Kinetic Study of the Ozonation of Atrazine

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The kinetic study of the ozonation of atrazine as a single contaminant characterized as COD was studied. A jet loop ejector reactor was used to improve the mixing and transfer of ozone in the reaction system. The results show a higher efficiency of atrazine degradation in alkaline pH during the first 45 minutes. At the same time, the dechlorination of atrazine is faster than in neutral pH. Respirometric measurements carried out with activated sludge were used to evaluate the effect of atrazine and the ozonation intermediates on microorganisms' oxygen uptake rate. The results showed that ozonation performed at an alkaline pH resulted in the formation of substances that are more rapidly biodegradable compared to substances formed by ozonation at neutral pH, as well as compared to atrazine.

Keywords
atrazine, dechlorination, immediate biodegradability, kinetic equation, ozonation, pH effect, radical mechanism, respirometric measurements, toxicity

Introduction

Atrazine, 6-chloro-4-N-ethyl-2-N-propan-2-yl-1,3,5-triazine-2,4-diamine, is a synthetic herbicide used to prevent the growth of dicotyledonous weeds in agricultural crops, such as sugarcane, hops or corn. In practice, there are more than 300 atrazine-based products.[1] The presence of atrazine and its chlorinated metabolites in the environment has a negative impact on living organisms in nature as well as on human health. It can be included in the group of neurotoxins, endocrine disruptors, teratogens, mutagens, and carcinogens. A typical manifestation of short-term exposure is an allergic reaction. In the case of long-term exposure through drinking water, it may lead to cardiovascular problems, motor disorders, limb paralysis or sperm mutagenesis.[2–6] In Europe, the use of products based on atrazine has been prohibited since 2005, following the decision of the European Commission 2004/248/EC. The presence of atrazine in the environment is current despite the ban on its use. At the end of 2017, the Regional Office of Public Health issued a ban on the use of drinking water for several municipalities located near the river island known as Žitný ostrov, which is the largest source of drinking water in Central Europe. The drinking water was classified as hazardous to health due to the reported exceedance of the highest limit value of atrazine during the operational monitoring.[7] Atrazine is a ubiquitous contaminant. Direct contamination of the environment occurred at the time of its intensive use. Depending on the nature of the environmental component, atrazine is able to persist in the environment for several years. Today, it can lead to contamination of surface and groundwater by secondary emissions from contaminated former agrochemical warehouses, waste dumps, and contaminated soils.[6,8–11] Water treatment technologies such as filtration or coagulation are not effective enough to remove micropollutants such as atrazine. Effective technologies for atrazine removal include adsorption, membrane filtration, and chemical oxidation.[8,12–18] Ozone-based processes are an increasingly attractive oxidation method. Ozone is a strong oxidizing agent, and it can be used to process large amounts of effluent with little or no formation of by-products. Ozone-based processes belong to the group of advanced oxidation processes (AOPs). These treatment methods are based on the generation of reactive radicals to remove pollutants. The advantage of these oxidation processes is that the persistent organic pollutants are transformed and degraded. In the best case, pollutants are completely mineralized into carbon dioxide and water.[19–21] Basically, ozone reacts with the pollutant through two mechanisms: direct and indirect pathway. In a direct pathway, molecular ozone selectively reacts with unsaturated bonds of an organic compound. The indirect pathway is based on non-selective radical reaction, mostly driven by hydroxyl radicals. Both pathways run simultaneously, and the rate of hy-

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droxyl radical formation is dependent on pH. Under acid conditions (pH < 4), the direct pathway prevails, while in alkaline pH (pH > 10) the indirect pathway predominates. The radical ozonation mechanism can also be initiated by UV, Fe^{2+}, hydrogen peroxide, formats, and humus substances.[22,23] The degradation of atrazine in water through ozone-based processes has already been studied by various researchers to identify the primary by-product formed, determine the reaction rate constants, and model the kinetics of oxidation. The ozone-based processes were usually performed in agitated glass reactor. For example, Liu *et al.*[24] reported that the removal rate of atrazine was always better with microbubble ozonation than with the macrobubble aeration system. Higher efficiency of atrazine degradation is achieved by catalytic ozonation. Lu *et al.*[25] reported more than 90 % atrazine degradation with O_3/H_2O_2. The heterogeneous catalytic ozonation using zero valent iron was highly efficient in degrading atrazine in aqueous solution.[26]

Atrazine contains a chlorine atom in its structure. Komtchou *et al.*[28] assumed that the initial step in the indirect ozonation reaction involves the removal of a hydrogen atom and the subsequent release of chlorine. One of the most common intermediates of atrazine through radical oxidation is cyanuric acid ($C_3H_3N_3O_3$), which supports the hypothesis that, upon reaction with HO•, the chlorine atom is removed and released into the solution. Therefore, an analysis of chlorine ion concentration was conducted. Based on this assumption that atrazine is dechlorinated by ozonation, its detoxification can also occur simultaneously.

