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Inhibition effects of petroleum products on nitrogen and phosphorous removal

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Inhibition effects of petroleum products on nitrogen and phosphorous removal

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Abstract. One of the main challenges in pet roleum-containing wastewater treatment in municipal wastewater treatment plants is their interference with the microbiological processes of nitrogen and phosphorus removal. The purpose of the study is to assess the effect of commercial petroleum products on the conversion of nitrogen and phosphorus compounds during the biological treatment of municipal wastewater in activated sludge systems. The presence of commercial petroleum products in wastewater was found to inhibit the process of conversion of NH_4-N and the absorption of PO_4-P in cells. The main inhibiting effect results from additives introduced into commercial petroleum products. Variations in the removal efficiencies of NH_4-N and PO_4-P are due to the variable distribution of commercial petroleum products in the mixed liquor of activated sludge. An increase in the degree of dispersion of commercial petroleum products, which results in an increase in the contact surface, increases the inhibitory effect on the activated sludge process. The toxic effect of gasoline is more pronounced in comparison with diesel fuel and hydraulic oil. During the first 30 minutes of incubation of samples with oil products, an increase in the concentration of PO_4-P in the solution was observed due to the death of microorganisms from toxic effects, mainly from gasoline.

1. Introduction

Biological methods are widely used in municipal wastewater treatment plants (MWWTP) for the removal of organic matter and nutrients. MWWTPs receive domestic and industrial wastewater as well as stormwater, which may contain a significant amount of oil products from gas stations, vehicle maintenance stations, and roads. The possibility of using aerobic and anaerobic conditions suspended and immobilised microorganisms and membrane bioreactors for the removal of such pollutants has been studied by many research groups since the early 1970s [1] and continuously thereafter [2, 3]. However, there are less studied aspects requiring better insight. There are many microorganisms that can degrade aliphatic and aromatic hydrocarbons of petroleum-containing wastewater, and they may also form associations that have an even greater destructive potential [4, 5].On the other hand, the composition of commercial petroleum products (CPP) is complex as they contain a variety of toxic compounds, such as polycyclic aromatic hydrocarbons and naphthenic acids, in different compositions and concentrations. Thus, some fractions of CPPs have an inhibitory effect on activated sludge systems as well as on the biological treatment process in general [6, 7] .

Additives such as antiknock agents, which reduce engine knocking and increase the fuel's octane rating, are reported to have a more pronounced effect on biocenosis than the CPPs themselves [8].

The situation becomes further complicated by the fact that there are significant fluctuations in the content of CPPs and their additives in the influents to MWWTPs. Accidental discharges of CPPs to the sewers make it even more difficult for microorganisms to adapt, leading to unstable treatment efficiencies at MWWTP [2].

Despite these challenges, biological methods are widely used for the treatment of CPP containing municipal wastewater, and there are efforts to improve the efficiency of treatment, including increased energy savings [9]**.**

For most recipients, the removal of nitrogen and phosphorus compounds (nutrients) in wastewater treatment is as important as the removal of organic and inorganic compounds. In the process of biological nitrogen removal, ammonia nitrogen (NH_4-N) is assimilated by the microorganisms in the activated sludge in the process of their growth or is oxidised to nitrite or nitrate by specific microorganisms, followed by a reduction to molecular nitrogen. As a rule, inhibiting substances have a stronger effect on nitrifying microorganisms than on denitrifying microorganisms [10]. The process of removing NH_4-N significantly slows down in the presence of CPPs exceeding 0.1 cm^3/dm^3, and the conversion process can be completely stopped at higher concentrations. The content of CPPs greater than 1 cm^3/dm^3 is harmful to the simplest microorganisms of activated sludge and completely disrupts the processes of nitrogen and phosphorus removal from wastewater. Such concentrations are possible when receiving oil-contaminated wastewater from enterprises, gas stations, and so on, especially in the event of accidents. It has also been reported that CPPs are dispersed in mixed liquor suspended solids (MLSS) as droplets and may adsorb onto filamentous bacteria [9].

Biological phosphorus removal occurs due to its removal from the P-accumulated biomass of excess activated sludge. The more phosphorus the activated sludge biomass accumulates, the more it will be removed from the system. Previously, authors reported that the removal of phosphate phosphorous (PO_4-P) from wastewater is difficult when the content of CPPs exceeds 0.5 cm^3/dm^3 [9].

