APPLICATION OF H_2O_2 TO OPTIMIZE AMMONIUM REMOVAL FROM DOMESTIC WASTEWATER

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Abstract

The paper presents the results of application of hydrogen peroxide (H_2O_2) for the optimization of the effects of ammonia nitrogen removal from domestic wastewater. The investigations were carried out at a model wastewater treatment plant consisting of a preliminary sedimentation tank and a sand filter with a horizontal flow of wastewater at a constant hydraulic load of 1.44 l/day. The efficiency of ammonia nitrogen removal was analyzed for different wastewater oxygenation levels: 0-10%, 10-20%, 20-30%, 30-40% and 40-50%, maintained by controlled application of a 0.1% H_2O_2 solution. It was demonstrated that the gradual increase in oxygen concentration in treated wastewater due to H_2O_2 dosing resulted in an increase in ammonia nitrogen removal from 39.0 to 81.2%. The best removal efficiency was obtained when the oxygenation level was in the range of 30-40%. It was also shown that application of hydrogen peroxide resulted in an effective removal of biochemical oxygen demand (BOD_5). The highest BOD_5 removal efficiency (94.3%) was obtained at the oxygenation level of 30-40%. The results indicate that oxygenation of wastewater with hydrogen peroxide can be applied for the optimization of the nitrification process in wastewater treatment plants.

Keywords: hydrogen peroxide (H_2O_2); ammonium nitrogen; domestic wastewater; wastewater treatment; nitrification

1. Introduction

Recent decades have seen an increasing interest in unconventional methods of degradation of pollutants present in wastewater, including nitrogen compounds. One of the methods which enjoy growing popularity is chemical oxidation. Among the oxidants commonly applied in the process, which include chloride and its compounds, potassium permanganate, ozone and hydrogen peroxide, only the last one does not form toxic oxidation by-products, and is thus sometimes referred to as an ecological oxidant [1]. Hydrogen peroxide is commonly applied in wastewater treatment, usually to assist biological treatment processes, since it is capable of degrading recalcitrant as well as toxic pollutants. It is applied for neutralization of cyanoalkaline wastewater and oxidation of sulfides. It has also been used for decolorization of industrial wastewater and for oxidation of recalcitrant organic compounds [2-4]. Besides, hydrogen peroxide can be used for removal of chromium as well as oxidation of aldehydes, toluene and anilines [1, 5]. Increased degradation of pollutants is achieved by joint application of hydrogen peroxide with ozone, UV radiation or iron ions [1, 6-7]; this allows for fast generation of hydroxyl radicals, which are highly reactive in the environment [8-9]. Application of this method together with biological treatment allows for neutralization of wastewater containing heavy metals, recalcitrant organics, including chlorinated hydrocarbons, phenolic compounds, pesticides, dyes and pharmaceuticals [7, 10-15].

Due to its properties, hydrogen peroxide significantly decreases the load of recalcitrant pollutants discharged to a biological treatment unit, at the same time protecting biological processes against toxic pollutants. Moreover, some concentrations of hydrogen peroxide stimulate the activity of aerobic bacteria, including nitrifiers, leading to intensification of ammonia nitrogen oxidation [1, 16]. Thus, hydrogen peroxide can be used as an alternative oxygen source in the biological treatment process, despite the fact that H_2O_2 is a strong oxidant [17]. In the investigations performed by Fiedurek [18] and Fiedurek and Gromada [19], hydrogen peroxide was automatically dosed to perform unconventional oxidation of the substrate in the process of gluconic acid production. A significant increase (over six-fold) in intracellular catalase activity was obtained while the dissolved oxygen concentration remained stable (30%+/-2%) [19]. Preliminary investigations of oxygen generation from 0.1% and 0.2% H_2O_2 solutions by microorganisms present in wastewater indicate that this procedure can be a convenient and inexpensive method of wastewater oxidation during ammonia nitrogen removal [20].