The goal of our work was to study the kinetics of atrazine degradation to obtain the most appropriate mathematical models for describing the kinetics of degradation. Zero-order, first-order, and second-order kinetic equations were used to describe the degradation kinetics of atrazine removal in this study. Another objective was to assess the effect of the ozonation process carried out by different reaction mechanisms on the biodegradability and inhibitory effects of ozonized atrazine during the process. Therefore, respirometric measurements were performed to study the effect of arsenic and degradation products on the activity of activated sludge microorganisms. Integration of experimental data into Monod, Haldane, Aiba-Edward, Tessier and Web equations was used. Therefore, a nonlinear regression parameterization procedure was used. Since previously published works primarily focused on concentration values of micropollutants, our work was centered on examining significantly higher levels of atrazine in model wastewater, i.e., at pollutant concentration levels. The main reason being the unavailability of a method for direct analysis of atrazine content in samples during the pandemic. Therefore, we evaluated the ozonation process using a model wastewater containing atrazine and its intermediates/ozonation products as one contaminant specified by chemical oxygen demand (COD). Another method based on chloride concentration was also used as an indirect parameter to determine the content of atrazine dechlorination in the ozonation process. For this determination, we utilized an argentometric titration according to Mohr.[29] From a practical standpoint, it is of interest to investigate the kinetics of ozonation in wastewater with a higher content of atrazine, such as in the case of contamination leaks or degradation of stored pesticide. To enhance the transfer of ozone from the gas phase to the liquid phase, we employed a new jet ozonation reactor, utilizing a Venturi ejector to generate microbubbles.

Methodology

Analytical methods and reagents

Analytical standard Atrazine PESTANAL® (Merck Slovakia Ltd) was used to prepare a model solution of atrazine with an approximate concentration of 0.1 mmol L^{-1}. A multimeter WTW Multi 3510 IDS with a SenTix[a] 940 pH electrode was used to monitor the pH of samples. The pH value of solutions was adjusted using H_2SO_4 and NaOH with concentration 1 mol L^{-1}. Chemical oxygen demand (COD) and chlorine ions were monitored during ozonation process. Cuvette tests LCI500 (Hach Lange) were used to determine the COD value spectrophotometrically at 440 nm. The chloride concentration was used as indirect parameter to determine the level of atrazine dechlorination in ozonation process. For this determination, argentometric titration according to Mohr was carried out.[29]

Ozonation experiments and kinetics study

Degradation and dechlorination were performed in a 3-L ozonation jet-loop reactor with external recirculation of reaction mixture (Fig. 1). An ozone generator LifeTech, Ltd., with a maximum ozone production of 5 g L^{-1} was used. The oxygen inflow was 12 L h^{-1} and ozone generator was set at 60 % of maximum power. A mixture of O_3 and O_2 was injected into the atrazine solution as a model wastewater sample through a Venturi ejector. At the same time, the ejector sucked the mixture of O_3 and O_2 from the reactor headspace. This, together with external circulation, should improve the efficiency of ozone utilization in the ozonation reactor.[30] External recirculation of the reaction mixture was ensured by a pump at a level of 30 L h^{-1}. The experi-