Thus, the purpose of this study was to assess the effect of CPPs, focusing especially on their additives, on the biological removal of nitrogen and phosphorus in MWWTPs to improve the understanding of the effects and underlying mechanisms.

2. Methods and materials of research

The wastewater samples (test water) used in this study were composed of a 1:1 proportion of return activated sludge (RAS) and the effluents from the primary sedimentation tanks of the Minsk city MWWTP, which has a capacity of 350 000 t/day.

Effect of commercial petroleum products (CPP): The effects were studied using gasoline (AI 95 brand), diesel fuel, and oil/heating oil, the composition of which are regulated and determined by the requirements of the technical regulations of the customs union between the Russian Federation and the republics of Kazakhstan and Belarus. In addition, CPPs sold in the Republic of Belarus meet European standards EN 228 and EN 590 [11].

Effect of additives to CPP: The effect of additives was studied in mixtures of gasoline and diesel fuel in a ratio of 1:1. To study the individual impacts, fractions of gasoline, diesel fuel, and hydraulic oil were also used. For comparison, crude oil fractions without additives were used.

The effect of oxygen availability and mass transfer was studied by varying the operating frequency of the shaker-incubator.

Setting up the experiment: 50 cm^3 of effluents from primary settlers and 50 cm^3 of the RAS were placed in 250 cm^3 flasks. CPPs were added in the amount of 0.1 or 0.5 cm^3/dm^3, referring to previous studies [9]. Since the primary effluent and RAS were collected at different times, giving variable

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concentrations, control samples were prepared without CPPs for comparison. The resulting mixture in the flasks was placed in a shaker-incubator at 150 or 240 min^{-1} and incubated for 1.5 or 4 hours at a temperature of 25°C. Samples were taken every 0.5 hours and were analysed after 4 hours of incubation.

The research included three stages:

1. I Commercial petroleum products (CPP) and crude oil fractions (without additives). Gasoline and diesel fuel were prepared in a ratio of 1:1. The resulting mixtures, whose density was 0.76 ± 0.01 g/cm^3, were placed in flasks with test water.
2. II As above (I), but with incubation in shaker-incubators at 150 and 240 min^{-1}. The range of mixing frequencies was selected based on preliminary experiments, where the data obtained indicate that the differences are not due to oxygen restriction.
3. III Individual CPPs in test waters. 0.1 or 0.5 cm^3/dm^3 of gasoline (density 0.72 ± 0.01 g/cm^3), diesel fuel (density 0.82 ± 0.01 g/cm^3), or hydraulic oil were added.

The content of PO_4-P was determined by the colourimetric method, based on interaction with ammonium molybdate with subsequent reduction of the resulting complex with ascorbic acid.

The content of NH_4-N was determined by the colourimetric method based on interaction with Nessler's reagent.

The reproducibility of the analytical results was within limits given in the methods used for analysis. Analytical methods followed national standards, which follows the Interstate Council for Standardization, Metrology, and Certification.

Experiments were carried out with three to five replications. Statistical processing of the data followed methods reported previously [12], calculating the arithmetic means and standard deviations.

3. Results and discussion

As noted above, the rate of NH4-N removal can be considered an indicator of the effectiveness of biological treatment, regardless of whether it is assimilated by active sludge organisms during its growth or is oxidised to nitrite and nitrate by specific microorganisms.

Figure 1 presents the results of the Stage I experiments showing NH_4-N removal efficiencies in test water with crude oil, which has no additives (figure 1a), and CPP which has additives (figure 1b) in two concentrations. No significant differences between the control sample and the samples with crude oil were noted during the first 60 minutes (figure 1a), confirming the assumptions of the experiment that there are no oxygen limitation conditions. Only a small impact of 0.5 ± 0.02 cm^3/dm^3 was noted at 90 minutes. The same figure shows that only a slight impact on NH_4-N removal is shown after 90 mins of incubation with crude oil compared with the control sample. On the other hand, CPPs (consisting of gasoline and diesel fuel in a 1:1 ratio) containing additives had a more pronounced impact on NH_4-N removal, confirming the influence of additives on the biological treatment process.

