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APPLICATION OF H₂O₂TO OPTIMIZE AMMONIUM REMOVAL

2 FROM DOMESTIC WASTEWATER

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24 25**Abstract**

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The paper presents the results of application of hydrogen peroxide (H_2O_2) for the optimization of 27the effects of ammonia nitrogen removal from domestic wastewater. The investigations were carried 28out at a model wastewater treatment plant consisting of a preliminary sedimentation tank and a sand 29filter with a horizontal flow of wastewater at a constant hydraulic load of 1.44 l/day. The efficiency of 30ammonia nitrogen removal was analyzed for different wastewater oxygenation levels: 0-10%, 10-20%, 3120-30%, 30-40% and 40-50%, maintained by controlled application of a 0.1% H_2O_2 solution. It was 32demonstrated that the gradual increase in oxygen concentration in treated wastewater due to H_2O_2 33dosing resulted in an increase in ammonia nitrogen removal from 39.0 to 81.2%. The best removal 34efficiency was obtained when the oxygenation level was in the range of 30-40%. It was also shown 35that application of hydrogen peroxide resulted in an effective removal of biochemical oxygen demand 36(BOD $_5$). The highest BOD $_5$ removal efficiency (94.3%) was obtained at the oxygenation level of 30-3740%. The results indicate that oxygenation of wastewater with hydrogen peroxide can be applied for 38the optimization of the nitrification process in wastewater treatment plants.

40 Keywords: hydrogen peroxide (H_2O_2); ammonium nitrogen; domestic wastewater; wastewater 41 treatment; nitrification

421. Introduction

Recent decades have seen an increasing interest in unconventional methods of degradation 44of pollutants present in wastewater, including nitrogen compounds. One of the methods which 45enjoy growing popularity is chemical oxidation. Among the oxidants commonly applied in the

46process, which include chloride and its compounds, potassium permanganate, ozone and 47hydrogen peroxide, only the last one does not form toxic oxidation by-products, and is thus 48sometimes referred to as an ecological oxidant [1]. Hydrogen peroxide is commonly applied 49in wastewater treatment, usually to assist biological treatment processes, since it is capable of 50degrading recalcitrant as well as toxic pollutants. It is applied for neutralization of 51cyanoalkaline wastewater and oxidation of sulfides. It has also been used for decolorization of 52industrial wastewater and for oxidation of recalcitrant organic compounds [2-4]. Besides, 53hydrogen peroxide can be used for removal of chromium as well as oxidation of aldehydes, 54toluene and anilines [1, 5]. Increased degradation of pollutants is achieved by joint application 55of hydrogen peroxide with ozone, UV radiation or iron ions [1, 6-7]; this allows for fast 56generation of hydroxyl radicals, which are highly reactive in the environment [8-9]. 57Application of this method together with biological treatment allows for neutralization of 58wastewater containing heavy metals, recalcitrant organics, including chlorinated 59hydrocarbons, phenolic compounds, pesticides, dyes and pharmaceuticals [7, 10-15].

Due to its properties, hydrogen peroxide significantly decreases the load of recalcitrant 61pollutants discharged to a biological treatment unit, at the same time protecting biological 62processes against toxic pollutants. Moreover, some concentrations of hydrogen peroxide 63stimulate the activity of aerobic bacteria, including nitrifiers, leading to intensification of 64ammonia nitrogen oxidation [1, 16]. Thus, hydrogen peroxide can be used as an alternative 65oxygen source in the biological treatment process, despite the fact that H₂O₂ is a strong 66oxidant [17]. In the investigations performed by Fiedurek [18] and Fiedurek and Gromada 67[19], hydrogen peroxide was automatically dosed to perform unconventional oxidation of the 68substrate in the process of gluconic acid production. A significant increase (over six-fold) in 69intracellular catalase activity was obtained while the dissolved oxygen concentration 70remained stable (30%+/-2%) [19]. Preliminary investigations of oxygen generation from 0.1% 71and 0.2% H₂O₂ solutions by microorganisms present in wastewater indicate that this 72procedure can be a convenient and inexpensive method of wastewater oxidation during 73ammonia nitrogen removal [20].

