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# GENERATION AND MANAGEMENT OF WASTEWATER FROM GROUND WATER TREATMENT

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**Keywords**: Water treatment, iron sludge, orthophosphates removal, sludge liquor.

**Abstract**: Use of various wastes containing iron or aluminium in wastewater treatment can be considered as an alternative method to expensive and commercial reagents. These wastes can be recycled thanks to this method, which is important from an environmental point of view. Washings generated during ground water treatment are rather useless but they are one of waste iron sources. The article demonstrates a description of two ground water treatment plants supplying the city of Koszalin with drinking water. On the basis of data from the last four years, a balance of the annual amount of iron sludge formed as a result of backwashing filter beds in both plants was performed. The amount of waste iron exceeds 10 Mg $Fe \cdot year^{-1}$. Research on waste iron usage to remove orthophosphates from a model solution and real sludge liquor from sludge digestion showed that iron sludge from washings can be efficiently used in wastewater treatment technology.

## INTRODUCTION

Wastes generated during production processes containing different forms of iron and aluminium are more and more attractive alternative to commercial reagents. In water and wastewater treatment technology, research is conducted on such diverse materials as: fly-ash [3], blast-furnace slag [7], red mud from bauxite refining [8], used alum precipitate [6], aluminium and iron wastes [4], iron deposits from hydrometallurgy processes [5], wastes from the mineral processing industry [22] and also natural zeolites modified by iron [1], and wastes from titanium white production from which a PIX coagulant – ferric sulfate (popular in Poland) is produced.

Recycling of iron and aluminium compounds is commonly used in the case of coagulation sludge from surface water treatment. Coagulants obtained in this way decrease the operating costs of the treatment plant. They can be also used to remove phosphorus from wastewater applying adsorption or chemical precipitation. Research on removing phosphorus during filtration performed on sludge containing 46% of aluminium (as $Al_2O_3$) showed that efficiency might vary between 30 and 90% depending on load (3.9–16.5 $g\ P \cdot m^{-2} \cdot d^{-1}$) and pH of solution. Adsorption ran more effectively when pH was decreasing. Together with pH decrease adsorption capacity was increasing (at pH = 4 capacity amounted to 4.52 $mg\ P \cdot g^{-1}$ and at pH = 9.0 capacity was of 1.74 $mg\ P \cdot g^{-1}$) [2, 13, 21].

Ground water treatment plants are also a source of wastes containing iron. Iron and manganese ions are main pollutants of ground water. They are oxidized and precipitated as hydroxides during treatment. During filter backwashing, washings are formed in an amount ranging between 2–5% of the total treated water amount in which the content of iron oxides may even reach 80–90% of solid phase [16, 17]. Research indicates that iron and aluminium sludge can be used in preliminary treatment to remove organic substances and suspension from wastewater during activated sludge process (sludge bulking control), during sludge fermentation, and to improve sludge dewatering properties [20].

In practice sludge generated during ground water treatment is not used. It is arduous waste because it must be periodically removed from the decanter which, in Poland, is the most frequently used means to store washings. Sedimented sludge is carried away to a wastewater treatment plant or pumped into the urban sewage system. In many countries research on possible uses of waste containing iron have been conducted. In Germany 40000 $Mg_{D.M}\cdot year^{-1}$ of iron sludge is generated during water treatment [10], whereas research conducted in the Netherlands showed that 5000 Mg of Fe may be obtained from the 12500 $Mg\cdot year^{-1}$ hydrated iron sludge generated during water treatment. This iron may successfully replace commercial coagulants. The annual demand for iron used in wastewater treatment processes in this country amounts to 15000 Mg and it could partly be satisfied by waste iron [18]. Use of iron sludge from water treatment without any processing is simple and cheap; however, this form of sludge is suitable only for a limited range of utilization methods. A large amount of research indicates that only acid treatment of iron sludge could be an alternative to commercial iron salts [14, 19].

On the basis of the two ground water treatment plants supplying the city of Koszalin with drinking water, this article describes the generation of washings, the balance of waste iron that can be recovered from washings and possibilities of using iron sludge to remove phosphate compounds from a model solution and from actual sludge liquor.