Ammonia nitrogen present in wastewater is removed in the process of nitrification [21]. *Nitrosomonas*, *Nitrosococcus*, *Nitrosolobus*, *Nitrosospira* and *Nitrosovibrio* participate in stage I of nitrification, while *Nitrobacter*, *Nitrococcus* and *Nitrospira* take part in stage II of the process [22]. Nitrification performance depends on many conditions, including temperature, pH, load of organic pollutants, presence and concentration of toxic substances, and concentration of nitrogen in the inflowing wastewater. Still, the most important factor is dissolved oxygen concentration [23]. The minimal dissolved oxygen concentration for proper performance of nitrification should be at least 1-2 mg O_2/l. Higher concentrations enhance nitrification performance [24].

The investigation of nitrogen removal optimization in wastewater treatment, also in constructed wetlands, has been one of the leading research directions in the recent years [25-39]. The methods of wastewater oxidation used so far for nitrogen removal in wastewater treatment plants (usually with air compressors) are energy-consuming. High capital and operating costs of conventional solutions result in continuous search for aeration methods which would be inexpensive in terms of investment and operation.

The aims of this study were to evaluate the potential of application of hydrogen peroxide for the optimization of removal of ammonia nitrogen from domestic wastewater and to define the optimum conditions for nitrification with the unconventional method of wastewater oxidation using a 0.1% solution of hydrogen peroxide (H_2O_2).

2. Materials and methods

2.1. Characteristics of experimental setup

The investigations were performed in a laboratory-scale model of a wastewater treatment plant consisting of a primary sedimentation tank (ST) and a sand filter with a horizontal subsurface flow of sewage - HF (A) at a constant flow of 1.44 l/day (which corresponded to hydraulic load of 0,016 m^3/m^2/day) (Fig. 1).

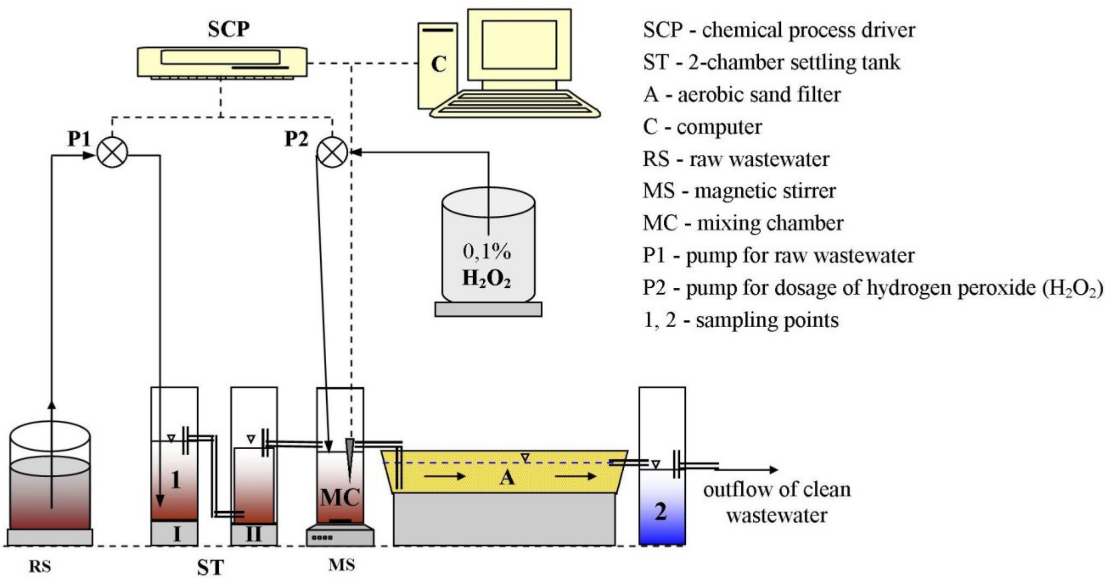

Fig.1. Schematic of the wastewater treatment plant model (WWTP)

The experimental set was unplanted, since the main research objective was to evaluate the impact of H_2O_2 on the efficiency of ammonia nitrogen removal in a filter without plants.

Table 1 summarizes the parameters of the component parts of the wastewater treatment plant model. The surface area of the sand filter was 0.091m^2 and its depth was 0.06 m. The slope of the bottom was 1% in the direction of sewage outflow. The substrate of the filter was coarse sand (ϕ=1-2 mm).