Figures 2a and 2b present the results from Stage II experiments for NH_4-N and PO_4-P removal, respectively, with shaking frequencies at 150 rpm^{-1} (thick lines) or 240 rpm^{-1} (thin lines) together with control samples.

The control samples (black lines) in figure 2 show that after 30 min of incubation, the shaking intensity (thin and thick lines) has an impact on the NH_4-N removal. However, this difference becomes insignificant after 60 mins of incubation.

The presence of 0.1 cm^3/dm^3 of CPP (a mixture of gasoline and diesel fuel) is shown in red lines. There is a significant and increasing difference in NH_4-N removal until 60 mins compared with the control sample, and the difference reduces thereafter and becomes negligible at 240 mins. No difference in the influence of shaking intensity was recorded after 90 min.

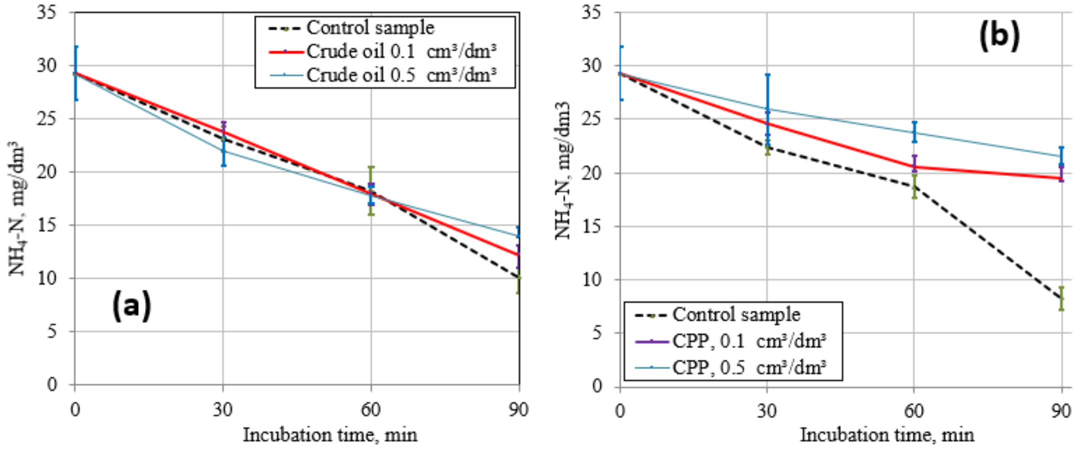

Figure 1. NH_4-N removal in test water containing 50% of RAS and 50% of effluent from primary settlers, with the presence of (1a) crude oil and (1b) commercial petroleum products (CPP) containing gasoline and diesel fuel in 1:1 proportion. Both tests had control samples (black, dotted line), with oil products of 0.1 cm^3/dm^3 (red/thick line) and 0.5 cm^3/dm^3 (blue/thin line).

The presence of 0.5 cm^3/dm^3 CPPs (blue lines) showed significant inhibition of the NH_4-N removal process, and the shaking intensity or extended incubation did not have any influence.

Figure 2b presents the results of the PO_4-P removal during the same experiments, and the observations are quite similar to NH_4-N removal. However, while only about 25% of NH_4-N was removed with the presence of 0.5 cm^3/dm^3 CPPs, over 70% removal of PO_4-P were observed.

The results show the influence of additives as well as CPPs on NH_4-N and PO_4-P removal even at concentrations as low as 0.1 cm^3/dm^3. At higher concentrations, the inhibition is very significant (a 25–75% reduction). The results also show that increasing shaking intensity reduces the impact of CPPs, indicating that increased contact between the nutrients and the biomass enhances the removal rates even in the presence of inhibiting agents. Increasing shaking intensity is also likely to increase the dispersion of CPPs, which seems to negatively influence the removal efficiencies, especially on PO_4-P removal at higher concentrations of CPPs.