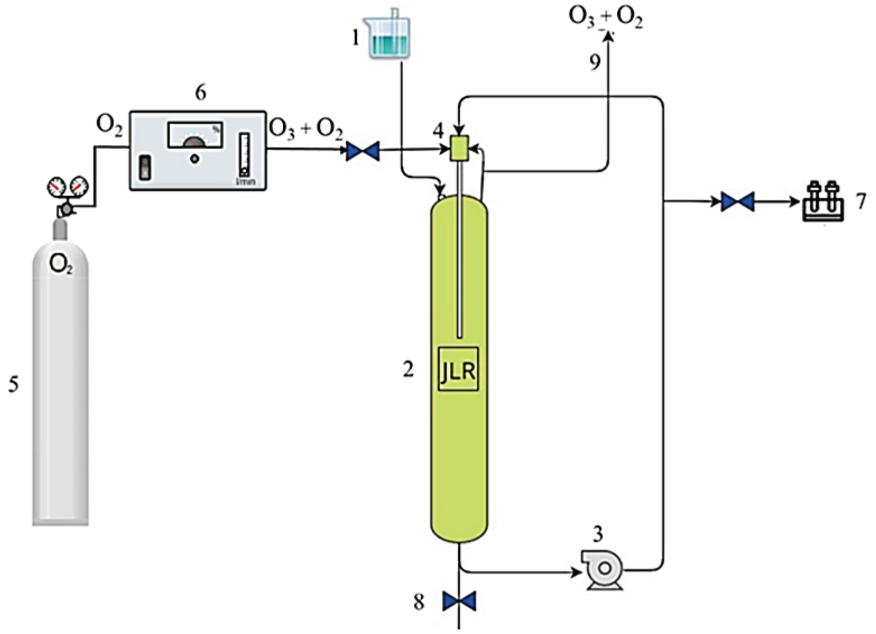

Fig. 1 – *Schematic diagram of ozonation reactor with external recirculation of reaction mixture (1 – sample input, 2 – ozonation reactor, 3 – pump, 4 – Venturi ejector, 5 – compressed oxygen cylinder, 6 – ozone generator, 7 – sampler, 8 – sample output, 9 – outlet gas mixture)*

ments were carried out at laboratory temperature of 20 °C for 45 minutes. We took 50-mL samples from the reactor at time intervals of 0, 5, 15, 30, 45, and 60 minutes. Outlet residual ozone was destructed in activated carbon column.

The concentrations of ozone in the gas phase at the inlet and outlet of the reactor were measured using a Life ODU 200 UV laboratory detector. The amount of ozone transferred (reacted and decomposed) from the gas phase to the liquid phase in the reactor during ozonation of atrazine samples was calculated using a macroscopic mass balance based on the gas phase inlet and outlet ozone concentrations (Eq. 1):

$$O_{3,\mathrm{trans}} = Q_g \int_0^t \frac{O_{3,\mathrm{in}} - O_{3,\mathrm{out}}}{V_\mathrm{R}} \mathrm{d}t \qquad (1)$$

where $O_{3,\mathrm{trans}}$ is transferred ozone [g L^{-1}], Q_g [Nm^{-3} min^{-1}] is oxygen gas flow containing generated O_3, while the concentration of ozone in the gas at the inlet is $O_{3,\mathrm{in}}$ [g Nm^{-3}], and the concentration of ozone in the gas at the outlet is $O_{3,\mathrm{out}}$ [g Nm^{-3}], and V_R is the volume of the reactor.[31] The values of ozone equilibrium concentration in aqueous phase were calculated from the concentration of ozone in the gas monitored at the outlet of the reactor using the Henry constant.

Respirometric measurements

Respirometric measurements with activated sludge were used for assessment of the effect on the endogenous respiration rate of activated sludge microorganisms and determination of immediate biological degradability. The simple respirometer (Fig. 2) was used. It consisted of a respirometric cell, stirrer, oxygen probe (FDO®925, WTW), and injector for testing sample. Continuous recording of dissolved oxygen in the respirometric cell was carried out with a multimeter WTW Multi 3510 IDS. The respirometric cell was filled with diluted activated sludge with an approximate concentration of total suspended solids of 1 g L^{-1}.[32] The gravimetric method was used to determine the concentration of total suspended solids in the activated sludge. The activated sludge was filtered through a 0.45 µm

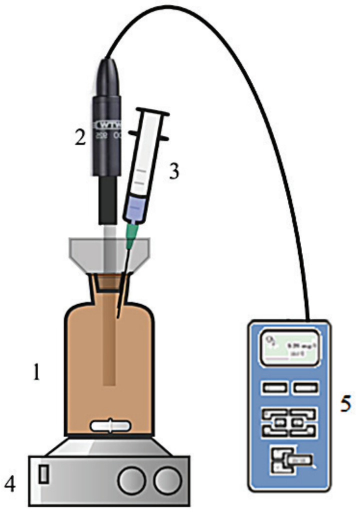

Fig. 2 – *Schematic diagram of simple respirometer (1 – respirometric cell, 2 – oxygen probe, 3 – sample injector, 4 – magnetic stirrer, 5 – recording device)*

Table 1 – *Composition of model wastewater*[33]

Compound	c (mg L^{-1})
glucose	36.9
peptone	38.4
starch	8.7
NH_4Cl	9.2
K_2HPO_4	2.7

pore size filter, and dried to constant weight at 105 °C.[29]

Respirometric measurements were performed with activated sludge microorganisms (solid retention time 15 days, organic load 0.2 kg kg^{-1} d^{-1} COD/TSS), which were cultivated in semicontinuous lab-scale model of activated sludge process. Model wastewater was used as a source of nutrients for the operation of the activated sludge model, and it was prepared from easily degradable organic substance of organic pollution. The composition of synthetic wastewater is shown in Table 1.[33] The initial activated sludge sample for the inoculation of the semicontinuous lab-scale model was obtained from a municipal wastewater treatment plant.

