Removal of phosphorus compounds from water experience from technological research

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Abstract. The aim of the technological research was to determine the technology which would enable reduction of the concentration of phosphorus compounds in water to the level of 0.02 mg PTot/dm³. The raw water during the study period was characterized by a pH of 6.66 to 7.62 and a variable concentration of phosphorus compounds ranging from 0.150 to 0.366 mg PTot/dm³, including phosphates in the range of 0.039 to 0.089 mg PO₄/dm³. The concentration of chlorides was below 10 mg Cl/dm³ and sulphates did not exceed 14 mg SO₄/dm³. Treated water was intended for soil application therefore its quality after treatment could not exceed the limit values set forth in the regulations in force during the study period. The conducted research has shown that the use of the coagulation process based on the ferric coagulant PIX 112 combined with rapid filtration ensures the required quality of the treated water, among other things, through lowering the concentration of PTot to 0.02 mg/dm³.

1 Introduction

The pollution of surface waters and, more and more often, also groundwaters can be attributed to a high extent to nitrogen and phosphorus compounds. Excessive concentrations of phosphorus in surface water bodies can have a serious negative impact on the natural environment. Phosphorus, just like nitrogen, is one of biogenic elements responsible, among other things, for the deterioration of the quality of water in rivers, streams and lakes, due to eutrophication and blooms. The main sources of phosphorus in surface water include insufficiently treated household and industrial wastewater and agricultural runoff resulting from inappropriate storage or application of natural and mineral fertilisers. In order to make surface water suitable for consumption and industrial and recreational uses and to prevent the occurrence of high phosphorus concentrations, effective water and wastewater treatment technologies must be employed before the effluent is discharged into receivers. The technologies applied in order to overcome the issue should not be too complex but, at the same time, should ensure satisfactory environmental outcomes. The right approach to the subject is to carry out pilot studies in order to select the optimum water treatment technology, define the unit process parameters and determine the size of the necessary investments. The results of technological research help to identify the appropriate process layout and estimated investment and operating costs. Designers receive specific guidelines for drawing up accurate technical documentation and thanks to a well thought-

out building design and execution plan the investment can be properly implemented, completed and commissioned, with the guaranteed achievement of the expected technological outcomes [1- 4].

Pursuant to the [5] currently in force in Poland, organophosphorus compounds are classified as substances particularly hazardous to the aquatic environment, causing water pollution which need to be effectively eliminated, while inorganic phosphorus compounds and free phosphorus are classified as substances particularly hazardous to the aquatic environment, causing water pollution whose content needs to be reduced. The target set in the Water Framework Directive [6] was to achieve a good ecological status of surface waters, including rivers, lakes, transitional and coastal waters in the European Union by the end of 2015, among other things, through the reduction of the phosphorus content in surface waters. The Water Framework Directive 2000/60/EC of 23 October, 2000 setting the legislative framework for the community actions in the water policy area is a result of many years of member states' collaborative effort aimed at better protection of the water quality, by way of implementing a common European water policy based on transparent, effective and coherent principles. The directive commits members states to rationally use and protect water resources, in line with the sustainable development guidelines. Consequently, mechanical wastewater treatment plants in Poland were expanded to include biological sections which enable removal of biogenic compounds from wastewater. Another way to prevent phosphorus occurrence in surface waters is to

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add reactive substances to the process of their treatment [7-13].

In this article, the authors will present the results of technological research concerning the treatment of water drained from a mine, to be discharged into surrounding lakes. The purpose of the studies was to identify the technology enabling removal of phosphorus from water to reduce its content to 0.02 mg/dm^3 . In addition to meeting this parameter, the quality of the treated water had to meet all requirements set forth in the Regulation of the Minister of Environment in force during the study period [14].

2 Methods

Technological research was conducted in March 2014. The pilot station was located at the intake of raw water. The layout of the process equipment used in the technological research is presented in Fig. 1.

Fig. 1. Process equipment layout during the pilot scale investigation.

