



Application of H₂O₂ to optimize ammonium removal from domestic wastewater



Krzysztof Józwiakowski^{a,*}, Michał Marzec^a, Jan Fiedurek^b, Agnieszka Kamińska^c, Magdalena Gajewska^d, Ewa Wojciechowska^e, Shubiao Wu^f, Jacek Dach^g, Andrzej Marczuk^h, Alina Kowlaczyk-Juško^a

^a Department of Environmental Engineering and Geodesy, University of Life Sciences in Lublin, Leszczyńskiego 7, 20-069 Lublin, Poland

^b Department of Industrial Microbiology, Maria Curie-Skłodowska University, Akademicka 19, 20-033 Lublin, Poland

^c Department of Applied Mathematics and Informatics, University of Life Sciences in Lublin, Głęboka 28, 20-612 Lublin, Poland

^d Department of Water and Wastewater Technologies, Gdańsk University of Technology, Narutowicza 11/12, Gdańsk 80-233, Poland

^e Department of Sanitary Engineering, Gdańsk University of Technology, Narutowicza 11/12, Gdańsk 80-233, Poland

^f Key Laboratory of Clean Utilization Technology for Renewable Energy, Ministry of Agriculture, College of Engineering, China Agricultural University, 100083 Beijing, PR China

^g Institute of Biosystems Engineering, Poznań University of Life Sciences, Wojska Polskiego 50, 60-637 Poznań, Poland

^h Department of Agricultural Machines and Transport, University of Life Sciences in Lublin, Głęboka 28, 20-612 Lublin, Poland

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ABSTRACT

The paper presents the results of application of hydrogen peroxide (H₂O₂) 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% H₂O₂ solution. It was demonstrated that the gradual increase in oxygen concentration in treated wastewater due to H₂O₂ 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 (BOD₅). The highest BOD₅ 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.

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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,

* Corresponding author.

E-mail address: krzysztof.jozwiakowski@up.lublin.pl (K. Józwiakowski).

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 sixfold) in intracellular catalase activity was obtained while the dissolved oxygen concentration remained stable ($30\% \pm 2\%$) [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*, *Nitrospira* 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 $0.016 \text{ m}^3/\text{m}^2/\text{day}$) (Fig. 1).

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 0.091 m^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 ($\phi = 1\text{--}2 \text{ mm}$).

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 (Table 2). The wastewater was collected from outflow of two chambers septic tank in household wastewater treatment plant with average flow of $0.6 \text{ m}^3/\text{day}$.

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 (Table 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 $\alpha = 0.05$.

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 (Table 3).

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 (Table 3). The concentrations of ammonia nitrogen, total nitrogen and BOD_5 in the inflow wastewater were $109.0\text{--}120.0$; $128.5\text{--}142.0$; and $47.8\text{--}86.0 \text{ mg/l}$, 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 (Table 3).

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