Ammonia nitrogen present in wastewater is removed in the process of nitrification [21]. 75*Nitrosomonas, Nitrosococcus, Nitrosolobus, Nitrosospira* and *Nitrosovibrio* participate in 76stage I of nitrification, while *Nitrobacter, Nitrococcus* and *Nitrospira* take part in stage II of 77the process [22]. Nitrification performance depends on many conditions, including 78temperature, pH, load of organic pollutants, presence and concentration of toxic substances, 79and concentration of nitrogen in the inflowing wastewater. Still, the most important factor is

80dissolved oxygen concentration [23]. The minimal dissolved oxygen concentration for proper 81performance of nitrification should be at least 1-2 mg O_2/I . Higher concentrations enhance 82nitrification performance [24].

83 The investigation of nitrogen removal optimization in wastewater treatment, also in 84constructed wetlands, has been one of the leading research directions in the recent years [25-8539]. The methods of wastewater oxidation used so far for nitrogen removal in wastewater 86treatment plants (usually with air compressors) are energy-consuming. High capital and 87operating costs of conventional solutions result in continuous search for aeration methods 88which would be inexpensive in terms of investment and operation.

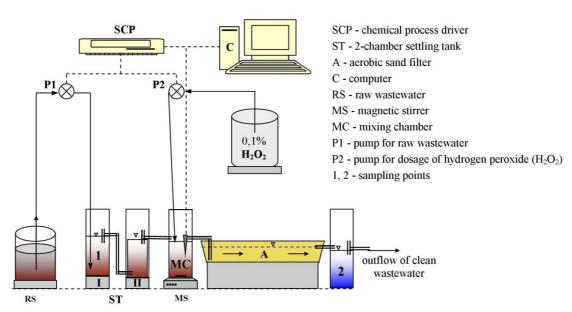
The aims of this study were to evaluate the potential of application of hydrogen peroxide 90 for the optimization of removal of ammonia nitrogen from domestic wastewater and to define 91 the optimum conditions for nitrification with the unconventional method of wastewater 92 oxidation using a 0.1% solution of hydrogen peroxide (H_2O_2).

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942. Materials and methods

952.1. Characteristics of experimental setup

The investigations were performed in a laboratory-scale model of a wastewater treatment 97plant consisting of a primary sedimentation tank (ST) and a sand filter with a horizontal 98subsurface flow of sewage - HF (A) at a constant flow of 1.44 l/day (which corresponded to 99hydraulic load of $0.016 \text{ m}^3/\text{m}^2/\text{day}$) (Fig. 1).



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

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102 The experimental set was unplanted, since the main research objective was to evaluate the 103impact of H₂O₂ on the efficiency of ammonia nitrogen removal in a filter without plants.

104 Table 1 summarizes the parameters of the component parts of the wastewater treatment 105plant model. The surface area of the sand filter was 0.091m² and its depth was 0.06 m. The 106slope of the bottom was 1% in the direction of sewage outflow. The substrate of the filter was 107coarse sand (ϕ =1-2 mm).

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Tab.1. Parameters of the wastewater treatment plant model

Parameters	Units	Primary	Sand filter	
		sedimentation tank		
		chambers I and II		
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]	[1]	1.059	5.499	
Active volume [V _{cz}]*	[1]	0.707	4.582	

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1112.2. Experimental procedures

112 During the investigations, an automatic dosing unit was used for dosing the 0.1% solution 113of H₂O₂ and for controlling the dissolved oxygenation level in treated wastewater in the range 114of 0-10%, 10-20%, 20-30%, 30-40% and 40-50%. The investigations were carried out for 10 115weeks (2 weeks with each level of wastewater oxidation).

The dissolved oxygen (DO) concentration of the treated wastewater was measured with an 117Oxyferm 120 electrode (Hamilton Comp.). The value of the reading was expressed as 118percentage of the initial level of saturation. The method of automatic H₂O₂ dosing and 119adjustment of the selected oxygenation level of the substrate was adapted from Fiedurek [18]. 120Consumption of hydrogen peroxide re-calculated for the 1% solution varied from 5 to 25 121ml/day and was dependent on the adopted level of wastewater aeration. The highest 122consumption of H₂O₂ was observed when the concentration of dissolved oxygen in the 123inflowing wastewater was 20-30%. The H₂O₂ solution was dosed to the mixing chamber (MC) 124upstream of the sand filter (A) (Fig. 1). Real wastewater after mechanical treatment was used. 125

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1272.3. Wastewater characteristics

128 During the whole investigation real domestic wastewater after mechanical treatment was 129used (Tab. 2). The wastewater was collected form outflow of two chambers septic tank in 130household wastewater treatment plant with average flow of 0.6 m³/day.

