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STUDY OF THE GLYPHOSATE-AMINE PESTICIDE MINERALIZATION IN WASTEWATER BY OZONATION TREATMENT

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Abstract

The main objective of the research was to study the efficiency of the glyphosate amine pesticide mineralization in wastewaters (real and model type of wastewaters respectively) using ozonation treatment as an advanced oxidation processes (AOP). The wastewater samples (model wastewater) were obtained by mixing a given volume of the stock solution prepared from glyphosate isopropyl-amine in different volumetric ratios with distilled water and with real wastewater obtained from a domestic wastewater plant, respectively. In case of model wastewater, the decomposition of glyphosate isopropyl-amine salt into ortophosphate, nitrite-, nitrate-ions and carbon dioxide products was studied. The efficiency of the oxidation process was determined by material balance calculations in terms of residual organic content, experimentally determined by COD_{Cr} method. During the experiments the changes of the chemical composition, due to the mineralization processes occurring in the model wastewater were monitored. The decomposition of the glyphosate isopropyl-amine was followed by analytical techniques in function of time. Mineralization efficiency of 13-14 % was achieved during the experiments carried out with model wastewater. The outcome of the experiments was used for a small-scale Hungarian wastewater plant having a capacity of 7,100 population equivalent. In the case of real effluent, the mineralization efficiency of 30 % was achieved. Based on the experimental results, it can be concluded that the ozonation treatment significantly increases the mineralization efficiency of model pesticide.

Key words: Advanced Oxidation Processes (AOP), glyphosate-amine pesticide, micropollutants, ozonation treatment, wastewater treatment

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1. Introduction

There are several new challenges in the field of wastewater treatment, which have continuously requested a significant innovation from the researchers and specialists. The organic UV filters, the disinfection of the wastewaters (Kunigk et al., 2018; Ramos et al., 2016) or the microwave treatment of the wastewaters (Moza and Mironescu, 2017; Wang N. and Wang P., 2016) could be mentioned among many others examples. The reuse of the water is a distinguished objective all over the world. The industry and the agriculture introduce and use new technological processes and solutions in order to efficiently decrease the water consumption. The intensive use of the pesticides increases due to the intensification of the agricultural production (Bannwarth et al., 2016). However, there are several disadvantageous impacts of using the pesticides, since the pesticides can get into the environment, especially into the surface and underground waters as well as finally into the human body (Silva et al., 2015).

Micropollutants are those compounds, which can be found in the natural waters in tiny amounts. The micropollutants block the ecological processes, which normally occur in natural waters, decrease the natural

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degradation processes in the environment and exhibit high biochemical stability (Gavrilescu, 2009). As it is presented in literature, several types of the micropollutants, denominated as refractory can be distinguished (Tokumura et al., 2016). These micropollutants (pesticides, dyestuffs, coloring agents, aromatic compounds, etc.) give unpleasant taste, odor to the water and generate sometimes volatile compounds.

However, these undesirable micropollutants can be efficiently decomposed if suitable advanced oxidation step is installed into the water/wastewater treatment process (Deletze et al., 2016; Giannakis et al., 2015; Kiss, 2015; Oller et al., 2011). The processes using ozone and hydrogen peroxide, as well as their combinations, belong to the family of advanced oxidation processes. The decomposition of the organic matters in waters and wastewaters is a complex multi-stage process (Stan et al., 2012). During the decomposition of the ozone free radicals are generated and present a high reactivity toward the organic pollutants.

