PRELIMINARY RESULTS FROM APPLICATION PHOSLOCK® TO REMOVE PHOSPHORUS COMPOUNDS FROM WASTEWATER

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ABSTRACT

The aim of the study is to assess the removal effectiveness of phosphorus compounds by using lanthanum-modified bentonite. This material was produced by the Australian company Phoslock® Water Solutions Pty Ltd. According to the company, Phoslock® has substantial capacity to bound phosphate anions. The investigation was carried out in steady conditions in laboratory model with beakers. The results of the study are related to the determination of hydraulic load, time of mixing and time of sedimentation. Research with synthetic wastewater was conducted in 4 beakers which were mixing by 5, 10, 20 and 30 minutes respectively. Samples for analyzing were taken from each beaker after 30 minutes, 1, 2, 3, 4 and 24 hours of sedimentation. Studies were conducted to determine the optimal dose of Phoslock® with a known concentration of phosphate anions PO_4^{3-} in artificial wastewater, time of mixing and time of sedimentation. All samples were taken before and after the treatment with Phoslock® and they were analyzed with following parameters: pH, total suspended solids, conductivity, turbidity, color and phosphate concentration. The carried out investigations confirmed high efficiency of phosphate anions $PO4^{3-}$ removal (over 95%), and the final concentration as average was 0.1 mg/dm³. The application of Phoslock® for phosphate anions PO_4^{3-} did not change the pH of final effluent.

Keywords: Phoslock, phosphorus removal, sorption, wastewater

INTRODUCTION

Eutrophication is a process of enrichment in nutrients in rivers, lakes or artificial reservoirs. It is caused by the presence of nutrients compounds, mainly phosphorus and nitrogen compounds. The negative effects of eutrophication, such as algal blooms and oxygen deficiency in the water, lead to substantial emission restrictions. Baltic Sea Action Plan [HELCOM, 2007] talks about the reduction of phosphorus compounds by 70% already for a small wastewater treatment plants up to 300 person equivalents (PE). Exacerbations on permissible concentrations of phosphorus and nitrogen compounds increases along with the number of PE [Council Directive 91/271/EEC, 1991, Polish Regulation (Year 2014, item 1800)].

The most common method of phosphorus removal is the chemical method, which consist in reducing phosphate by salts of iron and/or aluminum [Jozwiakowski et al. 2017, Nastawny et al., 2015]. However, this method is related to many problems like: with the disposal of produced sludge, generate high costs and is not suitable for use in many conventional wastewater treatment plants. Furthermore, with very good treatment effects, multiple methods of wastewater treatment does not provide phosphorus compounds removal to the expected level [Gajewska & Obarska-Pempkowiak, 2011, Gajewska et al., 2011, Paruch et al., 2011]

An alternative method of reducing concentration of phosphorus in the wastewater is binding phosphorus compounds while contact with material with high sorption capacity. We can distinguish adsorbents of anthropogenic origin, such as AAC (autoclaved aerated concrete) [Rennman G. & Rennman A., 2012], LECA [Karczmarczyk &

Bus, 2014] and Pollytag [Bus et al., 2014] and natural origin, such as rock opoka [Bus & Karcz-marczyk, 2014; Vohl et al., 2011] and POLONITE [Karczmarczyk et al., 2016, Rennman, 2008].

Modified clays, such as lanthanum-modified bentonite clay appearing under the technical name Phoslock®, belong to the adsorbent materials produced by man [Rennman G. & Rennman A., 2012]. The results of the experiments described by Van Oosterhout, Lurling [2013] showed that Phoslock® contributes to a significant reduction in growth of phytoplankton. According to Robb et al. [2003] during testing on natural waters, using of Phoslock®, dissolved phosphorus was reduced by 90%, to a level of 5 µg/dm³. Has also been proven that Phoslock® does no show harmful properties to living organisms [Van Oosterhout et al., 2014].

The aim of the work is to determine the sorption capacity of the Phoslock® material in steady conditions, towards potential application as a last stage of treatment in WWTP without biological phosphorous removal. Thus important in our investigation was the final quality of treated wastewater, which needs to meet the requirements of Regulation of Ministry from 2014, November 18. The study was carried out in the laboratory model. The subject of research was also the time of mixing, a period of sedimentation of absorbent material and the influence of Phoslock® on the basic parameters of the solution: pH, temperature, total suspended solids (TSS), chemical oxygen demand (COD), conductivity, turbidity and color.