Tab.1. Parameters of the wastewater treatment plant model

Parameters	Units	Primary sedimentation tank chambers I and II	Sand filter
Length [L]	[m]	-	0.390
Width [W]	[m]	-	0.235
Diameter [D]	[m]	0.075	-
Total depth [H]	[m]	0.240	0.060
Height of wastewater level (h)	[m]	0.160	0.050
Area [A]	[m^2]	-	0.091
Total volume [V]	[l]	1.059	5.499
Active volume [V_{cz}]*	[l]	0.707	4.582

2.2. Experimental procedures

During the investigations, an automatic dosing unit was used for dosing the 0.1% solution of H_2O_2 and for controlling the dissolved oxygenation level in treated wastewater in the range of 0-10%, 10-20%, 20-30%, 30-40% and 40-50%. The investigations were carried out for 10 weeks (2 weeks with each level of wastewater oxidation).

The dissolved oxygen (DO) concentration of the treated wastewater was measured with an Oxyferm 120 electrode (Hamilton Comp.). The value of the reading was expressed as percentage of the initial level of saturation. The method of automatic H_2O_2 dosing and adjustment of the selected oxygenation level of the substrate was adapted from Fiedurek [18]. Consumption of hydrogen peroxide re-calculated for the 1% solution varied from 5 to 25 ml/day and was dependent on the adopted level of wastewater aeration. The highest consumption of H_2O_2 was observed when the concentration of dissolved oxygen in the inflowing wastewater was 20-30%. The H_2O_2 solution was dosed to the mixing chamber (MC) upstream of the sand filter (A) (Fig. 1). Real wastewater after mechanical treatment was used.

2.3. Wastewater characteristics

During the whole investigation real domestic wastewater after mechanical treatment was used (Tab. 2). The wastewater was collected form outflow of two chambers septic tank in household wastewater treatment plant with average flow of 0.6 m^3/day.

Tab. 2. Average values (± standard deviation) of the selected parameters in the domestic wastewater after mechanical stage

Temperature [˚C]	pH	TN (mg/l)	NH_4^+–N (mg/l)	NO_3^-–N (mg/l)	NO_2^-–N (mg/l)	BOD_5 (mg/l)
18.6 ± 0.5	7.59-7.83	133.3 ± 9.1	116.5 ± 8.3	2.30 ± 4.22	0.40± 0.71	67.0 ±18.7

The wastewater discharged to pilot plant was characterized by relatively low concentration of organic matter expressed in BOD_5 and high concentration of total nitrogen mainly in form of the ammonia nitrogen. In consequence the mean ratio of BOD_5/ TN was very low and equal to 0.5 (Tab. 2).

2.4. Analytical methods

The samples were taken at two points of the pilot wastewater treatment plant model (Fig. 1). The following parameters were measured: temperature, pH, concentrations of ammonia nitrogen, nitrite nitrogen, nitrate nitrogen and total nitrogen, and BOD_5 for the different oxygenation levels. Temperature and pH were determined using a multiparameter measuring device Multi 340i produced by WTW. The concentration of ammonia nitrogen was measured with an MPM 2010 photometer produced by WTW, and the concentrations of nitrite and nitrate nitrogen – with an LF 300 photometer produced by Slandi. The total nitrogen concentration was determined using a PC spectro spectrophotometer manufactured by AQUALYTIC, after oxidation of the sample at 100°C in a CR4200 thermo reactor from WTW. BOD_5 was measured by the dilution method using Oxi 538 from WTW. Variance analysis of the results (ANOVA) was performed using STATISTICA 10. Division into homogenous samples was performed using the Tukey procedure at the significance level α=0.05.

3. Results and discussion

3.1. Effects of the application of H_2O_2 on ammonium nitrogen removal

In all the experimental series, real wastewater of a similar chemical composition was used (Tab. 3).

