shown as well as statistically significant influence of the air temperature on the change of the share of the \( \text{NaOH} \) fraction in the wastewater treatment plant in Radoszyce.

<table>
<thead>
<tr>
<th>Wastewater Treatment Plant</th>
<th>Bartkow</th>
<th>Barcza</th>
<th>Radoszyce</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca-EDTA</td>
<td>0.79</td>
<td>0.64</td>
<td>0.27</td>
</tr>
<tr>
<td>Na-EDTA</td>
<td>0.72</td>
<td>0.88</td>
<td>0.85</td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_4 )</td>
<td>0.93</td>
<td>0.93</td>
<td>0.20</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.84</td>
<td>0.81</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Together with the drop of the temperature, the phosphorus \( \text{H}_2\text{SO}_4 \) fraction shares in the case of the excess sludge from the mechanical-biological-chemical wastewater...
treatment plants (Fig. 6 and Fig. 7) and the shares of phosphorus NaOH fraction in the case of the sediment from the mechanical-biological wastewater treatment plant increase (Fig. 8).

Fig. 6. Influence of the air temperature on the change of the share of the $\text{H}_2\text{SO}_4$ fraction of phosphorus in the sediment from the wastewater treatment plant in Bartkow

Fig. 7. Influence of the air temperature on the change of the share of the $\text{H}_2\text{SO}_4$ fraction of phosphorus in the sediment from the wastewater treatment plant in Barcza
Conclusions

The analysis of the research results allows to state that:

– The shares of the phosphorus forms in the excess sludge change in one-year cycle according to the climatic conditions (the temperature of the surrounding). The dominating phosphorus factions in the spring-summer period were the fractions containing the mobile phosphorus and the bioavailable phosphorus, that is fractions obtained after the extraction by means of chelating reagents in comparison to the fractions containing the organic phosphorus i.e. the forms not available for plants.

– According to the present technological conditions in the particular wastewater treatment plants, the examined excess sludges are characterized by opposite shares of the speciation forms of phosphorus. In the sediments from wastewater treatment plants with integrated mechanical-biological-chemical methods of wastewater treatment, it is easy to notice bigger differences between the shares of the phosphorus forms easily and not easily available for plants in one-year cycle than in the sediments from the mechanical-biological wastewater treatment plant

The knowledge of the quantitative shares of the mobile phosphorus fractions according to the type of the applied technology of the wastewater treatment and the assumption of the cyclic changes of the phosphorus fraction shares may influence the process of its retrieval from the wastewater sediments. Thanks to the speciation analysis of this element in the wastewater sediments, the amount of the contained bioavailable (in other words: mobile, susceptible to migration in the soil-water environment) phosphorus can be estimated.

Fig. 8. Influence of the air temperature on the change of the share of the H_2SO_4 fraction of phosphorus in the sediment from the wastewater treatment plant in Radoszyce
References


SPECJACJA FOSFORU W OSADACH ŚCIEKOWYCH
Z WYBRANYCH Oczyszczalni Ścieków

Katedra Inżynierii i Ochrony Środowiska, Wydział Inżynierii Środowiska, Geomatyki i Energetyki Politechnika Świętokrzyska w Kielcach

Abstrakt: Celem pracy było scharakteryzowanie osadów ściekowych pochodzących z różnych typów oczyszczalni ścieków komunalnych pod względem występowania form specyficznych fosforu. Przeprowadzono...
wstępną analizę specyfikacyjną z wykorzystaniem ekstrakcji sekwencyjnej według Goltermana. Polega ona na wykorzystaniu odczynników chelatowych (Ca-EDTA i Na-EDTA) oraz roztworów NaOH i H2SO4. Pomiar ilości fosforu odbył się metodą spektrofotometryczną zgodnie z obowiązującymi normami. Wykorzystując powyższą metodę, zbadano ilości poszczególnych frakcji fosforu w osadach ścieków w osadach ścieków oraz stężenie fosforu ogólnego w ściekach oczyszczonych i surowych. Według Goltermana formą specyfikacyjną o największej доступności dla organizmów żywych jest fosfor zaadsorbowany na powierzchni cząstek osadów, czyli tak zwany fosfor mobilny. Wstępne wyniki wskazują, iż znaczny udział fosforu mobilnego w osadach ścieków występował w tych oczyszczalniach, gdzie stosowano zintegrowane metody oczyszczania ścieków (oczyszczalnie mechaniczno-biologiczno-chemiczne). Uzyskane rezultaty upoważniają do stwierdzenia, że w zależności od warunków fizyczno-chemicznych występujących w poszczególnych typach oczyszczalni ścieków, osady nadmierne charakteryzują się różnymi udziałami formy specyfikacyjnej fosforu mobilnego, co może wpływać na odzyskiwanie tego pierwiastka z osadów ścieków.

**Słowa kluczowe:** fosfor mobilny, osady ściekowe, specyfikacja