MATERIAL AND METHODS

Material

Phoslock® is the adsorbent with high binding capacity of phosphate ions. This preparation is produced from lanthanum-modified bentonite clay and developed by the Land and Water Division of Australia's CSIRO (Commonwealth Scientific and Industrial Research Organisation). Removal of phosphorus compounds is based on their adsorption on the surface of the material, where they form an insoluble complex. Particles of Phoslock® containing a significant amount of adsorbed ions of phosphorus PO_4^{3-} sediment on the bottom of the vessel [Phoslock general brochure]. Lanthanum is a chemical element that binds phosphate ions in a 1:1 ratio according to equation (1):

$$La^{3+} + + PO_4^{3-} \rightarrow LaPO_4 \qquad (1)$$
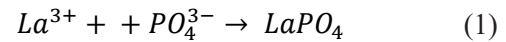
The product of the above reaction is rhabdophane, a stable mineral of low solubility. Rhabdophane is the only product of the setting process, and the lack of by-products is an important advantage during the process of wastewater treatment [Haghseresht et al., 2009, Zamparas et al., 2015].

Despite the relatively small size of the particles of Phoslock® material, with high specific surface area and pore volume (Table 1), the area of the adsorption reaches its maximum. Silicon oxide SiO_2 and aluminum oxide Al_2O_3 exist in the chemical composition of Phoslock® in the highest concentration (Table 2). According to Haghseresht et al. [2009], it contains approximately 49 mg of lanthanum per gram of Phoslock®, therefore the adsorption capacity of phosphorus cannot be higher than 10.6 mg per 1 gram of adsorbent.

The adsorbent material is capable to operate in a wide range of pH from 4 to 11 [Ross & Haghseresht, 2008]. The optimum pH for removal of phosphate ions using Phoslock® in the process of adsorption is in the range 5.0 – 9.0, while the maximum efficiency is achieved at a pH of 5.0 – 7.0. However, it is worth noting that the degree of phosphorus removal significantly decreases when the value of pH increased to 7.0 – 9.0 [PWS Report Number: IR 019/12, 2012].

Table 1. Physical characteristic of Phoslock® [Haghseresht et al., 2009]

Physical properties	Value
Specific surface area (m²/g)	39.3
Total pore volume (cm³/g)	0.171
Average particle size (µm)	22
Moisture content (%)	7 – 9
pH	7 – 7.5
Bulk Density (kg/m³)	910 – 960

Table 2. Chemical composition of Phoslock® [Haghseresht et al., 2009]

Chemical composition	Concentration (%)
SiO_2	63.36
Al_2O_3	14.73
MgO	2.76
Fe_2O_3	3.64
CaO	1.79
La_2O_3	0.058

Experiment design

In order to determine the sorption capacity of the Phoslock®, the model solution was prepared in 4 beakers with 2 dm³ capacity. To produce model solution, distilled water and a solution of potassium dihydrogen phosphate KH_2PO_4 (1 cm³ – 10 mgPO₄/dm³) was used. In each beaker were 1.5 dm³ of model solution with given concentration of phosphate phosphorus approx. of 15 mgPO₄-P/dm³, five series (repetitions) have been performed (Table 3).

Prior to the addition of Phoslock®, the following parameters of the solution was determined: the concentration of phosphate phosphorus, pH, temperature, total suspended solids (TSS), chemical oxide demand (COD), conductivity, turbidity and color. To each beaker 100 g of adsorbent was added. Stirring was provided by a magnetic stirrer (1000 rpm) in each beaker. Mixing times were 5, 10, 20 and 30 minutes. After period of mixing time followed sedimentation time. The sampling of the solution from each beaker was made after 0.5, 1, 2, 3, 4, and 24 hours of sedimentation. When reduction of the entire concentration of phosphorus from synthetic wastewater during each series was observed, the whole process was repeated. To emptied beakers, a model solution with given concentration was poured. The beakers were still filled with input amount of Phoslock® (100 g). The procedure was repeated until the exhaustion of sorption capacity of the material. In total, the process was repeated 5 times (5 series of investigation), resulting in the volume of treated wastewater equal to 7.5 dm³. In each beaker was taken 28 samples. All tests were conducted at room temperature approx. 20°C.