The oxidation processes can be used for the treatment of surface waters, underground waters, municipal, industrial and agricultural wastewaters (Taheri et al., 2017; Lutic et al., 2018; Lutic and Cretescu, 2016; Lutic et al., 2017). One of the most widely used oxidation agents in wastewater treatment is the ozone, which is an extremely strong oxidizing agent due to its high redox potential (pH=7; 2.07 V). Its oxidation potential can be explained by the role of the nascent oxygen formed during the decomposition of ozone, which by reacting with the organic compounds results in the decomposition of the micropollutants (Hoigné, 1997, Xiong et al., 2011). CO_2, H_2O and other inorganic species are the final products of the oxidation process according to the principle of thermodynamics (Mare et al., 2004). During the ozonation process, special attention should be paid onto the following parameters: temperature, pH, concentration of different organic compounds to be decomposed (Kasprzyk et al., 2003; Pohontu et al., 2011; Simion et al., 2015). The glyphosate-amine inhibits the synthesis of the amino acids in plants. The glyphosate-amine has been widely used in the agriculture as non-selective weed killing agent (Silva et al., 2011; Santos et al., 2010). Therefore, the glyphosate-amine was considered as a model pollutant for studying the decomposition process during the ozonation treatment.

The main objective of this research was to determine the efficiency of the glyphosate-amine pesticide mineralization in wastewater (real and model type wastewaters, respectively) using ozonation treatment as an advanced oxidation processes.

2. Experimental

In order to study the efficiency of the ozonation treatment on model and real wastewaters, a stock solution of glyphosate-amine pesticide was prepared using glyphosate isopropyl-amine salt [C_3H_9N-$C_3H_8NO_5P$] and distilled water (Schuette, 1998). The glyphosate-amine is a crystalline compound with high solubility in water (Manassero et al., 2010). The pesticide was manufactured by SINON Corporation and supplied by Cresco Chemical Ltd. The wastewater samples were obtained by mixing the glyphosate-amine in different volumetric ratios with real wastewater. The wastewater treatment plant receives 800 m^3/day wastewater with following parameters: BOD_5: 300 g O_2/m^3, COD_{cr}: 600 g O_2/m^3, TKN (Total Kjeldahl Nitrogen): 45 g nitrogen/m^3, and the phosphorous content: 12 g P-PO_4/m^3. The maximum treatment capacity of the wastewater treatment plant is 7,100 population equivalent (PE).

The glyphosate concentration of the stock model wastewater was 0.435 g/L, 0.97 g/L and 2.34 g/L respectively and the stock solution prepared this way was diluted before the experiments when it was mixed with real wastewater. The decomposition of the glyphosate-amine was studied using a compact ozone generator (MOBILO3-HC-MH3 type).

The capacity of the ozone generator was 0.5 g ozone/h. The ozone concentration was measured before and after the reactor, using the standard chemical method (IOA, 2018). The temperature of the wastewater samples was kept constant between 13 and 15 ^oC. The ozone solubility in water is relatively low. However, this disadvantage is compensated by the relative high oxidation potential of the ozone (Tokumura et al., 2009). The values for COD_{Cr} (HS, 1991) and BOD_5 (HS, 2000) were measured according to the pertaining European (IS, 2002) and Hungarian Standards (MSZ) as specified by the Hungarian regulations.

The nitrite (HS, 1985), nitrate (HS, 1979) and ortophosphate (HS, 1977) concentrations were measured according to the specific analytical methods stipulated by the Hungarian regulations. The tests were carried out in the experimental setup as depicted in Fig. 1.

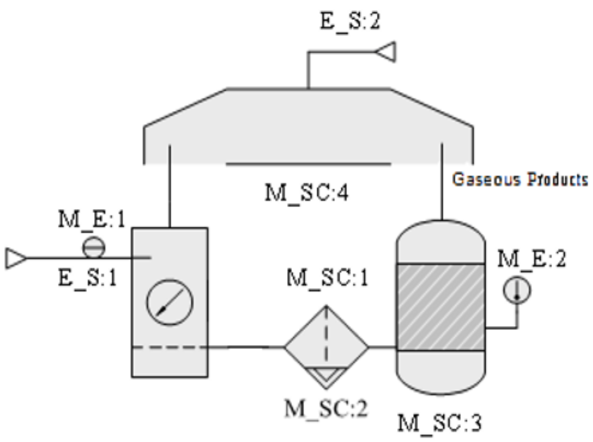

Fig. 1. Experimental setup used for the test of ozonation treatment of pesticide containing wastewaters (M_SC:1: ozone generator, M_SC:2: water trap, M_SC:3: reactor, M_SC:4: hood for exhaust ventilation, M_E:1: electrical measuring equipment, M_E:2: temperature measuring equipment, E_S:1/E_S:2: electric power supply)