Water was sampled from a ditch collecting water from different wells draining the mine grounds. Studies were performed using physical models of coagulation chambers, flotation chambers, a vertical sedimentation tank and a multi-stream sedimentation tank unit. The rate of raw water inflow to the pilot station was $1.5 \text{ m}^3/\text{h}$. The coagulant dosage and type were determined in a batch test. The selected coagulant was PIX 112. During the pilot scale process, coagulation in the sedimentation tank was boosted by adding a strongly anionic flocculant. After separation of the majority of sludge, water was

filtered by two connected, parallel rapid filters. The rapid filters were pipes with a diameter of 100 mm and a height of 2,500 mm. In the first filter, a 15 cm gravel support layer was topped with a 100 cm thick layer of quartz sand with a granulation of $d_{10}=0.71 \text{ mm}$ and $d_{60}=1.25 \text{ mm}$ and grain-size uniformity coefficient $WR=1.8$. In the second filter, a 15 cm gravel support layer was topped with a 100 cm thick layer of AG filter bed with a granulation of $d_{10}=0.59 \text{ mm}$, $d_{60}=1.65 \text{ mm}$ and $WR=1.8$. Both filters were equipped with an installation enabling control and measurement of the filtration rate and the intensity of backwashing with water. The filtration cycle lasted 48 hours and the filtration rate was 5 m/h . The filters were backwashed with raw water only, with a 50% filter bed expansion.

In order to control the effectiveness of phosphorus compounds removal from water and of the coagulation process, the following water quality parameters and indicators were determined for raw water, water after flotation, water past the vertical sedimentation tank and multi-stream sedimentation tank and the filtered water: temperature, pH, $PTot$, PO_4 , COD (Cr), Nog, N_{NH_4} , N_{NO_3} , Ca, Mg, Cl, SO_4 and Fe_{Tot} .

3 Results and interpretation

3.1 Selection of the coagulant type and dose

The study evaluated the effectiveness of PIX 112 coagulant used at the rate of 4 and 5 mg Fe/dm^3 and of PIX 112 after alkalization of the water samples with lime water to $pH \sim 9$. When the water became turbid, PIX 112 was added to $pH \sim 7.2$. Following coagulation, water samples were collected from selected vessels for analysis and the results obtained are presented in Table 1.

Table 1. Concentrations of total phosphorus and phosphates in the water after coagulation with selected doses of coagulant PIX 112 and calcium hydroxide.

Doses of coagulant mg Fe/dm^3	Concentrations of total phosphorus mg PTot/dm^3	Concentrations of phosphates $\text{mg PO}_4/\text{dm}^3$
Raw water	0.180	0.043
PIX 112 – 5 mg Fe/dm^3	0.010	0.020
PIX 112 – 4 mg Fe/dm^3	0.010	0.020
PIX 112 + $Ca(OH)_2$	0.010	0.020

In all water samples after the coagulation process and filtration through a medium-grade filter paper, the total phosphorus concentration was below $0.01 \text{ mg PTot/dm}^3$ and of phosphates below $0.02 \text{ mg PO}_4/\text{dm}^3$. The rate of 5 mg Fe/dm^3 was considered the optimum dose of PIX 112 coagulant for use in technological processes. The dose ensured formation of visible sludge flocs across the entire water mass. A similar effect was obtained by using PIX 112 in combination with lime, but the resulting flocs began to sediment during slow mixing and it would not be possible to remove them in the course of the flotation

process. Additionally, it was concluded that the use of two reagents and the need to control pH value would make the treatment process more complex. When PIX 112 coagulant was used at the rate of 4 mg Fe/dm³ sludge flocs formed later, were very small and water was not entirely clear.

3.2 Effectiveness of phosphorus compounds removal in the technological process with a flotation chamber and a rapid filter

Raw water during the study period demonstrated variable pH, ranging from 6.66 to 7.62. Variability was also observed with regard to phosphorus concentrations from 0.150 to 0.366 mg PTot/dm³, including phosphates in the range from 0.039 to 0.089 mg PO₄/dm³. Chloride concentrations were below 10 mg Cl/dm³ and sulphates did not exceed 13.9 mg SO₄/dm³.

The determined quality parameters and indicators for raw water and water after flotation are presented in Table 2a and 2b, while Fig. 2a and Fig. 2b shows changes in the total phosphorus concentrations in water after flotation and rapid filtration.

Table 2a. Water quality indicators and parameters for raw water.