Tab. 3. Characteristics of wastewater with different levels of oxygenation

Parameters	Level of wastewater oxygenation (% O_2)									
	0-10		10-20		20-30		30-40		40-50	
	In	Out	In	Out	In	Out	In	Out	In	Out
Temperature [˚C]	18.3	18.2	19.2	18.9	19.0	18.7	18.3	17.8	18.3	18.1
pH	7.6-7.8	7.9-8.1	7.6-7.7	8.1-8.2	7.8-7.8	7.5-7.6	7.7-7.8	7.5-7.6	7.6-7.7	7.4-7.5
Ammonium nitrogen [mg/l]	117.0	80.0	109.0	74.9	120.0	38.0	117.0	22.0	119.0	29.5
Nitrate nitrogen [mg/l]	0.11	0.11	0.11	12.20	1.15	63.20	8.36	85.50	1.81	84.50
Nitrite nitrogen [mg/l]	0.09	0.02	0.06	0.83	1.22	7.65	0.59	2.35	0.11	4.79
Total nitrogen [mg/l]	133.0	91.0	129.5	100.5	128.5	107.0	134.0	117.0	142.0	126.5
BOD_5 [mg/l]	47.8	24.1	55.0	12.5	86.0	12.7	77.4	4.4	69.0	61.4

The pH of discharged wastewater fluctuated insensibly between 7.6 and 7.8. Also the temperature of wastewater during the investigations varied insignificantly in the range from 18.3 to 19.2°C. Both monitored parameters were close to the nitrification process optimum (Tab. 3). The concentrations of ammonia nitrogen, total nitrogen and BOD_5 in the inflow wastewater were 109.0-120.0; 128.5-142.0; and 47.8-86.0 mg/l, respectively. The only significant variable was oxygen concentration in the wastewater discharged to the pilot plant model (sand filter). At the same time, it was noted that the increase in the oxygenation level resulted in higher concentrations of nitrates and nitrites in wastewater (Tab. 3).

The efficiency of ammonia nitrogen removal in the WWTP at different ranges of oxygenation with a division into uniform groups is presented in Figure 2.

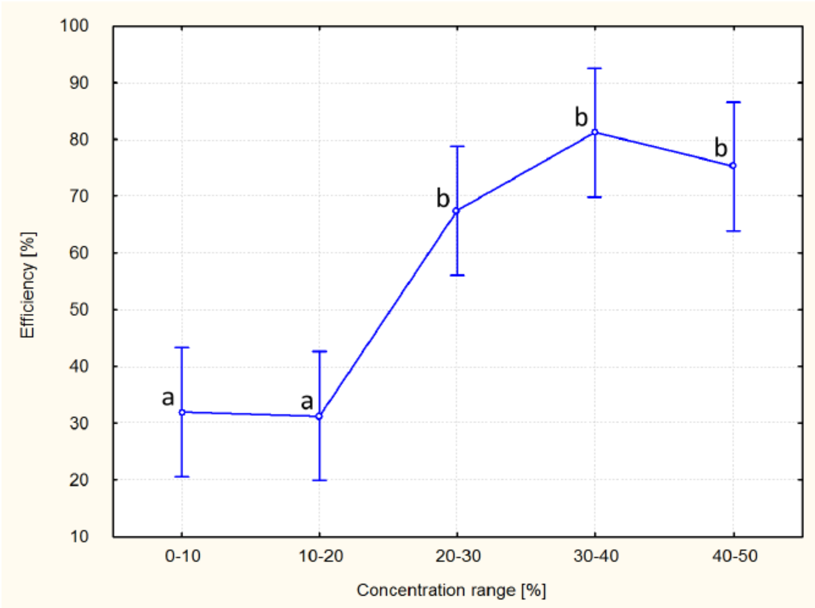

Fig. 2. The influence of the oxygenation level on the efficiency of ammonia nitrogen removal; the significances of differences between mean values are marked with letters a, b at p≤0.05