## WASHINGS GENERATED DURING WATER TREATMENT

Koszalin is supplied with drinking water from two ground water intakes equipped with water treatment plants: in Koszalin and in Mostowo (20 km from Koszalin). Currently both plants operate below their maximum capabilities due to a decrease in the amount of water taken by inhabitants in recent years. The water permit for WTP-Koszalin allows a maximum water intake of 19200 $m^3\cdot d^{-1}$, whereas for WTP-Mostowo it is 54000 $m^3\cdot d^{-1}$. During the last four years the total daily amount of treated water decreased in both plants by 23%.

Water taken from both intakes has good quality in general but its chemical parameters are diverse. Iron and manganese concentrations in water from Koszalin intake are several times higher (2.50 mg $Fe\cdot dm^{-3}$ and 0.30 mg $Mn\cdot dm^{-3}$) than their concentrations in Mostowo intake (0.40 mg $Fe\cdot dm^{-3}$ and 0.13 mg $Mn\cdot dm^{-3}$).

Both technological systems are mainly based on the removal of iron and manganese compounds from water during aeration and gravity filtration. The plants are equipped with an installation for the disinfection of the water with sodium hypochlorite currently not being used. In WTP-Koszalin there is a two-stage rapid filter system: 1$^{st}$-stage deironing filters, 2$^{nd}$-stage demanganization filters. Each deironing filter bed is backwashed with air and water every 24 hours while the demanganization filter bed every 260 hours. The washings are directed to the clarifier and iron sludge is removed and transported to the municipal wastewater treatment plant once a month.

In WTP-Mostowo iron and manganese are removed from raw water in a one-stage process. Filtration is conducted on two-layer filters – deironing occurs on the upper layer while demanganization runs on the lower one. Backwashing of the filter beds is performed every 72 hours. Washings are directed to a clarifier. The physical and chemical parameters (iron, total suspended solids and sulfates' analysis) of the supernatant liquid are under continuous control, and that water is discharged to a nearby pond, whereas the precipitated sludge is stored in a sludge tank and transported to the municipal wastewater treatment plant every few weeks.

In WTP-Koszalin, 17570 $m^3$ of washings are generated monthly (average value of 4 recent years), however WTP-Mostowo generates 10230 $m^3$ (Fig. 1). In comparison to the amount of treated water, the amount of washings in WTP-Koszalin is of 5.2 to 7.0%, whereas in WTP-Mostowo washings range from 1.7 to 3.1% (Fig. 2). The significantly lower amount of wastewater observed in WTP-Mostowo results from the characteristic of raw water, the lower amount of iron compared to the Koszalin intake and resulting treatment technology – longer filter runs in WTP-Mostowo.

On the basis of the analyses of the amount and quality of treated water in recent four years, a balance of the iron waste amount in tested water treatment plants was performed (Tab. 1). A reduced assumption was adopted that the iron amount in washings is the difference in iron concentration in raw and treated water.

When comparing the iron amount that is sent with raw water to the treatment system and is removed with washings to decanters, it was calculated that 8466 kg Fe·year$^{-1}$ is generated in WTP-Koszalin and 1890 kg Fe·year$^{-1}$ in WTP-Mostowo. It yields over 10 Mg of iron in the form of iron hydroxides sludge in total per year (Fig. 3).