Water quality indicators and parameters	Unit	Raw water date/sampling time		
		19.03	20.03	28.03
		14.00	8.00	8.00
Temp.	°C	10.40	12.20	10.60
pH	-	6.66	7.06	7.37
Alkalinity	mval/dm ³	-	7.80	-
Turbidity	NTU	12.80	14.50	18.10
Fe _{Tot}	mgFe/dm ³	1.14	2.35	2.18
Mn	mgMn/dm ³	0.427	0.416	-
P _{Tot}	mgP/dm ³	0.207	0.366	0.101
PO ₄	mgPO ₄ /dm ³	0.045	0.046	0.066
BOD ₅	mgO ₂ /dm ³	1.00	1.50	1.60
COD	mgO ₂ /dm ³	9.80	7.70	8.50
N _{Tot}	mgN/dm ³	1.300	1.200	1.230
N _{NH4}	mgN/dm ³	0.686	0.648	0.696
N _{NO3}	mgN/dm ³	0.089	0.067	0.064
Ca	mgCa/dm ³	113.90	114.40	128.70
Mg	mgMg/dm ³	18.10	18.40	20.00
Cl	mgCl/dm ³	9.90	9.90	9.20
SO ₄	mgSO ₄ /dm ³	13.90	11.80	11.90

Doses of coagulant PIX 112 = 5.0 – 5.5 mg Fe/dm³
 Doses of flocculant = 0.25 – 0.50 mgPAA/ dm³

Table 2b. Water quality indicators and parameters for water after flotation.

Water quality indicators and parameters	Unit	Water after flotation date/sampling time	
		19.03	20.03
		14.00	8.00
Temp.	°C	10.40	12.50
pH	-	6.72	6.85
Alkalinity	mval/dm ³	-	7.40
Turbidity	NTU	10.50	15.40
Fe _{Tot}	mgFe/dm ³	1.91	1.90
Mn	mgMn/dm ³	0.406	0.431
P _{Tot}	mgP/dm ³	0.053	0.051
PO ₄	mgPO ₄ /dm ³	0.010	0.020
BOD ₅	mgO ₂ /dm ³	1.10	0.60
COD	mgO ₂ /dm ³	6.00	7.00
N _{Tot}	mgN/dm ³	1.430	1.380
N _{NH4}	mgN/dm ³	0.688	0.740
N _{NO3}	mgN/dm ³	0.065	0.071
Ca	mgCa/dm ³	116.40	115.90
Mg	mgMg/dm ³	18.60	18.60
Cl	mgCl/dm ³	9.40	10.10
SO ₄	mgSO ₄ /dm ³	27.60	28.70

Doses of coagulant PIX 112 = 5.0 – 5.5 mg Fe/dm³
 Doses of flocculant = 0.25 – 0.50 mgPAA/ dm³

High concentrations of iron compounds and substantial turbidity values were observed in the water past the flotation chamber. The high water turbidity and elevated concentrations of iron compounds indicating an increased suspended solids content accelerated the filtration bed colmatation process and reduced the filtration cycles. Despite that, water after filtration – with minor exceptions – demonstrated acceptable concentrations of phosphorus compounds.

The results presented in Fig. 2 show that after the filtration of water through a quartz sand filter and through an AG filter, the content of phosphorus compounds was equal to 0.02 mg PTot/dm³ or lower in 77% and 86% of cases, respectively. The average total phosphorus concentration past the quartz sand filter was 0.021 mg PTot/dm³ and past the AG filter 0.016 mg TP/dm³.

The studies have proven that it is necessary to use the water filtration process in order to achieve the required concentrations of total phosphorus and phosphates in treated water.

Fig. 2a. The concentration of total phosphorus in water after coagulation with sludge flotation and filtration through a quartz sand filter.

Fig. 2b. The concentration of total phosphorus in water after coagulation of sludge flotation and filtration through AG filter.

3.3 Effectiveness of phosphorus compounds removal from water in the technological process with a vertical sedimentation tank and a rapid filter.

The vertical sedimentation tank removed suspended post-coagulation solids from water more effectively than the flotation chamber, as demonstrated by the lower turbidity and lower iron compounds concentrations.

The turbidity values and concentrations of iron compounds in the water past the flotation chamber and the vertical sedimentation tank are presented in Table 3. It was undeniably an effect of the sedimentation tank's lower capacity versus the flotation chamber by ca. 60%.

Table 3. Turbidity and the iron concentration in water past the flotation chamber and the sedimentation tank.

Water Quality Indicators	Equipment	Average value
Turbidity [NTU]	Flotation chamber	13.4
	Sedimentation tank	4.3
The iron concentration [mgFe/dm ³]	Flotation chamber	4.1
	Sedimentation tank	1.9

The results of coagulation and rapid filtration in the technological process with a vertical sedimentation tank are presented in Fig. 3a and Fig. 3 b and Table 4.

Fig. 3a. Total phosphorus concentration in the water past the sedimentation tank and past the quartz sand filter.

Fig. 3b. Total phosphorus concentration in the water past the sedimentation tank and past the rapid AG filter.