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

Temperature	nII.	TN	$\mathrm{NH_4}^+\!\!-\!\!\mathrm{N}$	NO ₃ -N	$NO_2^ -N$	BOD_5	
[°C]	pН	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(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	

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135 The wastewater discharged to pilot plant was characterized by relatively low concentration 136of organic matter expressed in BOD₅ and high concentration of total nitrogen mainly in form 137of the ammonia nitrogen. In consequence the mean ratio of BOD₅/ TN was very low and equal 138to 0.5 (Tab. 2).

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1402.4. Analytical methods

The samples were taken at two points of the pilot wastewater treatment plant model (Fig. 1421). The following parameters were measured: temperature, pH, concentrations of ammonia 143nitrogen, nitrite nitrogen, nitrate nitrogen and total nitrogen, and BOD₅ for the different 144oxygenation levels. Temperature and pH were determined using a multiparameter measuring 145device Multi 340i produced by WTW. The concentration of ammonia nitrogen was measured 146with an MPM 2010 photometer produced by WTW, and the concentrations of nitrite and 147nitrate nitrogen – with an LF 300 photometer produced by Slandi. The total nitrogen 148concentration was determined using a PC spectro spectrophotometer manufactured by 149AQUALYTIC, after oxidation of the sample at 100°C in a CR4200 thermo reactor from 150WTW. BOD₅ was measured by the dilution method using Oxi 538 from WTW. Variance 151analysis of the results (ANOVA) was performed using STATISTICA 10. Division into 152homogenous samples was performed using the Tukey procedure at the significance level $153\alpha = 0.05$.

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1573. Results and discussion

1583.1. Effects of the application of H₂O₂ on ammonium nitrogen removal

159 In all the experimental series, real wastewater of a similar chemical composition was used 160(Tab. 3).

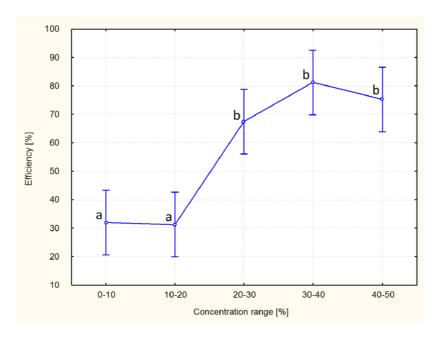
161 Tab. 3. Characteristics of wastewater with different levels of oxygenation

	Level of wastewater oxygenation (% O ₂)									
Parameters	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
pН	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

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163 The pH of discharged wastewater fluctuated insensibly between 7.6 and 7.8. Also the 164temperature of wastewater during the investigations varied insignificantly in the range from 16518.3 to 19.2°C. Both monitored parameters were close to the nitrification process optimum 166(Tab. 3). The concentrations of ammonia nitrogen, total nitrogen and BOD₅ in the inflow 167wastewater were 109.0-120.0; 128.5-142.0; and 47.8-86.0 mg/l, respectively. The only 168significant variable was oxygen concentration in the wastewater discharged to the pilot plant 169model (sand filter). At the same time, it was noted that the increase in the oxygenation level 170resulted in higher concentrations of nitrates and nitrites in wastewater (Tab. 3).

171 The efficiency of ammonia nitrogen removal in the WWTP at different ranges of 172oxygenation with a division into uniform groups is presented in Figure 2.



175 Fig. 2. The influence of the oxygenation level on the efficiency of ammonia nitrogen removal; 176 the significances of differences between mean values are marked with letters a, b at $p \le 0.05$ 177

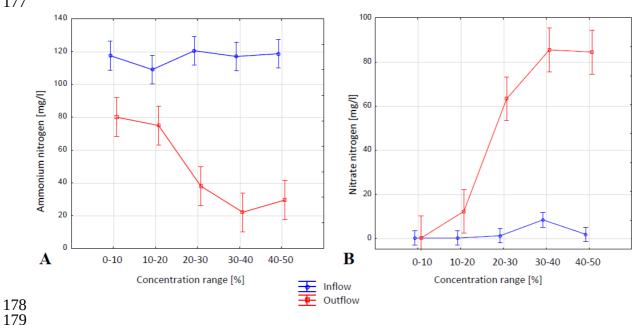


Fig. 3. Concentration of ammonia nitrogen (A) and nitrate nitrogen (B) at the inflow and outflow at different oxygenation levels of treated wastewater