Physical and chemical analysis

Before the designation of the individual parameters of synthetic wastewater, the samples were subjected to filtration in order to determine total suspended solids (TSS). The content of TSS was performed by gravimetric method, which was calculated on the basis of the formula (2):

$$Z = \frac{(m_2 - m_1)}{V} * 1000 \qquad (2)$$

where: Z – concentration of total suspended solids (TSS) [mg/dm³],
m_1 – mass of the filter before filtration [g]
m_2 – mass of the filter after filtration [g],
V – sample volume [dm³]

The concentration of the phosphorus phosphate was marked by using the cuvette tests HACH Lange LCK 049 (1.6 – 30 mg/dm³ of PO₄-P), LCK 348 (0.5 – 5.0 mg/dm³ of PO₄-P) and LCK 349 (0.05 – 1.5 mg/dm³ of PO₄-P). The content of COD was determined by using the cuvette test HACH Lange LCK 314 (15 – 1500 mg/dm³ O₂). Measurement of turbidity and color was performed by using a spectrophotometer HACH Lange DR3900. The temperature and pH were measured using a pH meter WTW inoLab pH 720, and conductivity was defined by conductivity meter HACH Lange HQ40D Multi.

Sorption capacity of Phoslock® for each of the mixing times are calculated according to the formula [Nastawny et al., 2015]:

$$q = \frac{(C_0 - C)}{m} * V \qquad (3)$$

where: q – the value of sorption [mg/g],
C_0 – initial concentration of phosphorus in the solution [mg/dm³],
C – final concentration of phosphorus in the solution [mg/dm³],
m – mass of the adsorbent [g],
V – the volume of solution [dm³]

RESULTS AND DISCUSSION

Effect of Phoslock® on phosphorus reduction

The study showed a significant sorption capacity of Phoslock®. In order to exhaustion sorption capacity of 100 g of material, the process of the experience had to be repeating 5 times. The total amount of adsorbed PO₄-P and sorption

Table 3. Initial concentration of PO₄-P in input samples ("0") in each series

Series	1st (0 hour)	2nd (24 hours)	3rd (72 hours)	4th (96 hours)	5th (120 hours)
Initial concentration [mg/dm³]	15.2	15.0	16.1	15.1	15.6

value calculated according to [Nastawny et al., 2015] are given in Table 4.

In 1st series, the concentration of phosphorus significantly decreased after 30 minutes of sedimentation with the effectiveness over 99%. After the first three series for each time of mixing the content of phosphorus compounds has been reduced from the initial value of 15 mg/dm³ to a value of 0.1–0.2 mg/dm³ at the end of the series. While conducting 4th series, a less sudden decrease in the concentration of PO_4-P was noticed, but the reduction rate fluctuated around 90%. After 5th series, the phosphorus level decreased by only 80% to approx. 3 mg/dm³, that was the moment of exhaustion of sorption capacity of the adsorption material.

For each mixing time were achieved similar results, so it has not shown correlation between the effectiveness of phosphorus compound removal and time of mixing.

During the field research described by Haghseresht [2009], were received 95% reduction of concentration of phosphorus compounds. The laboratory experiment, made by Zamparas [2015], was carried out at pH 7, at room temperature of 25±1°C. After 250 minutes of contact time, the study showed reduction efficiency of 87%. The work of Van Oosterhout and Luring [2013] shows

the binding of phosphorus by the absorbent material Phoslock® with effectiveness close to 100%. According to Ross [2008], in the optimal pH range, sorption capacity was designated at level 4.37 mg/g, therefore this experiment demonstrated a higher efficiency of Phoslock® (Table 4).

Effect of Phoslock® on total suspended solids (TSS)

Figure 1 shows the changes in TSS during the experiment. The initial value of the total suspended solids was 0–1 mg/dm³ and was very low due to the use of synthetic wastewater. Phoslock® material caused the release of suspension after use. The increase in TSS followed along with the course of the experiment.

The highest TSS was obtained after 20 and 30 minutes of mixing which occurred in the 4th series (72 h) after 30 minutes of sedimentation reached a value of 1000 mg/dm³ (for 5 and 10 minutes mixing time) and 1398 mg/dm³ and 1740 mg/dm³ for 20 and 30 minutes of mixing respectively. In the 5th series, samples were not collected after 30 minutes of sedimentation, due to difficulties with filtrating too much amount of suspension. TSS value dropped to approx. 10 mg/dm³ after 3 hours of sedimentation in each series of measure-

Table 4. The value of sorption capacity of Phoslock® material for each time of mixing