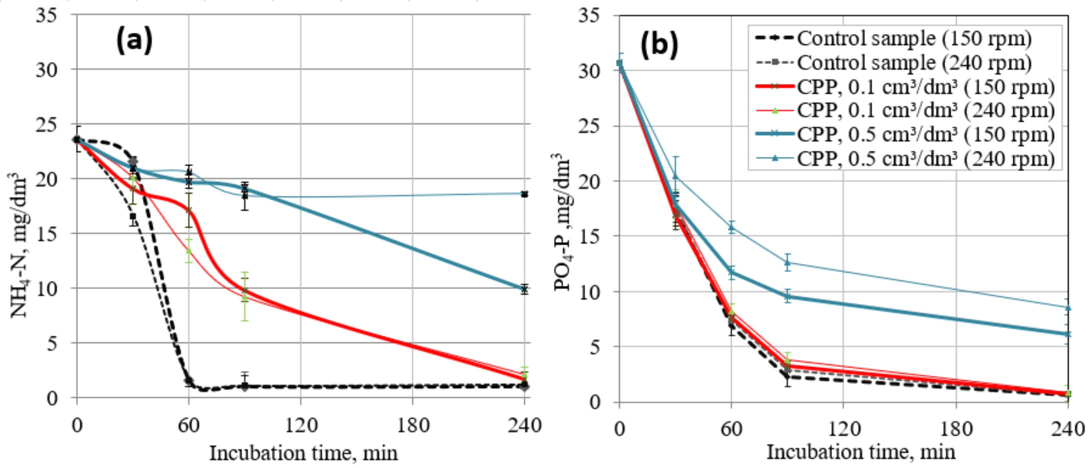

Figure 2. Influence on (a) NH_4-N and (b)PO_4-P removal at 150 rpm (thick line)and 240 rpm (thin line) of the CPPs (1:1: mixture of gasoline and diesel fuel) and shaking intensity (150 and 240 rpm) on test water (1:1 mixture of RAS and effluent from primary settling), over incubation time.

The Stage III experiments were devoted to identifying the impact of the three oil products (gasoline, diesel fuel, and hydraulic oil). Figures 3a and 3b present the results of NH_4-N removal with the presence of 0.1 cm^3/dm^3 and 0.5 cm^3/dm^3, respectively. Figure 4a and 4b present the results for PO_4-P removal.

The removal of NH_4-N when adding 0.1 cm^3/dm^3 gasoline reached only 35.0 ± 3.3%, even after 240 minutes of incubation (figure 3a), while 0.5 cm^3/dm^3 of gasoline fully inhibited the process (figure 3b). The presence of diesel fuel and hydraulic oil only slightly slowed down the biological process; after 90 mins of incubation, the concentration of NH_4-N in these samples was 2–2.5 times higher compared with the control sample. However, after 240 min of incubation, complete removal of NH_4-N was observed at 0.1 cm^3/dm^3 of these oil pollutants, while it was in the range of 2.1–3.2 mg/dm^3 when the concentration of pollutants was 0.5 cm^3/dm^3.