183Results for oxygenation up to 20%

The oxygenation levels 0-10% and 10-20% brought similar effects in terms of ammonia 185nitrogen depletion in wastewater flowing through the sand filter. The decrease in 186concentration was slightly higher than 31% (Fig. 2), and the concentration of ammonia 187nitrogen downstream of the sand filter was at a fairly high level of 75-80 mg/l (Fig. 3A). An 188analysis of pH and temperature fluctuations did not show any significant changes which could

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189confirmed enhancement of nitrification process. Moreover the small change in wastewater pH 190towards alkaline could have resulted from ammonification of organic nitrogen. In this 191condition of high supply of N-NH₄⁺ ions, the achieved results could be explained by the too 192low oxygen concentration. According to many authors, ammonia ions are known as inhibitors 193of nitrification [40-41]. Also, the character of wastewater flow through the filter (horizontal -194plug flow) certainly has not enhance the oxygenation and in consequence not favor the 195nitrification process. Despite the fact that the filter surface was not isolated from the air, 196horizontal flow of wastewater enabled fast and uniform oxygen supply to microbial cells, 197limiting the rate of many biochemical transformations, including ammonia nitrogen oxidation 198[25, 42]. The low nitrification efficiency can also be explained by slow growth of some 199groups of nitrifiers. Directly after certain environmental conditions are established, the 200number of nitrifying bacteria is low and increases with time. A stable level is usually reached 201after several days [43-44].

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203Results for oxygenation over 20%

204 An analysis of achieved results indicates that the efficiency of ammonia nitrogen removal 205increased at higher levels of oxygenation. At the oxygenation level of 20-30%, removal 206efficiency of ammonia nitrogen in the pilot plant was equal to 68.5%, at the level of 30-40% it 207was 81.2%, and at the level of 40-50% - 75.1% (Fig. 2). Statistical analysis indicated that 208these values significantly differed from the results obtained at the two lower oxygenation 209levels discussed above (Fig. 2). The results of our study are in accordance with previous 210study by Fiedurek and Gromada [19], whose observed that a significant (over 6-fold) increase 211in intracellular catalase activity was achieved at a stable dissolved O2 concentration (30% ± 2122%).

So far it has been demonstrated that the efficiency of ammonia nitrogen removal in single-213 214stage horizontal flow (HF) constructed wetlands (CWs) does not exceed 54%, for high NH₄-N 215concentrations [45]. According to Vymazal [42], the 50% threshold in such CW systems 216cannot be exceeded because of low oxygen transfer which sets a limit on nitrification [37, 39, 21746-48]. Much more higher removal efficiency of ammonium nitrogen had been confirmed for 218hybrid and vertical flow CWs. In such system it is possible to achieve very effective removal 219of nitrogen compounds up to 90% due to better oxygenation which is achieved by changeable 220flow in hybrid system or by intermittent discharge in VF system or by force aerated beds 221(FAB) [36, 49-52].

According many authors aeration of wastewater before discharge to HF beds could be 222 223applied to overcome problem of lack of oxygen [53-54]. A study conducted by Jamieson et al. 224[55] in a model wastewater treatment system indicated that nitrogen removal efficiency could 225be increased from 50.5 to 93.3% by aeration with compressed air. Nitrogen removal 226efficiencies similar to those obtained in the present study at an oxygenation level of 30-40% 227were reported by Ju et al. [29] in their model-scale investigations performed with a vertical 228flow filter in a novel electrolysis-integrated tidal flow CW system. Liu et al. [56] achieved 22997% efficiency of nitrogen removal in lab-scale investigations using zeolites as substrates. 230According to Araya et al. [57] combination of zeolite as the support medium and the aeration 231strategy with a suggested cycle of 4 h/d in a single CW demonstrated the importance of 232aeration for the regeneration of adsorption sites and the maintenance of the COD and NH⁺⁴–N 233removal efficiencies above 70% over time.

In our studies application of higher doses of hydrogen peroxide and maintaining a 235wastewater oxygenation level of 30-40% or 40-50% had the best effect on the activity of 236nitrifying bacteria and ammonia nitrogen oxidation. Under these conditions, the ammonia 237nitrogen concentration decreased to an average level of 22.0-29.5 mg/l at the outflow (Fig. 2383A). At the same time, at the oxygenation level of 30-50%, the concentration of nitrates 239reached a maximum (Fig. 3B).