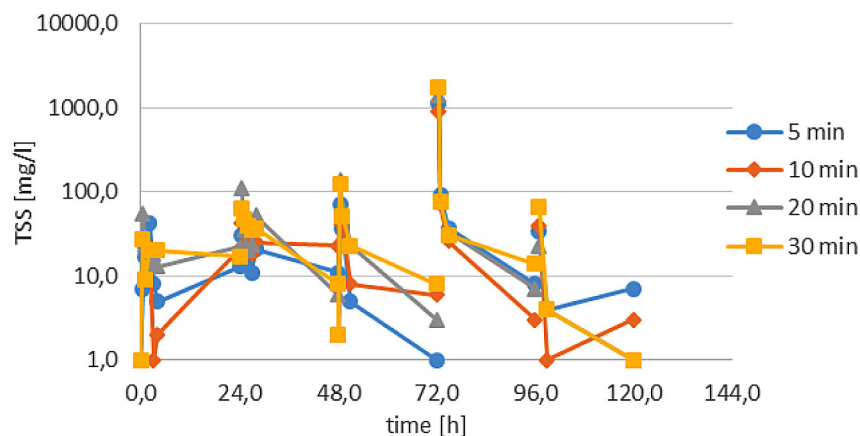| Time of mixing	Summary load of PO_4-P C_0 [mg]	Final load of PO_4-P C [mg]	Quantity of adsorbed PO_4-P [mg]	Sorption q [mg/g]
5 min		2.41	74.59	5.59
10 min	77.00	2.39	74.61	5.60
20 min		3.33	73.67	5.53
30 min		2.70	74.30	5.57

Figure. 1. Characteristic of total suspended solids (TSS) during the investigation (logarithmic scale)

ments for 5 and 10 minutes mixing time, while for 20 and 30 minutes mixing time after 24 hours of sedimentation.

From the measurement of TSS, we can infer, that the multiple use of the same deposits (resuspension) and extended mixing time negatively affects to a solution with Phoslock®. In each of the following series were precipitated higher amount of suspended solids, which was impossible to filtering after 30 minutes of sedimentation (clogging a filter).

Effect of Phoslock® on conductivity

The conductivity of the input samples ("0") was approx. 100 µS/cm (Fig. 2). During the 1st series of tests, with using Phoslock®, the conductivity has increased to values in the range 1000–1400 µS/cm (longer time of mixing gave higher conductivity). With every next carried out series conductivity decreased gradually: after the 2nd series dropped to the value of 400 µS/cm, after the 3rd series to approx. 150 µS/cm, after 4th series – 100 µS/cm, while after 5th series reached the value of approx. 90 µS/cm, so the level of conductivity was similar to the input sample ("0"), or even slightly lower. It has been observed similar characteristics for each mixing time. We can conclude, that the Phoslock®, releases dissolved substances in the early stage of action, while as a result of the resuspension followed by resorption of the dissolved compounds, the conductivity drops down again.

Effect of Phoslock® on pH and chemical oxygen demand (COD)

During the measurements, there has been a slight increase in the value of pH (Fig. 3). Experience has proceeded in the pH range from approx. 6.45 to 7.50. Only in the 3rd series, after 24 hours of sedimentation was observed
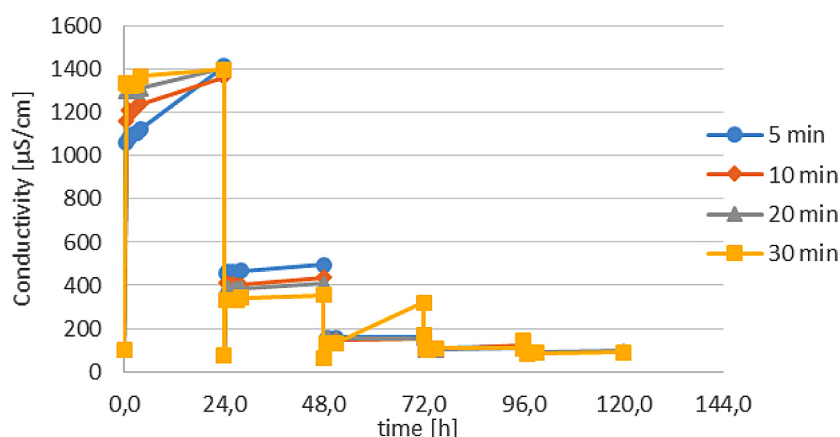