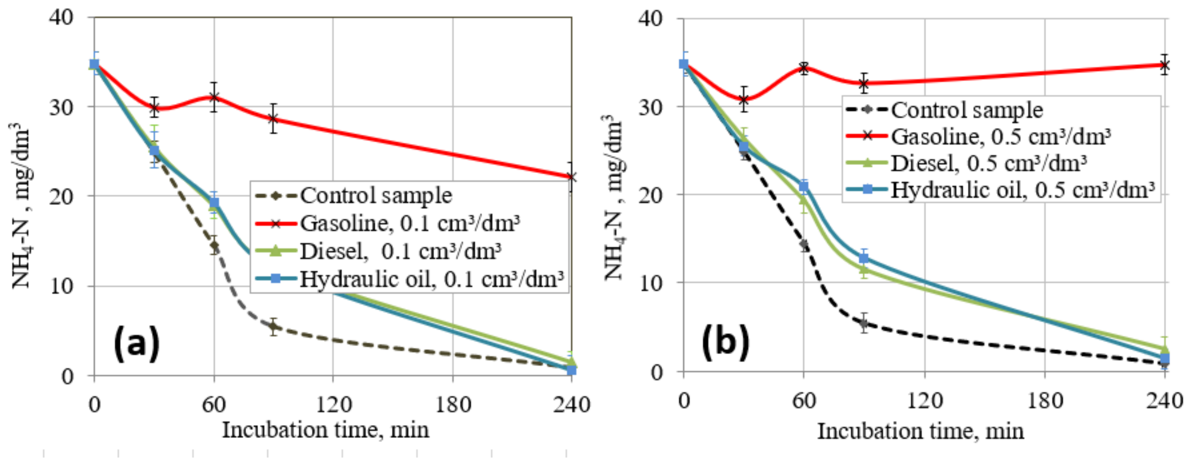

Figure 3. Influence of the concentration of various oil products (gasoline: red, diesel fuel: green, and hydraulic oil: blue) at (a) 0.1 cm^3/dm^3 and (b) 0.5 cm^3/dm^3 over incubation time on NH_4-N removal. The control sample has zero oil products (dotted line).

The results of the PO_4-P removal are given in figure 4. The inhibition trends are comparable to the NH_4-N removals shown in figure 3.

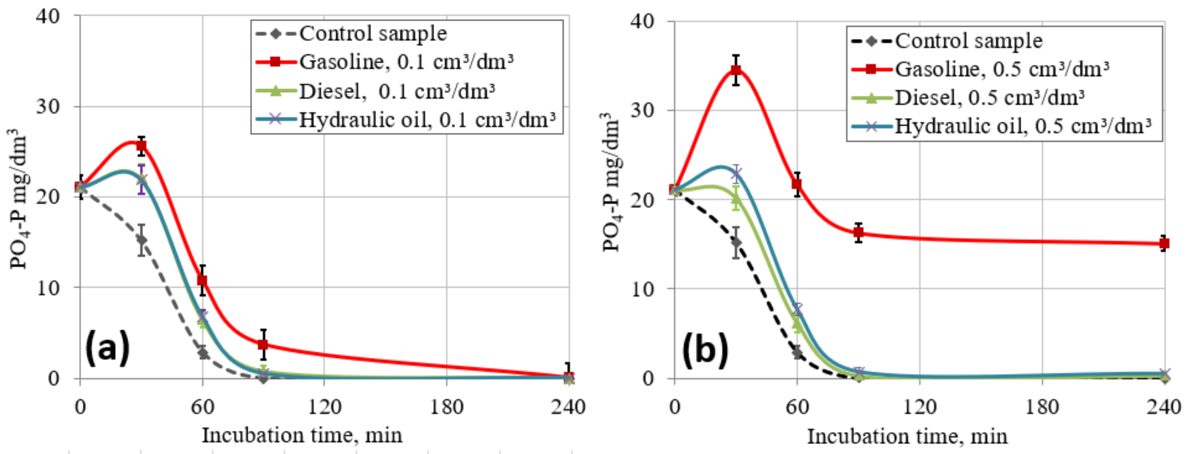

Figure 4. Influence of the concentration of various oil products (gasoline: red, diesel fuel: green, and hydraulic oil: blue) at (a) 0.1 cm^3/dm^3 and (b) 0.5 cm^3/dm^3 over incubation time on PO_4-P removal. The control sample has zero oil products (dotted line).

Figure 4 shows that PO_4-P removal is comparable to the control sample after 240 minutes of incubation. However, the presence of gasoline slows down the process to a greater extent: at 30, 60, and 90 minutes of incubation, the content of PO_4-P in samples with diesel fuel and hydraulic oil is 1.5–2.5 times higher than the control samples, while it is 1.7–4.4 times higher with the presence of gasoline.

When the gasoline content was 0.5 cm^3/dm^3, about 40% of PO_4-P was removed after 240 minutes, while a similar content of diesel fuel or hydraulic oil did not show any inhibiting impact after 90 minutes of incubation.

During the first 30 minutes of incubation of samples with oil products, an increase of PO_4-P in the solutions was observed. Increasing dosages of gasoline from 0.1 to 0.5 cm^3/dm^3, the PO_4-P in the solutions was increased by 17.0 ± 1.6 and 39.0 ± 2.8%, respectively, while for diesel fuel and hydraulic oils, they were in the range of 8.0 ± 0.8%.

As mentioned above, this study examined only aerobic conditions when PO_4-P is absorbed by microorganisms. However, the study was not intended to examine whether this PO_4-P is used simply for cell growth or is a part of a cycle based on the assimilation of PO_4-P under aeration conditions and its release from cells in the absence of oxygen. Nevertheless, the observed increase of PO_4-P (release from cells) at the beginning of the process under aeration conditions was unexpected.