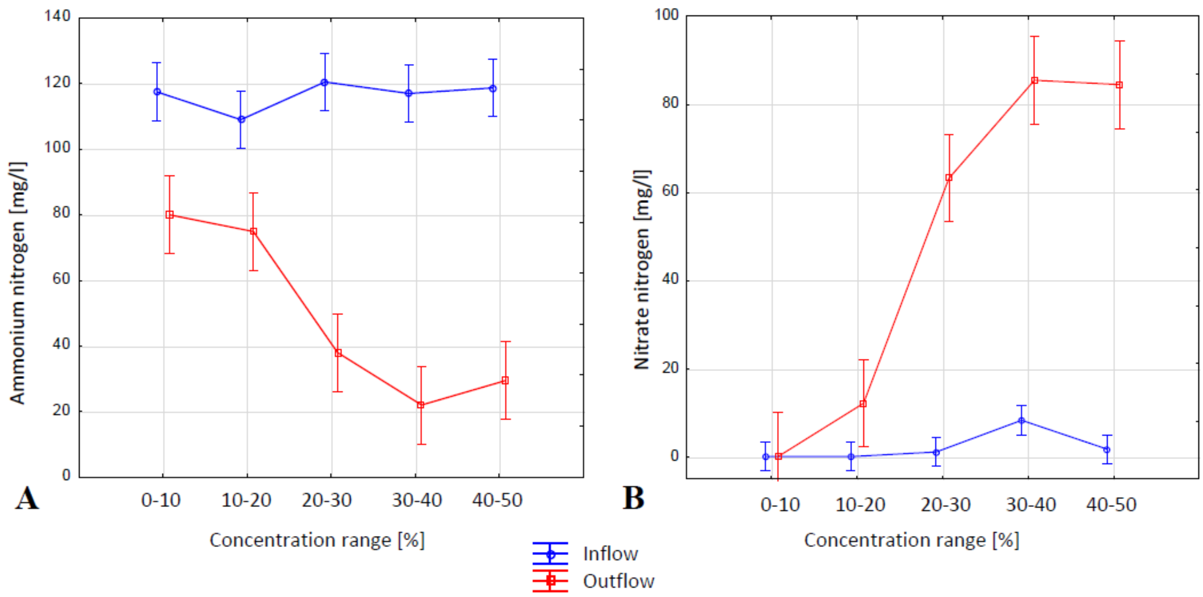

Fig. 3. Concentration of ammonia nitrogen (A) and nitrate nitrogen (B) at the inflow and outflow at different oxygenation levels of treated wastewater

Results for oxygenation up to 20%

The oxygenation levels 0-10% and 10-20% brought similar effects in terms of ammonia nitrogen depletion in wastewater flowing through the sand filter. The decrease in concentration was slightly higher than 31% (Fig. 2), and the concentration of ammonia nitrogen downstream of the sand filter was at a fairly high level of 75-80 mg/l (Fig. 3A). An analysis of pH and temperature fluctuations did not show any significant changes which could confirmed enhancement of nitrification process. Moreover the small change in wastewater pH towards alkaline could have resulted from ammonification of organic nitrogen. In this condition of high supply of N-NH_4^+ ions, the achieved results could be explained by the too low oxygen concentration. According to many authors, ammonia ions are known as inhibitors of nitrification [40-41]. Also, the character of wastewater flow through the filter (horizontal - plug flow) certainly has not enhance the oxygenation and in consequence not favor the nitrification process. Despite the fact that the filter surface was not isolated from the air, horizontal flow of wastewater enabled fast and uniform oxygen supply to microbial cells, limiting the rate of many biochemical transformations, including ammonia nitrogen oxidation [25, 42]. The low nitrification efficiency can also be explained by slow growth of some groups of nitrifiers. Directly after certain environmental conditions are established, the number of nitrifying bacteria is low and increases with time. A stable level is usually reached after several days [43-44].

Results for oxygenation over 20%

An analysis of achieved results indicates that the efficiency of ammonia nitrogen removal increased at higher levels of oxygenation. At the oxygenation level of 20-30%, removal efficiency of ammonia nitrogen in the pilot plant was equal to 68.5%, at the level of 30-40% it was 81.2%, and at the level of 40-50% - 75.1% (Fig. 2). Statistical analysis indicated that these values significantly differed from the results obtained at the two lower oxygenation levels discussed above (Fig. 2). The results of our study are in accordance with previous study by Fiedurek and Gromada [19], whose observed that a significant (over 6-fold) increase in intracellular catalase activity was achieved at a stable dissolved O_2 concentration (30% ± 2%).

So far it has been demonstrated that the efficiency of ammonia nitrogen removal in single-stage horizontal flow (HF) constructed wetlands (CWs) does not exceed 54%, for high NH_4-N concentrations [45]. According to Vymazal [42], the 50% threshold in such CW systems cannot be exceeded because of low oxygen transfer which sets a limit on nitrification [37, 39, 46-48]. Much more higher removal efficiency of ammonium nitrogen had been confirmed for hybrid and vertical flow CWs. In such system it is possible to achieve very effective removal of nitrogen compounds up to 90% due to better oxygenation which is achieved by changeable flow in hybrid system or by intermittent discharge in VF system or by force aerated beds (FAB) [36, 49-52].