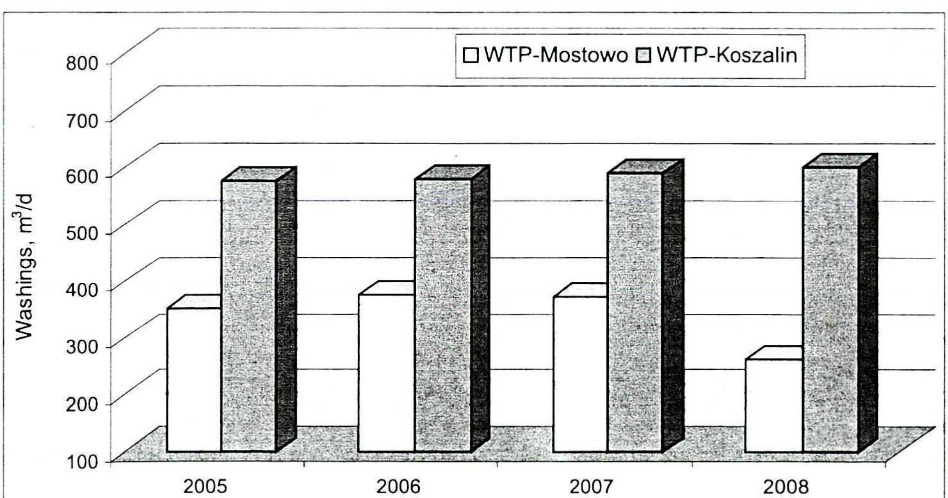


Fig. 1. Average amount of washings in WTP-Koszalin and WTP-Mostowo in 2005–2008

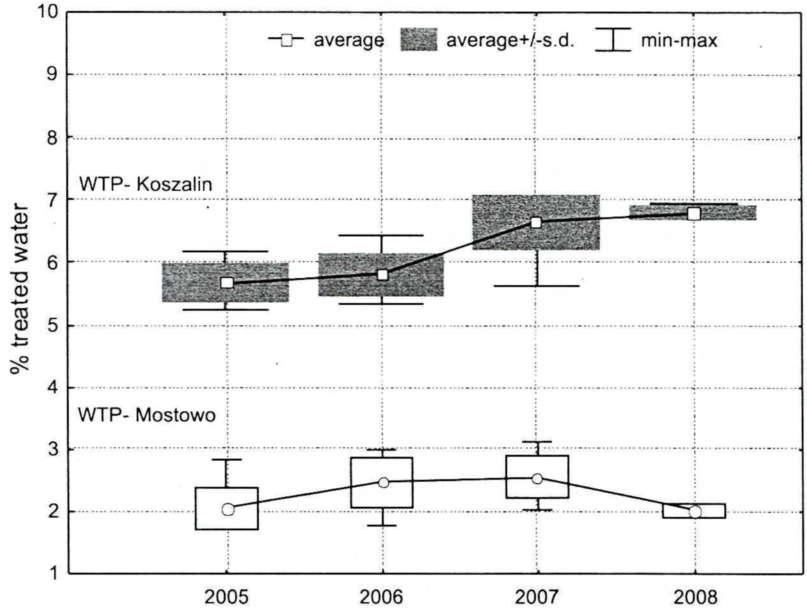


Fig. 2. Percentage of washings compared to total amount of treated water

Table 1. Balance of waste iron in washings of ground water treatment plants in Koszalin and Mostowo (C – concentration, L – load)

| Parameter | Unit | WTP-Koszalin | WTP-Mostowo |
|---|---|---|---|
| Amount of raw water | [$m^3 \cdot year^{-1}$] | 3400000 | 5400000 |
| $C_{Fe}$ in raw water | [$g \cdot m^{-3}$] | 2.50 | 0.40 |
| $L_{Fe}$ in raw water | [kg $Fe \cdot year^{-1}$] | 8500 | 2160 |
| $C_{Fe}$ in treated water | [$g \cdot m^{3}$] | 0.01 | 0.05 |
| $L_{Fe}$ in treated water | [kg $Fe \cdot year^{-1}$] | 34 | 270 |
| Amount of washings | [$m^3 \cdot year^{-1}$] | 210000 | 123000 |
| $C_{Fe}$ in washings | [$g \cdot m^{-3}$] | 40.31 | 15.37 |
| $L_{Fe}$ in washings | [kg $Fe \cdot year^{-1}$] | 8466 | 1890 |

This sludge is not further used in any way and it is an inconvenient waste that is periodically transported to a wastewater treatment plant. This was the reason why laboratory tests were carried out in order to determine possible uses of waste iron from WTP-Koszalin to remove orthophosphates from a model solution and from real sludge liquor.