We can consider two reasons for this increasing concentration of PO_4-P: the release of PO_4-P from cells due to a decrease in the concentration of oxygen and the death of some microorganisms due to the toxic effects of oil products. Further, with intensive mixing, the mixture is saturated with oxygen, the mass exchange is normalised, and phosphorus is absorbed by microorganisms in the MLSS.

Only aerobic conditions were examined during this study. Transformations of nitrogen compounds were evaluated by changes in the content of NH_4-N, regardless of whether it increases assimilation in the active sludge or undergoes nitrification. PO_4-P removal was also evaluated without distinguishing whether it was assimilated by active sludge organisms or if it was a part of the cycle based on the assimilation of PO_4-P under aerobic conditions and/or its release from cells in the absence of oxygen. In any case, this allows us to judge the impact of oil products on the biological treatment process.

The conversion of NH_4-N to nitrite and nitrate is an oxidative process that occurs in the presence of oxygen. When wastewater enters treatment facilities, the oxygen that it can capture during mixing is spent primarily on the oxidation of organic compounds; thus, nitrification is unlikely in conditions of high organic content. Therefore, it is reasonable to assume that the effluent after primary settling in this experiment contained nitrogen mainly as NH_4-N.

The results of this study confirm the previously reported trends [6, 7, 13] and provide quantitative indications of the impact of the presence of oil products in wastewater on biological nutrient removal treatment due to the inhibitory effect on the activated sludge process.

4. Conclusion

Additives introduced into commercial petroleum products (CPP) have a noticeable inhibitory effect on the conversion of NH4-N, while crude oil, which has no additives, has only a marginal effect, especially at lower concentrations. It is also established that additives in CPPs have a higher inhibitory impact than the petroleum products themselves.

This study has further documented that CPPs have a more pronounced inhibitory effect on NH_4-N removal than on the PO_4-P removal process.

Among the oil products, gasoline was found to be more inhibitory than diesel fuel or hydraulic oil on biological processes. The presence of 0.1 cm^3/dm^3 gasoline reduced the NH_4-N removal to 35.0 ± 3.3% even at incubation periods of 240 minutes. The increase of the gasoline concentration to 0.5 cm^3/dm^3 led to complete inhibition of the process.

During the first 30 minutes of incubation of samples with oil products, the concentration of PO_4-P in the solution was increased above the original levels. When adding 0.1 and 0.5 cm^3/dm^3 of gasoline, PO_4-P was increased by 17.0 ± 1.6% and 39.0 ± 2.8%, respectively. Only 8.0 ± 0.8% increase of PO_4-

P was observed with diesel fuel and hydraulic oils. This phenomenon is explained by the death of microorganisms with PO_4-P release due to the toxic effect of gasoline. Figure 5 shows the main conclusions.

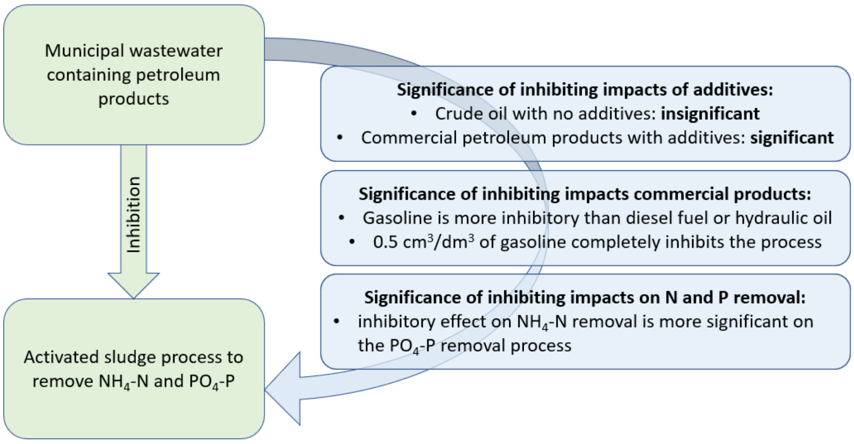

Figure 5. Graphical abstract of the main conclusions.

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