Figure 2. Characteristic of the conductivity during the investigation time
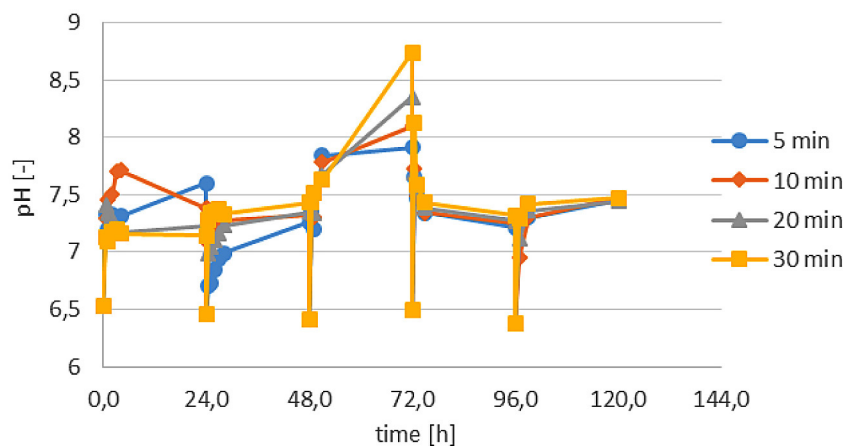

Figure 3. Values of pH during the investigation

an increase of pH to the value of 8.74 for 30 minutes mixing time. During the experiment, the optimal pH range of 6.0 – 9.0 was obtained, to achieve the most effective reduction [PWS Report Number: IR 019/12, 2012].

The values of chemical oxygen demand (COD) subjected to fluctuations from 12.20 mgO_2/dm^3 to 0 mg O_2/dm^3. COD value in input sample ("0") was about 6.50 mg O_2/dm^3. In the 1st and the 2nd series, COD of the solution increased slightly, while in the subsequent series COD steadily decreased to reach finally values close to 0 mg O_2/dm^3 (Fig. 4).

There was no effect of mixing time on the conversion of pH and COD of the solution.

Effect of Phoslock® on color and turbidity

Carried out experiment has shown a significant impact of absorbent material Phoslock® on color and turbidity of the solution. The readings for the input samples ("0") for color were 2–5 $mgPt/dm^3$ and for turbidity were 0.1–1.0 mg/dm^3. After the 1st series, both the color and turbidity changed slightly, but after each subsequent series, the values increased significantly. In the 2nd series for 20 minutes mixing time, color varied within 400–500 $mgPt/dm^3$ and turbidity reached 143.7 mg/dm^3, while for 30 minutes mixing time did not perform measurement of a spectrophotometer (absorbance>3.5). Only after 24 hours of sedimentation, were received lower values: color 278 $mgPt/dm^3$, turbidity 75.1 mg/dm^3. In each subsequent series were received higher values and in many samples values was impossible to read. In 4th series measurements have been made for the input samples ("0") and after 24 hours of sedimentation, which attains a value in the range of 300–400 $mgPt/dm^3$ for color and 80–100 mg/dm^3 for turbidity. For 30 minutes mixing time parameters has not been tested. In the 5th series, readings were made only for 20 minutes mixing time after 24 hours of sedimentation (color: 372 $mgPt/dm^3$, turbidity 95.9 mg/dm^3) (Fig. 5, 6).

Experiment conducted by Van Oosterhout and Luring [2013] also indicates a significant increase in turbidity after the application of Phoslock® (from 0.15 mg/dm^3 to 218 mg/dm^3) and its decrease along with time of sedimentation (after 6 h of sedimentation – 13 mg/dm^3, after 24 hours of sedimentation – 6.5 mg/dm^3).

CONCLUSIONS

Experiment has shown very high sorption capacity of Phoslock® around 5.60 mg/g. The amount of PO_4-P removed from the solution was approx. 74 mg, which gives more than 95% of phosphorus removal efficiency from synthetic wastewater during the entire test. Experiment showed no relationship between the mixing time and the degree of reduction of phosphorus compounds. After the experiment, it is concluded that the optimal condition for the process in steady condition is (I) mixing time should not exceeded 10 min and (II) sedimentation time is 3h.