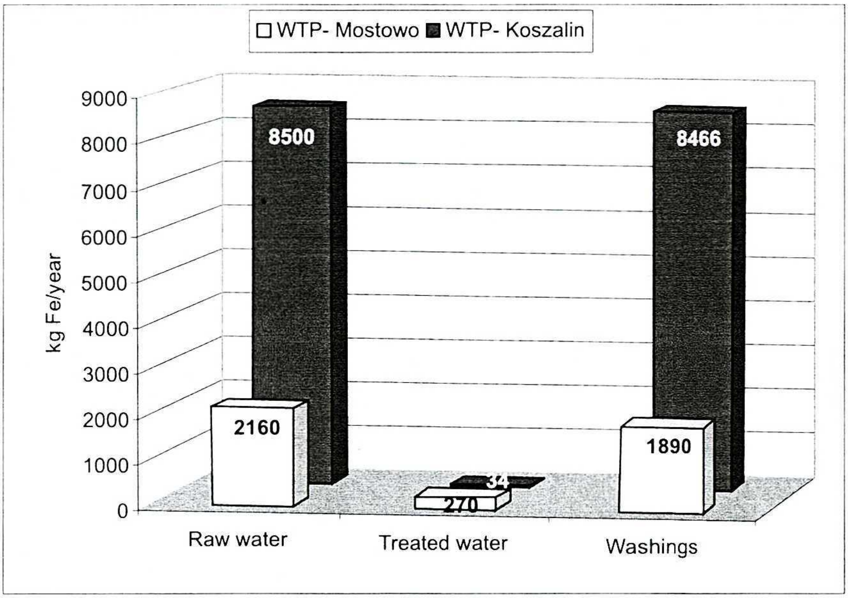


Fig. 3. Average amount of iron in raw water, treated water and washings in tested plants

## EXPERIMENTAL PROCEDURES

Research was carried out on iron sludge obtained from washings the deironing filter beds of the water treatment plant in Koszalin. Sludge taken from the decanter was dried at room temperature; next it was sifted on sieves with a mesh diameter of 0.75 mm to remove filter bed grains. The total iron content amounted to 600 mg $Fe \cdot g^{-1}$ of air-dried sludge.

Research was conducted under static conditions with a model solution of $KH_2PO_4$ with a concentration range from 13.4 to 114 mg $P \cdot dm^{-3}$. The pH was controlled with HCl and NaOH solutions. Kinetics of removing orthophosphates was performed at initial concentrations of 25, 50 and 100 mg $P \cdot dm^{-3}$ and waste iron to phosphorus ratio Fe:P = 20:1. Samples were mixed in shaker in 250 $cm^3$ conical flasks (200 $rev \cdot min^{-1}$) during 0–24 h, and they were then centrifuged (12000 $rev \cdot min^{-1}$, t = 5 min), and the concentration of $PO_4^{3-}$ ions determined. After kinetics determination, the influence of independent variables, such as the initial concentration of orthophosphates and Fe:P ratio, was analyzed. The final concentration of orthophosphates and percentage of removal of orthophosphates were output variables. Verification of the results was conducted with sludge liquid taken from the "Jamno" wastewater treatment plant in Koszalin (after sludge digestion). The concentration of orthophosphates in sludge liquor ranged from 12 to 124 mg $P \cdot dm^{-3}$. Analyses were made after centrifuging.

## DISCUSSION OF RESULTS

Research on the kinetics of adsorption of $PO_4^{3-}$ ions from the model solution was carried out at a constant dose of iron sludge and different initial concentrations of orthophosphates (Fig. 4). With regard to the high intensity of the process during early hours, an optimal time of 3 hours was established. The effectiveness of removing orthophosphates ranged from 28 to 41% with an upward trend observed when the initial concentration of $PO_4^{-3}$ ions was increased. Extension of the contact time of the model solution with iron sludge to 24 hours did not significantly influence process effectiveness (3–5% increase).

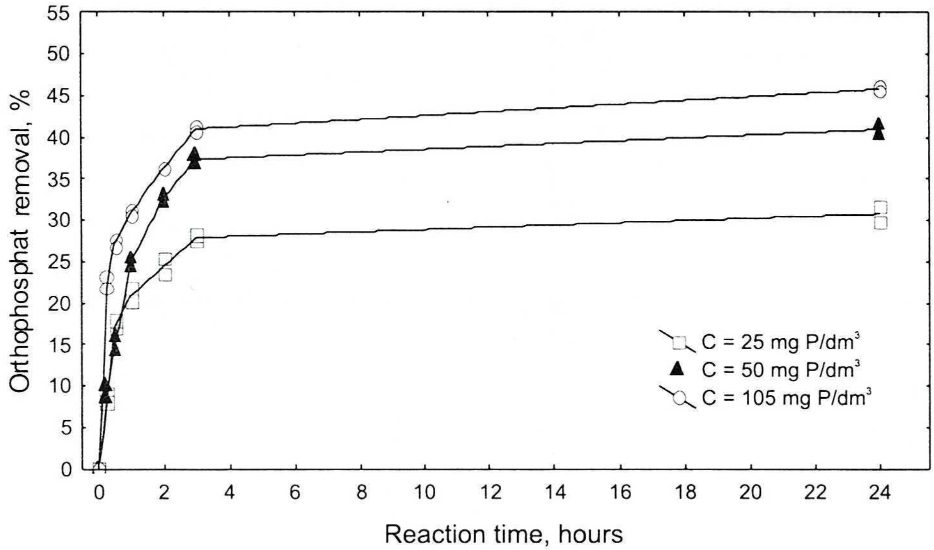


Fig. 4. Influence of reaction time on percentage effectiveness of removing orthophosphates, Fe:P = 20:1, pH ≈ 7