The following methodology was used for the ozonation treatment of pesticide containing wastewaters. A volume of 250 mL pesticide solution after proper dilution was measured into the reaction vessel and the ozone feed was started (Fig. 1). The amount of ozone introduced into the reactor was continuously measured and controlled. New stock solutions were used for every experiment. The duration of the experiments was changed between 15 and 90 min. The organic content of samples was analyzed in terms of COD_{cr}. In addition, nitrite, nitrate and orthophosphate concentrations were determined according to the standard analytical methods as described above.

3. Results and discussion

3.1. Experimental results

The goal of the experimental run was to study the decomposition of the glyphosate-amine by using ozonation treatment. In the first run (2.34 g/L initial glyphosate-amine concentration) the reaction time of the oxidation reaction was changed between 15 and 180 min respectively. These reaction times (15, 30, 45, 60, 75, 90, 120, 180 min) correspond to 0.125, 0.25, 0.375, 0.5, 0.75, 1.0 and 1.5 g ozone/L dosage. The experiments were carried out with three different initial glyphosate concentrations and the results are presented in Fig 2. During the measurements, the COD_{cr} values were determined and the changes in COD in the function of time/ozone dosage were plotted. The experimental results obtained during the treatment of the model wastewaters with ozone will be further presented. The change of the COD values in the function of the ozone dosage is illustrated in Fig.2,

The mineralization transforms the complex organic compounds to mineral substances (Ahmed et al., 2010) by the oxidation of the pesticide with ozone. The mineralization efficiency can be seen in Fig. 2 in the function of ozone dosage. In Fig. 2 the initial COD_{cr} values correspond to the initial concentration of glyphosate-amine pesticide containing model wastewater. During the ozonation treatment, the COD_{cr} values decreased in the function of time due to the conversion of the heavily biodegradable compounds. In addition to the first run, additional experiments were carried out. In the 2nd run (0.97 g/L initial glyphosate-amine concentration) and in the 3rd run (0.435 g/L initial glyphosate-amine concentration) decreasing amounts of the pesticide were used. In the 2nd and 3rd runs the reaction time was changed between 15 and 180 min as well, which represent higher ozone dosages from 0.125 through 1.5 g ozone/L. It can be concluded that higher mineralization efficiency can be achieved in case of lower initial glyphosate-amine concentration on increasing the ozone dosage. At higher initial glyphosate-amine concentration of 2.34 g/L, a decrease of 5.72 % COD_{cr} was observed at 0.125 g ozone/L dosage.

By increasing the ozone dosage to 0.25 g ozone/L, the chemical oxygen demand decreased to 9.89 %, and at ozone dosage of 0.375 g ozone/L the chemical oxygen demand decreased to 12.16%. In case of lower glyphosate-amine concentration of 0.97 g /L and at ozone dosage of 0.375 g ozone/L a decrease of 5.89 % in COD_{cr} was obtained. At the lowest glyphosate-amine concentration (0.435 g/L) upon increasing the ozone dosage up to 1.5 g/L 13.36 % decrease in the chemical oxygen demand was achieved. The COD_{cr} removal efficiency (in case of 3rd run) increased in the function of the ozone dosage. 0.5 g/L ozone dosage resulted in COD_{cr} removal of 7.9 %, 1.0 g/L ozone dosage resulted in COD_{cr} removal of 10.8%, and 1.5 g/L ozone dosage resulted in COD_{cr} removal of 12.5%.