A comparison of Fig. 2 and Fig. 3 shows that as a result of lower concentration of suspended solids past the vertical sedimentation tank (Table 3), the effectiveness of phosphorus compounds removal from water increased. After passing through the quartz sand filter, only one out of seven water samples contained more than 0.02 mg PTot/dm³, while past the AG filter excessive values were recorded in two cases out of eight.

Worth emphasising is the fact that the average total phosphorus concentrations past both filters were significantly lower than 0.02 mg PTot/dm³ and amounted to 0.014 mg PTot/dm³ for the quartz sand filter and to 0.017 mg PTot/dm³ for the AG filter.

The high effectiveness of phosphorus compounds removal from water in the technological process with the vertical sedimentation tank was related to its limited capacity (0.6 m³/h), approximately 60% lower than the capacity of the flotation chamber.

The multi-stream sedimentation tank, on the other hand, can be an alternative for the vertical sedimentation tank.

The results of the studies carried out on one multi-stream sedimentation tank are presented in Fig. 4. Given the results presented in Fig. 4, if the effectiveness of suspended solids removal is measured in terms of the maximum turbidity of treated water not exceeding 4 NTU and of the iron concentration close to 1 mg Fe/dm³

(similar to the average value past the vertical sedimentation tank), the estimated capacity of one unit approximates 13 l/h.

Table 4. Water quality indicators and parameters for the water past the sedimentation tank.

Water quality indicators and parameters	Unit	Water past the sedimentation tank date/sampling time		
		19.03	20.03	28.03
		14.00	8.00	8.00
Temp.	°C	10.4	13.1	-
pH	-	6.6	6.88	-
Alkalinity	mval/dm ³	-	7.40	-
Turbidity	NTU	4.97	9.30	4.34
Fe _{Tot}	mgFe/dm ³	1.95	2.90	1.98
Mn	mgMn/dm ³	0.418	0.420	-
P _{Tot}	mgP/dm ³	0.510	0.092	0.060
PO ₄	mgPO ₄ /dm ³	0.010	0.011	<0.01
BOD ₅	mgO ₂ /dm ³	1.20	1.80	1.00
COD	mgO ₂ /dm ³	6.6	8.7	7.9
N _{Tot}	mgN/dm ³	1.290	1.420	1.460
N _{NH4}	mgN/dm ³	0.562	0.730	0.823
N _{NO3}	mgN/dm ³	0.080	0.730	0.072
Ca	mgCa/dm ³	115.4	111.7	122.3
Mg	mgMg/dm ³	18.6	18.5	19.4
Cl	mgCl/dm ³	9.5	9.6	9.6
SO ₄	mgSO ₄ /dm ³	27.8	30.8	23.4

Doses of coagulant PIX 112 = 5.0 – 5.5 mg Fe/dm³

Doses of flocculant = 0.25 – 0.50 mgPAA/ dm³

Fig. 4. Turbidity and iron compounds in the water past multi-stream sedimentation tank depending on its capacity.

Based on that value, the capacity of the entire multi-stream sedimentation tank made of pipes with a diameter

of 0.05 m can be determined. Due to the inclined position at the angle of 60° and the length of 100 cm, it will consist of 19 x 18 pipes, i.e. the total of 342 pipes. Assuming the unit capacity of 13 l/h, the overall capacity of the whole set will be 4.15 m³/h.

4 Conclusions

The conducted technological research proved that was possible to treat mine drainage water with the effectiveness ensuring conformance with the requirements of the Regulation of the Minister of Environment of 2006 [14] and, additionally, to achieve reduction of the phosphorus compounds concentration to 0.02 mg PTot/dm³. The study results remain valid also in the context of the limits set forth in the currently applicable Regulation of the Minister of Environment of 2014 [5].

The technological process in the Water Treatment Plant encompassing coagulation and the PIX 112 iron coagulant, sedimentation and rapid filtration would ensure appropriate quality of treated water.

Due to the low effectiveness of suspended solids removal and relatively high energy consumption of the flotation process, the idea of using flotation chambers was abandoned. Instead, a more effective multi-stream sedimentation tank was proposed.

The filtration of water after the process of coagulation and sedimentation should be carried out using rapid filters with quartz sand or AG filter beds.

The results of the technological research enabled the development of the technological and construction concept of the water treatment plant. Based on the concept, estimated investment and operating costs were estimated. All the documents were used by the Investor in the decision making process regarding the future steps to be taken.

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