Research on the influence of the iron sludge dose (Fe:P ratio) and the initial concentration of orthophosphates on the effectiveness of their removal were conducted at assumed optimal contact time (Tab. 2). The Fe:P ratio and initial concentration were independent variables in tests, whereas the percentage removal of orthophosphate ions was a dependent (output) variable. The relationship between independent variables and the dependent variable was analyzed applying approximation relative to the central point. A characteristic feature of the central point method is that the calculated approximation curves for a given dependent variable always run through one common point of intersection assuming that analyzed independent variables do not interact with each other.

Independent variables:

$x_1 = S$ – Fe:P ratio

$x_2 = C$ – initial concentration [mg P·dm$^{-3}$]

Dependent (output) variables:

$y_1 = R$ – removal of orthophosphates [%]

Table 2. Results of research on removing orthophosphates with iron sludge at diverse initial concentrations and Fe:P ratio values

| Fe:P | Concentration of orthophosphates [mg P·dm$^{-3}$] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C = 114.0 | | C = 84.5 | | C = 50.0 | | C = 34.0 | | C = 25.0 | | C = 13.4 | |
| 2:1 | 104.23 | 102.31 | 73.27 | 72.84 | 45.22 | 45.74 | 29.92 | 30.36 | 23.03 | 22.60 | 11.82 | 12.01 |
| 5:1 | 91.69 | 94.83 | 67.12 | 66.18 | 41.59 | 42.09 | 27.45 | 26.94 | 20.95 | 20.50 | 11.25 | 11.00 |
| 10:1 | 81.21 | 82.67 | 56.06 | 58.61 | 37.34 | 36.96 | 25.04 | 24.85 | 19.55 | 19.12 | 10.60 | 10.31 |
| 20:1 | 63.72 | 65.72 | 48.43 | 47.95 | 32.03 | 30.58 | 22.05 | 21.76 | 17.09 | 17.35 | 9.68 | 9.50 |
| 30:1 | 50.10 | 51.22 | 40.02 | 38.23 | 26.20 | 27.25 | 20.56 | 20.32 | 16.20 | 16.07 | 9.38 | 9.40 |

The influence of the Fe:P ratio on percentage removal of orthophosphates is shown in Figure 5. Obtaining 25% removal of orthophosphates was observed at Fe:P = 10:1, whereas an increase of removal up to 46% required higher iron amount reaching Fe:P = 30:1. The effectiveness of removing orthophosphates improved together with an increase in initial concentration of $PO_4^{3-}$ ions (Fig. 6).

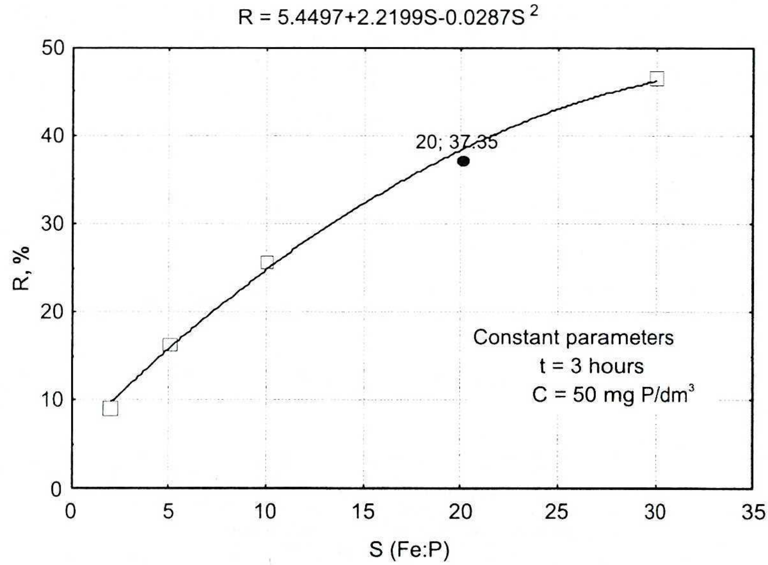


Fig. 5. Influence of Fe:P ratio (S) on average percentage removal of orthophosphates from model solution (R), pH ≈ 7