The conductivity of the solution was subjected to significant fluctuations. It was observed that resuspension of Phoslock® reduces its ability to change the conductivity. There was no relationship between the mixing time and conductivity
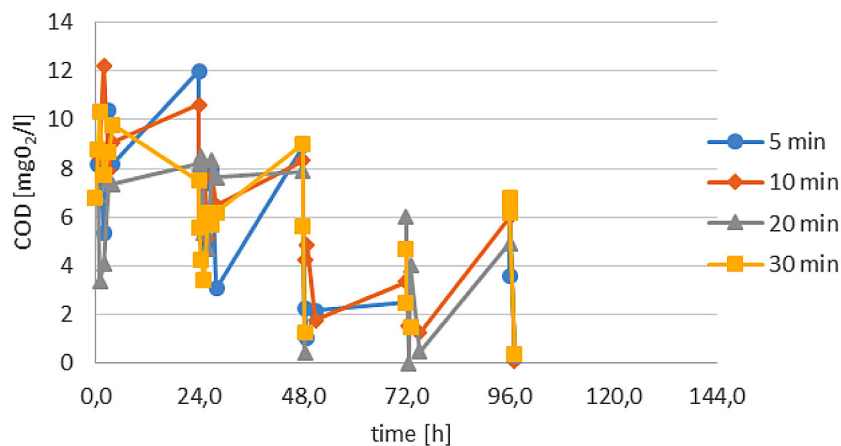

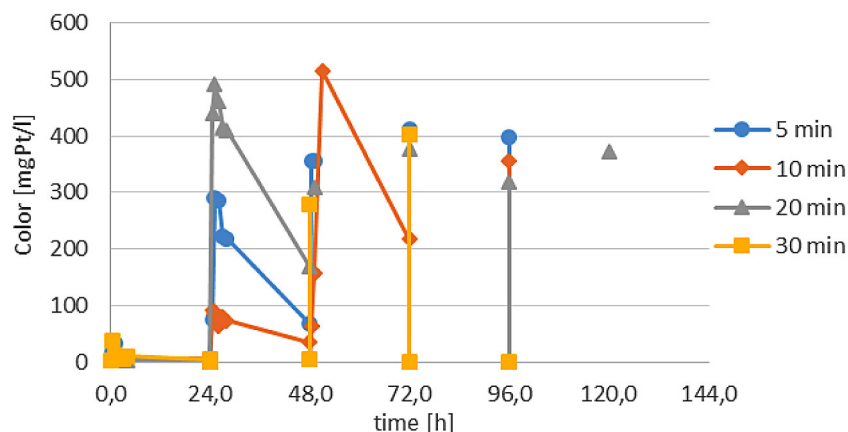**Figure 4.** Values of COD during the investigation

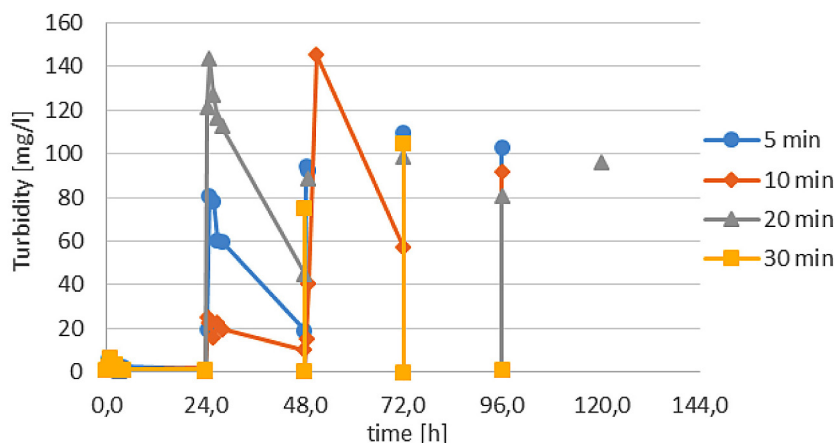**Figure 5.** Values of color during the investigation

Figure 6. Values of turbidity during the investigation

fluctuations. It has been found, that the Phoslock® material causes a small increase in pH of the solution regardless of the mixing time and the number of ongoing series.

The value of COD was subjected to slight changes, where the mixing time did not affect the course of these changes. Repeating the experience on the same deposit resulted in the decrease in COD of solution. The experiment has shown that a longer mixing time adversely affects to color and turbidity of the solution. The worst results were obtained with 30 minutes mixing time, while the lowest values of these parameters were obtained for 10 minutes mixing time. For further studies on the Phoslock®, time of mixing should be reduced to 10 minutes. There is a need for further investigation to mitigate the adverse color and turbidity in wastwater due to application of Phoslock®.

Acknowledgements

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