The data of the three experimental runs, using different glyphosate-amine concentrations were studied by correlation analysis. The strength of the interrelations between the experimental runs was studied by the Pearson linear correlation coefficient. If the coefficient exhibits a value higher than 0.9 it means that strong correlation exists among the variables (Zhou et al., 2016).

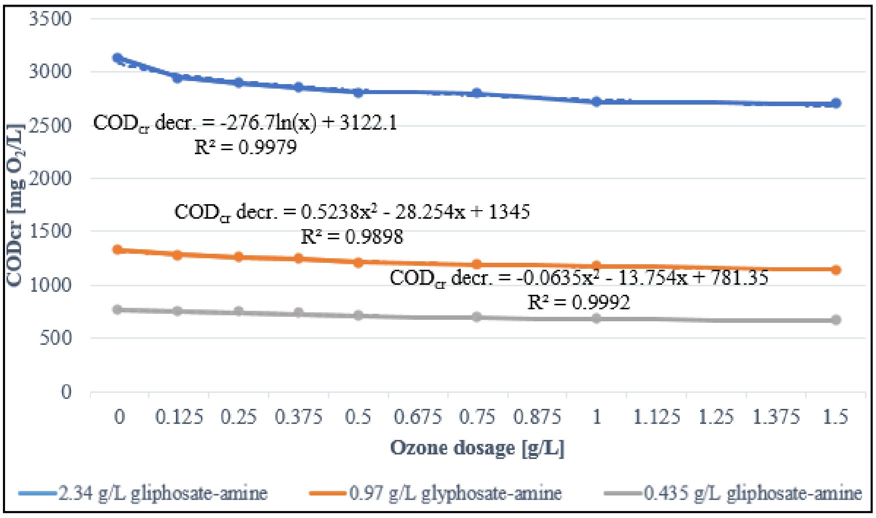

Fig. 2. The decrease of the CODcr in function of the ozone dosage in the case of model glyphosate-amine wastewater

Table 1. Measured water parameters during the decomposition of the glyphosate-amine (at 2.34 g/L initial concentration)

Treatment time [min]	*Ozone dosage [g O_3/L]*	*COD_{cr} [mg O_2/L]*	*BOD_5 [mg O_2/L]*	*Nitrite [mg N-NO_2/L]*	*Nitrate [mg N-NO_3/L]*	*Orthophosphate [mg P-PO_4/L]*
0	0.000	3184	169	0.0087	0.77	0.0013
15	0.125	3001	63	3.95	5.17	0.0203
30	0.250	2865	94	6.78	8.96	0.0778
45	0.375	2795	38	11.07	8.96	0.0778
60	0.5	2770	0	n.a.	n.a.	n.a.
90	0.75	2762	42	n.a.	n.a.	n.a.
120	1.0	2681	8	n.a.	n.a.	n.a.
180	1.5	2664	0	n.a.	n.a.	n.a.