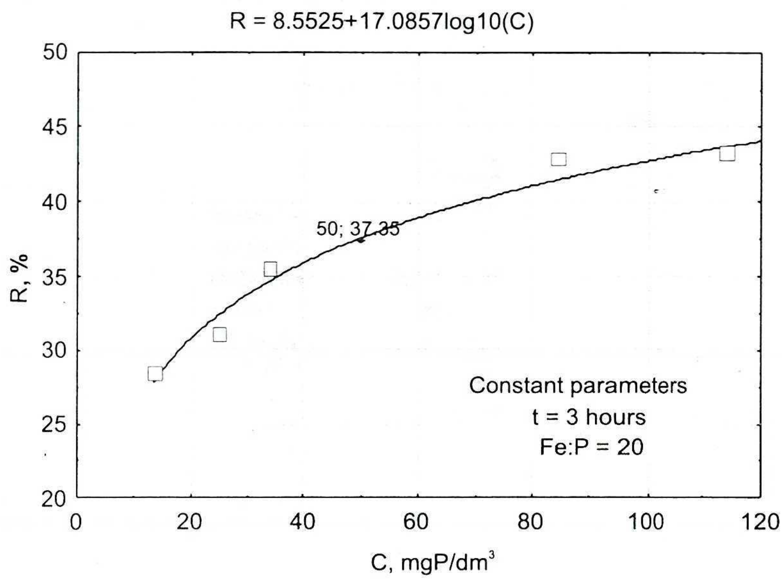


Fig. 6. Influence of initial concentration of orthophosphates (C) on average percentage removal of orthophosphates from model solution (R), pH ≈ 7

Obtained relationships were approximated using the central point method and the resulting equation (relationship in Fig. 5) at first stage approximation is shown below:

$$R_s(S) = 5.4497 + 2.2199 \cdot S - 0.0287 \cdot S^2 \quad (1)$$

Approximation constant in central point $C_s = R_s(20)$ was of $C_s = 38.37$.

Approximated equation for relationship in Figure 6 at second stage approximation is as follows:

$$R_C(C) = 8.5525 + 17.0857 \cdot \log_{10}(C) \quad (2)$$

General equation after approximation at I and II stage:

$$R_{SC}(S,C) = R_s(S) + R_C(C) - C_S \quad (3)$$

Approximation constant in central point $C_{SC} = R_{SC}(20,50)$ was of $C_{SC} = 37.58$.

Final equation:

$$R_{SC}(S,C) = 2.2199 \cdot S - 0.0287 \cdot S^2 + 17.0857 \cdot \log_{10}(C) - 24.3655 \quad (4)$$

A three-dimensional graph being a solution to equation (4) determining the percentage removal of orthophosphates in function of initial concentration and Fe:P ratio value is shown in Figure 7. This equation can be applied to model solution at S (Fe:P) range of 2–30 for initial concentration C = 13–114 mg P·dm$^{-3}$ and reaction time of 3 hours.