The obtained results indicate clearly that application of H₂O₂ resulted in the optimization of 240 241the nitrification process in the analyzed WWTP model.

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2433.2. Effects of H₂O₂ application on BOD₅ removal

The study also confirmed that the application of hydrogen peroxide leads to an effective 244 245decrease in BOD₅ concentration. The efficiency of BOD₅ removal in the wastewater treatment 246plant model at different ranges of oxygenation, with a division into uniform groups, is 247presented in Figure 4. The Anova confirmed significant differences in BOD₅ removal 248efficiency at the different oxygenation levels. The Tukey test indicated that significantly the 249highest efficiency of BOD₅ removal (94.3%) and the lowest BOD₅ concentration (4.4 mg/l) 250were obtained at the oxygenation level of 30-40% (Fig. 4, 5). At the aeration level of 40-50%, 251the decrease of BOD₅ removal efficiency to 11% was observed and the concentration of BOD₅ 252at the effluent increased considerably (Fig. 4, 5). One of potential explanations is that 253increasing the dose of H₂O₂ over 40% most probably inhibited the biological processes, due to 254oxygenation of microbes. Too high concentration of H₂O₂ could lead to lysis of cells and in the

255consequence the organic matter content increases. Also the remain fraction of relatively 256hardly degradable organics and Org-N could be decomposed to less complexes compounds in 257such conditions and during the analytical procedure could be recognized as increased of 258BOD₅ concentration [4, 7].

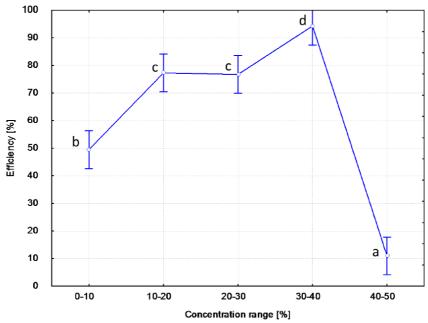


Fig. 4. The influence of oxygenation level on the efficiency of BOD₅ removal; the significances of differences between mean values are marked with letters a, b, c, d at p≤0.05

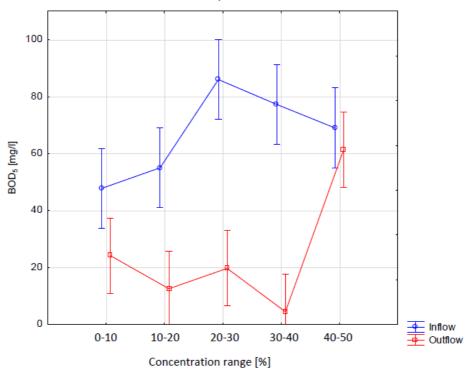


Fig. 5. Concentration of BOD₅ at inflow and outflow at different oxygenation levels of treated wastewater

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267 During the conventional processes of pollutants removal mineralization of organic matter 268demands 1 mg of oxygen per 1 mg of decompose organic matter expressed as BOD₅, in the 269same time for nitrification of 1mg N-NH4 is required about 4.3 mg of oxygen. Thus many 270authors arise the problem of competitions between mineralization of organics (heterotrophic 271bacteria) and nitrification process (autotrophic bacteria) in many wastewater treatment plants. 272Such statement is particularly true in low -coats systems for wastewater treatment like 273treatment wetlands technology [41, 58]. In such systems due to limited oxygen conditions 274both organics and oxidation of ammonia nitrogen can be limited and insufficient [49].

The effect of BOD₅ removal in the analyzed model at the oxygenation level of 30-40% 276(94.3%) was higher than that obtained during long-term operation of single-stage HF systems 277[42, 45] and comparable to that obtained in hybrid VF-HF systems [59;], VF-VF-HF systems 278[59] and VF-HF systems at the initial stage of operation, without plants [61].

The efficiencies of BOD₅ removal in constructed wetlands treating different types of 280wastewater are usually high, at the level of 90-99%, while the nitrogen removal could varied 281significantly from 20 up to 90% [41, 49]. Hybrid constructed wetlands have been reported to 282effectively remove organic matter also from high-strength wastewater [39, 49] as well as in 283case of unfavorable C:N ratio [36].