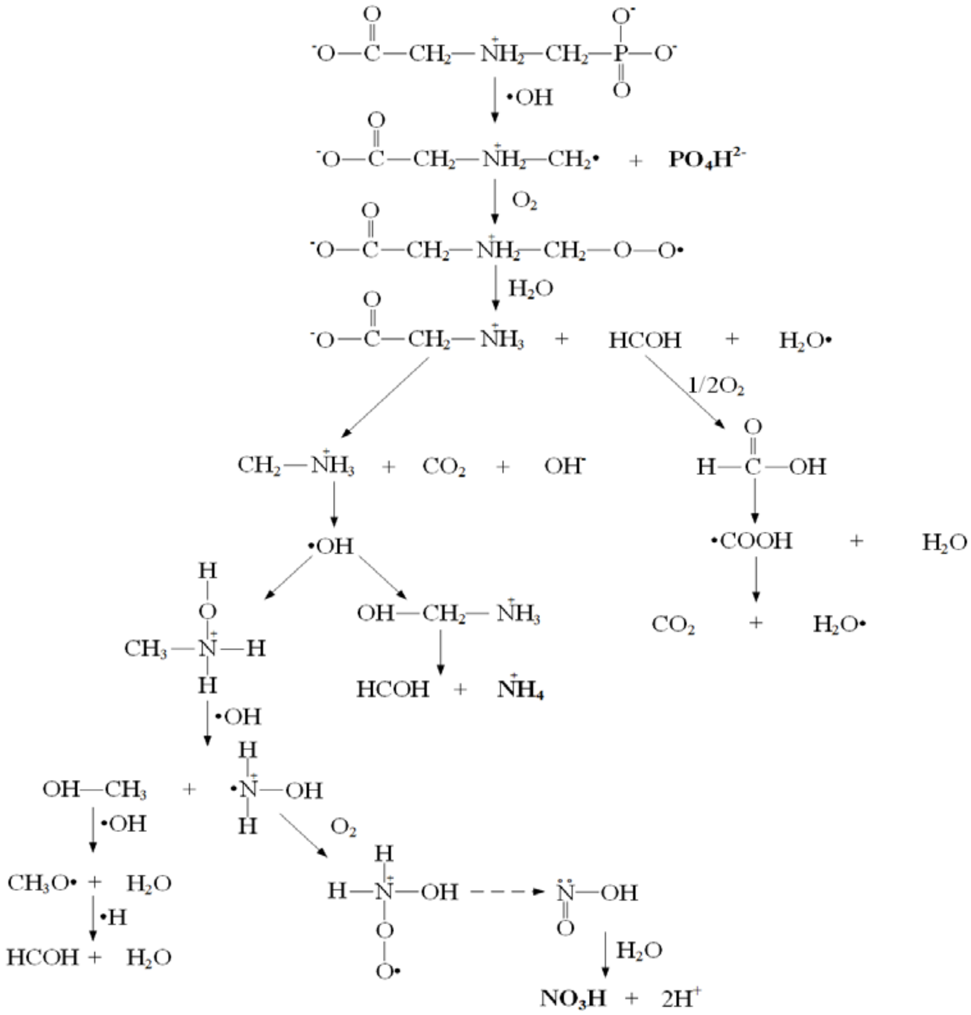

Fig. 3. The mechanism of glyphosate isopropyl-amine decomposition during the oxidation reaction (Manassero et al., 2010)

The data presented in Fig. 2 showed good correlation among the variables as evidenced by the high correlation coefficients which were higher than 0.98. During the reaction, nitrite, nitrate and orthophosphate are formed, which indicate the decomposition of the glyphosate. The ion concentrations and the COD_{Cr} values measured during the decomposition are summarized in Table 1.

Based on these experimental results it can be assumed that the decomposition of the glyphosate-amine follows the mechanism presented in Fig. 3. The chemical oxidation of the glyphosate-isopropyl amine pesticide is accompanied by the formation of orthophosphate-, nitrite- and nitrate-ions as it can be seen in Fig. 3. The oxidation of the glyphosate takes place through the thermodynamical equilibrium (CO_2 and H_2O formation) (Pera-Titus et al., 2004).

Based on the obtained results it can be seen that intermediate products form during the decomposition of the glyphosate-amine, which increase the BOD_5 values. During the oxidation of an organic compound with hetero atoms such as: oxygen, nitrogen and phosphorous having a general chemical formula $C_nH_xO_yN_zP_t$ the following reaction takes place:

$$C_nH_xO_yN_zP_t + O_2 = nCO_2 + qH_2O + zNH_3 + tPO_4 \quad (1)$$

By substitution of the glyphosate-amine into Eq. (1) and assuming that the ammonia and orthophosphate are not oxidized further during the reaction, the amount of oxygen needed for the oxidation of 1 mol of glyphosate-amine is 19.5 mol O_2.

3.2. Case study on a Hungarian wastewater treatment plant

The objective of this experimental run was to study the micropollutant removal efficiencies with using the effluent of an existing municipal waste water treatment facility. The effluent of the wastewater plant allowed to investigate the efficiency of the post-treatment technology namely the ozonation under real conditions. The wastewater samples were taken from the effluent of Veszprem County wastewater treatment plant.