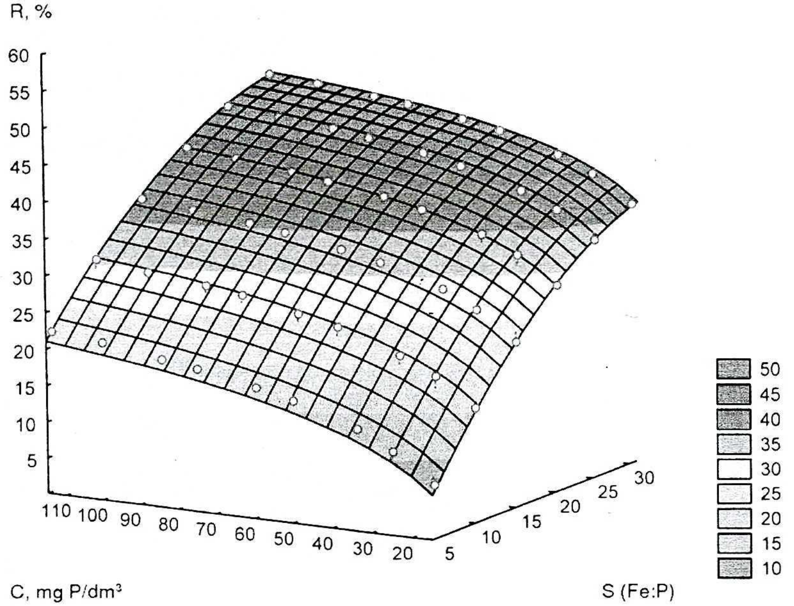


Fig. 7. Influence of initial concentration (C) and Fe:P ratio (S) on percentage removal of orthophosphates (R). Reaction time of 3 hours, pH ≈ 7

Verification of the equation determined for the model solution and evaluating the practical usefulness of iron sludge was performed using sludge liquor. This is generated during the processing and disposal of wastewater and it poses a major problem for wastewater treatment plants that remove phosphorus in biological processes. A large amount of phosphorus is released to sludge liquor during thickening and dewatering of a fermented sludge. Due to recirculation of sludge liquor to the wastewater treatment plant, the phosphorus contribution in the load observed in raw wastewater may amount to 40% [11]. Disturbance of the dephosphatation process initiated by sludge liquor inflow may be eliminated by chemical precipitation with coagulants or substitute materials such as iron sludge.

Performed tests confirmed that iron sludge is highly useful for removing orthophosphates from sludge liquor (Fig. 8). Effectiveness varied from 19% to almost 70%, depending on initial concentration (12–124 mg P·dm$^{-3}$) and dose (defined by ratio of Fe:P = 5–25). Comparison of the effectiveness of removing orthophosphates at a selected initial concentration of 76.6 mg P·dm$^{-3}$ also revealed that the use of iron sludge is more efficient to remove orthophosphates from sludge liquor by 15–27% compared to the model solution (Fig. 9).

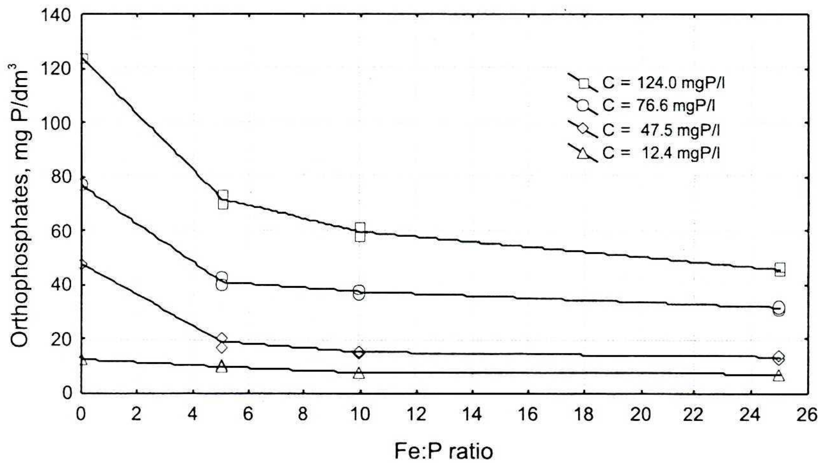


Fig. 8. Removal of orthophosphates from sludge liquor in function of initial concentration (C) and Fe:P ratio value. Reaction time of 3 hours, pH ≈ 7