According many authors aeration of wastewater before discharge to HF beds could be applied to overcome problem of lack of oxygen [53-54]. A study conducted by Jamieson et al. [55] in a model wastewater treatment system indicated that nitrogen removal efficiency could be increased from 50.5 to 93.3% by aeration with compressed air. Nitrogen removal efficiencies similar to those obtained in the present study at an oxygenation level of 30-40% were reported by Ju et al. [29] in their model-scale investigations performed with a vertical flow filter in a novel electrolysis-integrated tidal flow CW system. Liu et al. [56] achieved 97% efficiency of nitrogen removal in lab-scale investigations using zeolites as substrates. According to Araya et al. [57] combination of zeolite as the support medium and the aeration strategy with a suggested cycle of 4 h/d in a single CW demonstrated the importance of aeration for the regeneration of adsorption sites and the maintenance of the COD and NH^{+4}−N removal efficiencies above 70% over time.

In our studies application of higher doses of hydrogen peroxide and maintaining a wastewater oxygenation level of 30-40% or 40-50% had the best effect on the activity of nitrifying bacteria and ammonia nitrogen oxidation. Under these conditions, the ammonia nitrogen concentration decreased to an average level of 22.0-29.5 mg/l at the outflow (Fig. 3A). At the same time, at the oxygenation level of 30-50%, the concentration of nitrates reached a maximum (Fig. 3B).

The obtained results indicate clearly that application of H_2O_2 resulted in the optimization of the nitrification process in the analyzed WWTP model.

3.2. Effects of H_2O_2 application on BOD_5 removal

The study also confirmed that the application of hydrogen peroxide leads to an effective decrease in BOD_5 concentration. The efficiency of BOD_5 removal in the wastewater treatment plant model at different ranges of oxygenation, with a division into uniform groups, is presented in Figure 4. The Anova confirmed significant differences in BOD_5 removal efficiency at the different oxygenation levels. The Tukey test indicated that significantly the highest efficiency of BOD_5 removal (94.3%) and the lowest BOD_5 concentration (4.4 mg/l) were obtained at the oxygenation level of 30-40% (Fig. 4, 5). At the aeration level of 40-50%, the decrease of BOD_5 removal efficiency to 11% was observed and the concentration of BOD_5 at the effluent increased considerably (Fig. 4, 5). One of potential explanations is that increasing the dose of H_2O_2 over 40% most probably inhibited the biological processes, due to oxygenation of microbes. Too high concentration of H_2O_2 could lead to lysis of cells and in the consequence the organic matter content increases. Also the remain fraction of relatively hardly degradable organics and Org-N could be decomposed to less complexes compounds in such conditions and during the analytical procedure could be recognized as increased of BOD_5 concentration [4, 7].

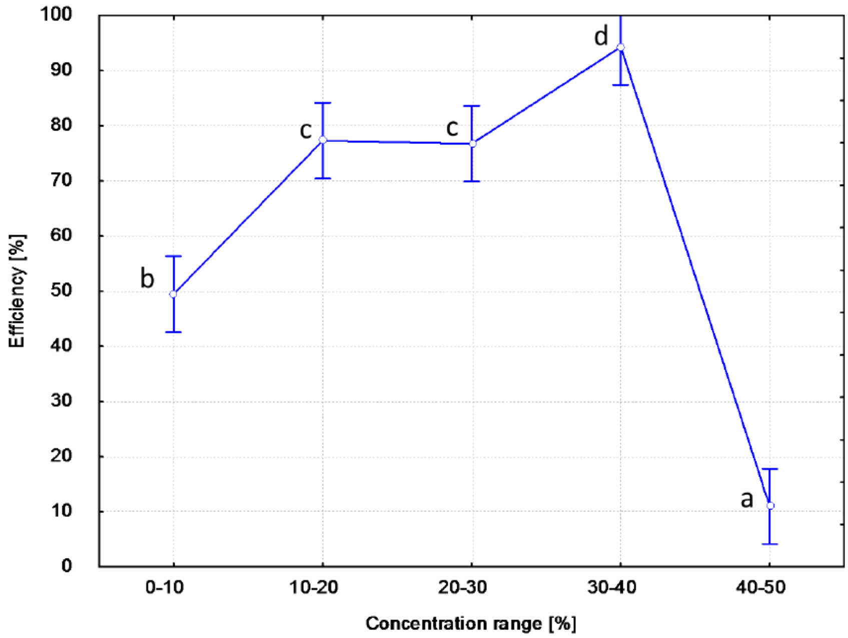

Fig. 4. The influence of oxygenation level on the efficiency of BOD_5 removal; the significances of differences between mean values are marked with letters a, b, c, d at $p \leq 0.05$