Prior to the ozonation treatment a known amount of glyphosate was added to the wastewater samples to monitor the micropollutant removal efficiency. From the stock solution sample was taken and it was added into the 10 L of treated wastewater sample and it was thoroughly mixed by a stirrer. The obtained mixture had a glyphosate concentration of 48.59 µg/L which is typical for real wastewaters contaminated by micropollutants. A volume of 400 mL mixture was used up for the oxidation experiments at different ozone dosage (between 0.125 and 0.375 g ozone/L), during a period of 45 min. Blank experiment -as given above- was carried out with the ozonation of the real wastewater without glyphosate-amine under the same experimental conditions. The experimental results for the glyphosate-amine removal efficiency were calculated with taking the COD value of the real wastewater after ozonation into consideration. The chemical oxygen demand values -after deducting the COD value of the real wastewater- are summarized in Fig. 4.

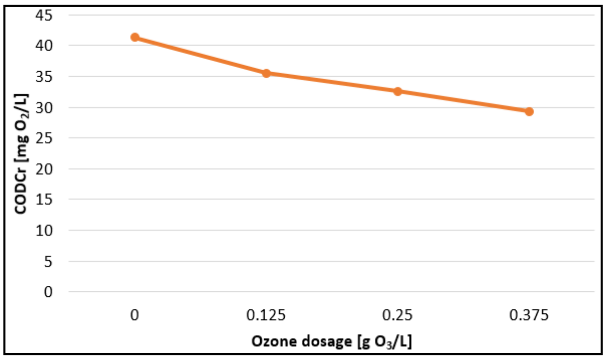

Fig. 4. The change of COD_{Cr} as a function of ozone dosage in case of glyphosate containing real wastewater

The mineralization degree of the glyphosate-amine, G_{min} is calculated using the following (Eq. 2):

$$G_{min} = \frac{C}{C_0} \times 100 \qquad (2)$$

where: C is the COD value assigned to the specified ozone dosages; C_0 is the COD value corresponding to the initial glyphosate amine concentration

The mineralization degrees show the decomposition efficiencies related to the glyphosate-amine content of the real wastewater after deducting the COD value of the real wastewater. The obtained figures are summarized in Table 2. Based on the experimental measurements and calculations carried out, it can be concluded that the efficiency of glyphosate-amine oxidation by ozone treatment is moderate, it is around 30%. However, in the present case the COD_{cr} value of the treated effluent decreased and reached a value of 29.32 mg oxygen/L (30% decrease) which is acceptable from the point of view of the environmental regulations.

Table 2. The experimental results of the ozonation treatment of the glyphosate-amine containing real wastewater

Ozone dosage *[g O_3/L]*	*COD_{cr}* *[mg O_2/L]*	*G_{min}* *[%]*
0	41.32	0.00
0.125	35.53	14.02
0.25	32.55	21.23
0.375	29.32	29.05

4. Conclusions

Experimental tests had been carried out for the decomposition of a model wastewater samples using glyphosate-amine pesticide. Different pesticide concentrations were used for the experiments and real wastewater samples were mixed with the given pesticide as well as to learn the efficiency of the decomposition process.

It can be observed from the experimental results that the oxidation process shows up a mineralization efficiency of 12.2% (initial pesticide concentration of 2.34 g/L) at 45 min reaction time and at an ozone dosage of 0.375 g ozone/L in case of model wastewater.

The experimental results were taken for correlation studies, which showed that the efficiency of the mineralization experiments did not change significantly by using glyphosate-amine solutions with different concentrations.

The efficiency of the ozonation treatment was studied in case of a Hungarian wastewater treatment plant. Based on the correlation among the standard wastewater parameters experimentally determined, the decomposition of the glyphosate-amine was confirmed, and the mineralization efficiency was around 30%, which is in compliance with the pertaining environmental specifications.

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