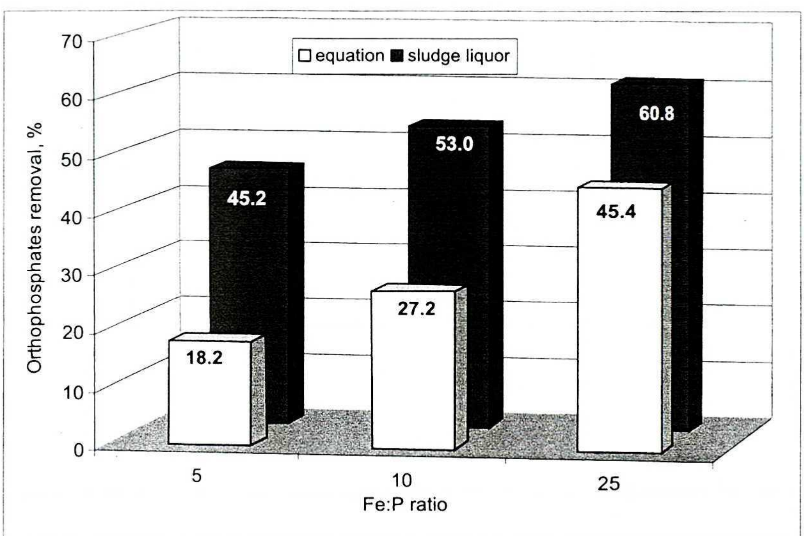


Fig. 9. Percentage value of orthophosphates removal from sludge liquor and value calculated based on equation for model solution depending on value of Fe:P ratio. Initial concentration of 76.6 mg P·dm$^{-3}$, reaction time of 3 hours, pH ≈ 7

The major difference observed between results obtained from research on model solution and those obtained from research on removing orthophosphates from sludge liquor might result from conditions under which the process of removal occurred. Those conditions might influence the properties of iron sludge. The form of iron in water depends above all on pH and redox potential. Together with an increase of indexes, iron ions are converted into sludge ($FeCO_3$, $Fe(OH)_2$, $Fe(OH)_3$). At low pH and low redox potential, changes in the properties of the iron sludge surface may occur (change of surface charge), which influences the effectiveness of adsorption and changes of iron form. Iron may become partly dissolved or reduced; thus its chemical activity would increase [9, 12, 15].

Under laboratory conditions at neutral reaction, removing orthophosphates proceeded as a result of adsorption. At low redox potential (typical for sludge liquor from anaerobic sludge digestion) iron ions from sludge might be partly reduced and dissolved, which would influence the increase of effectiveness in removing orthophosphates during precipitation. Explanation of that issue requires further research.

## CONCLUSIONS

- With regards to different efficiency and iron concentration in raw water, tested ground water treatment plants generate 2.3% of washings (WTP-Mostowo) and 6.2% (WTP-Koszalin), compared to the amount of treated water (data from the last four years).
- Annual amount of waste iron generated from washings amounted to 8466 kg $Fe \cdot year^{-1}$ in WTP-Koszalin, while it amounted to 1890 kg $Fe \cdot year^{-1}$ in WTP-Mostowo, which gives more than 10 Mg of waste iron per year.
- Washing without any processing can be used to remove orthophosphates from wastewater.
- During the early most effective 3 hours of contact of model solution with the iron sludge, 28–41% percentage effectiveness of removing orthophosphates was reached.
- The higher effectiveness of removing orthophosphates was obtained with increase of initial concentration and Fe:P ratio.
- Verifying tests on real sludge liquor showed an increase in effectiveness of removing orthophosphates by 15–27% compared to determined equation for model solution.
- Increase of iron sludge effectiveness to remove orthophosphates from sludge liquor may indicate a positive role of reducing conditions (confirming tests required).
- The high effectiveness of removing orthophosphates from sludge liquor by iron sludge may be an interesting alternative to commercial coagulants to decrease the internal supply of wastewater treatment plant with biogenic compounds. It can be a useful method of iron sludge utilization.

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## POWSTAWANIE I ZAGOSPODAROWANIE WÓD ODPADOWYCH Z UZDATNIANIA WODY PODZIEMNEJ

Wykorzystywanie w procesach oczyszczania ścieków różnorodnych odpadów zawierających żelazo lub glin może stanowić alternatywę dla drogich reagentów komercyjnych oraz sposób na ich skuteczne zagospodarowanie, istotne z punktu widzenia ochrony środowiska. Jednym ze źródeł żelaza odpadowego są popłuczyny powstające podczas uzdatniania wody podziemnej, które nie są w praktyce wykorzystywane. W artykule przedstawiono charakterystykę dwóch stacji uzdatniania wody podziemnej zaopatrujących miasto Koszalin. Na podstawie danych z ostatnich 4 lat przeprowadzono bilans rocznej ilości żelaza odpadowego powstającego z płukania złóż filtracyjnych na obu stacjach, których ilość przekracza 10 Mg·rok$^{-1}$. Badania nad zastosowaniem osadów z popłuczyn do usuwania ortofosforanów z roztworu modelowego oraz z rzeczywistych wód osado-

wych po procesie fermentacji osadów ściekowych wykazały możliwość skutecznego wykorzystania żelaza odpadowego w technologii oczyszczania ścieków.