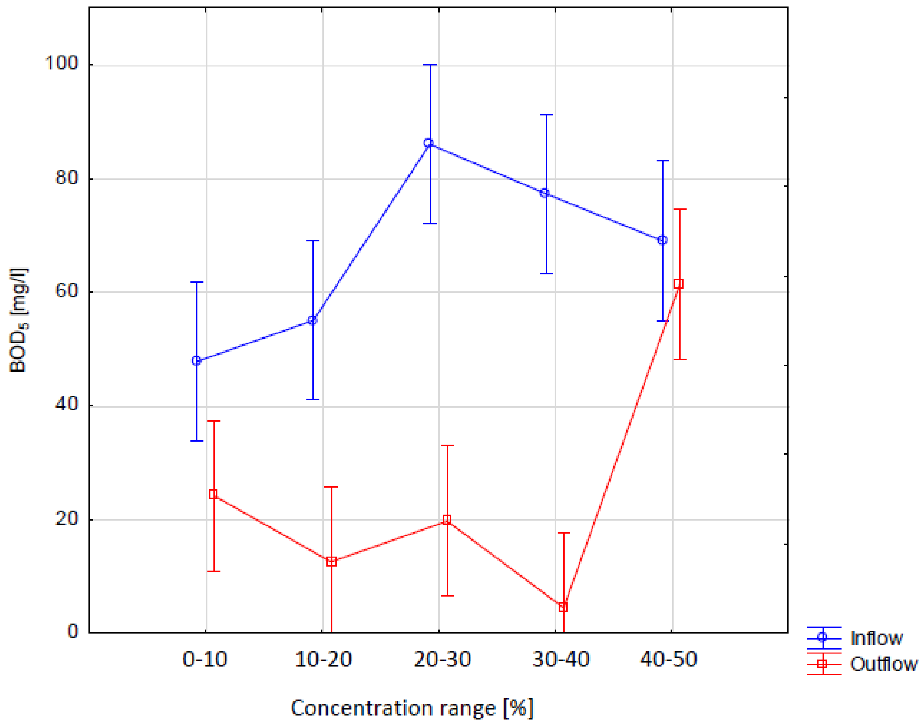

Fig. 5. Concentration of BOD_5 at inflow and outflow at different oxygenation levels of treated wastewater

During the conventional processes of pollutants removal mineralization of organic matter demands 1 mg of oxygen per 1 mg of decompose organic matter expressed as BOD_5, in the same time for nitrification of 1mg N-NH4 is required about 4.3 mg of oxygen. Thus many authors arise the problem of competitions between mineralization of organics (heterotrophic bacteria) and nitrification process (autotrophic bacteria) in many wastewater treatment plants. Such statement is particularly true in low –coats systems for wastewater treatment like treatment wetlands technology [41, 58]. In such systems due to limited oxygen conditions both organics and oxidation of ammonia nitrogen can be limited and insufficient [49].

The effect of BOD_5 removal in the analyzed model at the oxygenation level of 30-40% (94.3%) was higher than that obtained during long-term operation of single-stage HF systems [42, 45] and comparable to that obtained in hybrid VF-HF systems [59;], VF-VF-HF systems [59] and VF-HF systems at the initial stage of operation, without plants [61].

The efficiencies of BOD_5 removal in constructed wetlands treating different types of wastewater are usually high, at the level of 90-99%, while the nitrogen removal could varied significantly from 20 up to 90% [41, 49]. Hybrid constructed wetlands have been reported to effectively remove organic matter also from high-strength wastewater [39, 49] as well as in case of unfavorable C:N ratio [36].