2853. 3. Economic aspects of H₂O₂ application

The results of the study indicate that hydrogen peroxide can be an attractive alternative to 287conventional methods of wastewater aeration, bringing similar effects but at a lower energy 288consumption. Evaluation of the actual costs of the application of the two types of methods is 289quite complicated and has to be based on an assumed effect. Each of the methods has a 290specific character and is defined by completely different factors. In the case of traditional 291aeration, the major factor is energy consumption during aeration defined as aeration capacity 292per unit power [62]. Assuming that the expected effect is to achieve a strictly defined 293optimum level of oxygenation (40%), this factor varies from 0.25 to 0.30 kWh/m³. It is worth 294noting that in practice the capacity of aerators as well as the efficiency of aeration depend on a 295number of indirect factors, such as pressure, temperature, depth and technology of air 296injecting as well as the level of consumption per unit aeration [63].

In the case of hydrogen peroxide dosing, the basic characterizing factor is reagent 298consumption. Basing on the experience gained in this study, it can be concluded that to obtain 299the oxygenation level of 30-40% approximately 0.25 kg/m³ of 50% hydrogen peroxide has to 300be used. Calculations based on the average prices of energy and hydrogen peroxide indicate

301that the costs of H_2O_2 dosing are higher than aeration with compressed air. These estimations 302can significantly change with time and be different for different countries. Moreover, they are 303only based on operation costs and do not include capital or amortization charges that are 304considerably higher in the case of aeration with compressed air.

305 Apart from various applications in chemical degradation of the pollutants present in 306wastewater, hydrogen peroxide can also be used to significantly aid biochemical treatment. 307Due to the fact that microorganisms are able to produce oxygen from a 0.1% solution of H_2O_2 , 308dosing of hydrogen peroxide can be a convenient and cost-effective way of intensifying 309nitrification at the early stages of wastewater treatment, when wastewater contains low 310oxygen concentrations [20]. As it was indicated earlier, increasing of hydrogen peroxide doses 311combined with filtration of wastewater improves the efficiency of nitrogen removal. The 312highest removal efficiency was obtained at the oxygenation levels of 30-40% and 40-50%. 313Because the investigations were performed in a model-scale set-up and the investigation 314conditions were similar during the various experiments, it can be concluded that the decrease 315in ammonia nitrogen concentration in wastewater resulted from the application of hydrogen 316peroxide in the form of a 0.1% solution and was not related to other factors such as the grain 317size of the filter material or filtration rate [64].

318 The pilot investigations of the wastewater treatment plant model with a sand filter indicate 319that aeration with hydrogen peroxide can be used to optimize nitrification and increase 320ammonia nitrogen and BOD_5 removal efficiency at different WWTPs. Application of this 321method could also bring positive effects for WWTPs with activated sludge [65-66] as well as 322sand filters or drainage systems (which are known to have a low ammonia nitrogen removal 323efficiency). However, application of this method would require further investigations under 324laboratory and technical-scale conditions.

Recently there is an increasing interest in multistage constructed wetlands all over the 326world. The systems with alternately vertical and horizontal flow beds, are capable of effective 327removal of nitrogen and organic matter, fulfilling the criteria of sustainability development 328[67]. Application of H_2O_2 in multistage wetland systems as well as in other technological 329solutions of wastewater treatment can optimize ammonia removal and help to control 330eutrophication of surface waters.

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3355. Conclusions

336 Hydrogen peroxide can be applied as a source of oxygen for microorganisms and as an 337agent intensifying biochemical transformations during ammonia nitrogen oxygenation in the 338nitrification process.

339 In the present study, the efficiency of ammonia nitrogen removal in the sand filter with a 340horizontal flow of wastewater was directly dependent on the dose of H_2O_2 and thus the level 341of wastewater oxygenation. The highest removal efficiency of ammonia nitrogen was 342obtained at the oxygenation levels of 30-40% and 40-50%, while the lowest removal 343efficiency was obtained at 0-10% and 10-20% oxygenation. The differences in removal 344efficiency between the various oxygenation levels were statistically significant. Application of 345high doses of hydrogen peroxide in combination with wastewater filtration can result in 346ammonia nitrogen removal exceeding 80%.

347 It was demonstrated that application of hydrogen peroxide also results in effective removal 348of BOD₅. The highest BOD₅ removal efficiency (94.3%) was obtained at the oxygenation 349level of 30-40%, and such level of oxygenation is advanced as optimal for both organic and 350ammonium nitrogen removal in WWTP which needs the improvement towards fulfill the 351requirements of final effluent.

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353Acknowledgments

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