3. 3. Economic aspects of H_2O_2 application

The results of the study indicate that hydrogen peroxide can be an attractive alternative to conventional methods of wastewater aeration, bringing similar effects but at a lower energy consumption. Evaluation of the actual costs of the application of the two types of methods is quite complicated and has to be based on an assumed effect. Each of the methods has a specific character and is defined by completely different factors. In the case of traditional aeration, the major factor is energy consumption during aeration defined as aeration capacity per unit power [62]. Assuming that the expected effect is to achieve a strictly defined optimum level of oxygenation (40%), this factor varies from 0.25 to 0.30 kWh/m^3. It is worth noting that in practice the capacity of aerators as well as the efficiency of aeration depend on a number of indirect factors, such as pressure, temperature, depth and technology of air injecting as well as the level of consumption per unit aeration [63].

In the case of hydrogen peroxide dosing, the basic characterizing factor is reagent consumption. Basing on the experience gained in this study, it can be concluded that to obtain the oxygenation level of 30-40% approximately 0.25 kg/m^3 of 50% hydrogen peroxide has to be used. Calculations based on the average prices of energy and hydrogen peroxide indicate that the costs of H_2O_2 dosing are higher than aeration with compressed air. These estimations can significantly change with time and be different for different countries. Moreover, they are only based on operation costs and do not include capital or amortization charges that are considerably higher in the case of aeration with compressed air.

Apart from various applications in chemical degradation of the pollutants present in wastewater, hydrogen peroxide can also be used to significantly aid biochemical treatment. Due to the fact that microorganisms are able to produce oxygen from a 0.1% solution of H_2O_2, dosing of hydrogen peroxide can be a convenient and cost-effective way of intensifying nitrification at the early stages of wastewater treatment, when wastewater contains low oxygen concentrations [20]. As it was indicated earlier, increasing of hydrogen peroxide doses combined with filtration of wastewater improves the efficiency of nitrogen removal. The highest removal efficiency was obtained at the oxygenation levels of 30-40% and 40-50%. Because the investigations were performed in a model-scale set-up and the investigation conditions were similar during the various experiments, it can be concluded that the decrease in ammonia nitrogen concentration in wastewater resulted from the application of hydrogen peroxide in the form of a 0.1% solution and was not related to other factors such as the grain size of the filter material or filtration rate [64].

The pilot investigations of the wastewater treatment plant model with a sand filter indicate that aeration with hydrogen peroxide can be used to optimize nitrification and increase ammonia nitrogen and BOD_5 removal efficiency at different WWTPs. Application of this method could also bring positive effects for WWTPs with activated sludge [65-66] as well as sand filters or drainage systems (which are known to have a low ammonia nitrogen removal efficiency). However, application of this method would require further investigations under laboratory and technical-scale conditions.

Recently there is an increasing interest in multistage constructed wetlands all over the world. The systems with alternately vertical and horizontal flow beds, are capable of effective removal of nitrogen and organic matter, fulfilling the criteria of sustainability development [67]. Application of H_2O_2 in multistage wetland systems as well as in other technological solutions of wastewater treatment can optimize ammonia removal and help to control eutrophication of surface waters.

5. Conclusions

Hydrogen peroxide can be applied as a source of oxygen for microorganisms and as an agent intensifying biochemical transformations during ammonia nitrogen oxygenation in the nitrification process.

In the present study, the efficiency of ammonia nitrogen removal in the sand filter with a horizontal flow of wastewater was directly dependent on the dose of H_2O_2 and thus the level of wastewater oxygenation. The highest removal efficiency of ammonia nitrogen was obtained at the oxygenation levels of 30-40% and 40-50%, while the lowest removal efficiency was obtained at 0-10% and 10-20% oxygenation. The differences in removal efficiency between the various oxygenation levels were statistically significant. Application of high doses of hydrogen peroxide in combination with wastewater filtration can result in ammonia nitrogen removal exceeding 80%.

It was demonstrated that application of hydrogen peroxide also results in effective removal of BOD_5. The highest BOD_5 removal efficiency (94.3%) was obtained at the oxygenation level of 30-40%, and such level of oxygenation is advanced as optimal for both organic and ammonium nitrogen removal in WWTP which needs the improvement towards fulfill the requirements of final effluent.

Acknowledgments

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