Specific substrate oxygen consumption rate of activated sludge microorganisms was calculated as difference of total oxygen consumption rate after adding sample and endogenous oxygen consumption rate:

$$r_{X,ox} = r_{X,ox,t} - r_{X,ox,en} \qquad \text{(Eq. 2)}$$

where $r_{X,ox}$ is the specific rate of substrate removal (mg O_2 g^{-1} h^{-1}), $r_{X,ox,t}$ is total oxygen consumption rate (mg O_2 g^{-1} h^{-1}), and $r_{X,ox,en}$ is endogenous oxygen consumption rate (mg O_2 g^{-1} h^{-1}), when oxygen is solely consumed for the oxidation of stock substances and cell mass of decayed microorganisms. Specific respiration rate values of microorganism were used to obtain substrate removal kinetic parameters, and quantify the inhibitory effect of the substance (atrazine and its by-products of ozonation) on the activated sludge microorganisms respiration activity.[32] Several kinetic equations listed in Table 2 were applied.

Processing of experimental data

Kinetic equations of zero (Eq. 8), first (Eq. 9) and second (Eq. 10) order were applied to describe the reaction kinetics:

$$\mathrm{COD}_t = \mathrm{COD}_0 - k_0\, t \qquad \text{(Eq. 8)}$$

$$\mathrm{COD}_t = \mathrm{COD}_0\, \exp\left(-k_1\, t\right) \qquad \text{(Eq. 9)}$$

$$\mathrm{COD}_t = \frac{\mathrm{COD}_0}{1 + \mathrm{COD}_0\, k_2\, t} \qquad \text{(Eq. 10)}$$

where t is time (min), COD_0 and COD_t are the initial and in time t COD values (mg L^{-1}), and k_0, k_1, k_2 are kinetics constants of corresponding kinetics orders (mg L^{-1} min^{-1}, min^{-1}, mg^{-1} L min^{-1}).[39]

Dechlorination kinetics of atrazine was described according to the following equation:

$$c_t = c_{\max} - \left(c_{\max} - c_0\right)\, \exp\left(-R_\mathrm{D} \cdot t\right) \qquad \text{(Eq. 11)}$$

Table 2 – *Kinetic models used for respirometric measurements evaluation*

Author(s)	Kinetics equation		Literature
Monod	$r_{X,ox} = r_{X,max} \dfrac{S}{K_\mathrm{S} + S}$	(Eq. 3)	34
Haldane	$r_{X,ox} = r_{X,max} \dfrac{S}{K_\mathrm{S} + S + S^2/K_i}$	(Eq. 4)	35
Aiba-Edward	$r_{X,ox} = r_{X,max} \dfrac{S \cdot \exp\left(-S/K_i\right)}{K_\mathrm{S} + S}$	(Eq. 5)	36
Tessier	$r_{X,ox} = r_{X,max} \left[\exp\left(-S/K_i\right) - \exp\left(-S/K_\mathrm{S}\right)\right]$	(Eq. 6)	37
Webb	$r_{X,ox} = r_{X,max} \dfrac{S\left(1 + S/K_i\right)}{K_\mathrm{S} + S + S^2/K_1}$	(Eq. 7)	38

where t is time (min), c_0 and c_t are the initial and in time t chloride mass concentrations (mg L^{-1}), $c_{\max}$ is maximum chlorides concentration (mg L^{-1}), and R_D is dechlorination rate constant (min^{-1}).[40]

It is known that there was one chloride in the atrazine molecule. Based on the molecular weights, it was possible to calculate the chloride content in atrazine with a molar concentration of 0.1 mmol L^{-1} which equaled 21.568 mg L^{-1} of atrazine. According to Eq. 12, atrazine with molar concentration of 0.1 mmol L^{-1} contained 3.5 mg L^{-1} of chloride:[43]

$$c_{\mathrm{Cl-ATR}} = m_{\mathrm{ATR}} \frac{1 \cdot \mathrm{M(Cl)}}{\mathrm{M(ATR)}} \qquad \text{(Eq. 12)}$$

where $c_{\mathrm{Cl-ATR}}$ is mass concentration of chloride in atrazine molecule (mg L^{-1}), m_{ATR} is mass concentration of atrazine (21.568 mg L^{-1}), M (Cl) is molar mass of chlorine (35.45 g mol^{-1}), and M (ATR) is molar mass of atrazine (215.68 g mol^{-1}). According to the theory of conservation of mass, the theoretical amount of chloride in atrazine during ozonation in time can be calculated using the known amount of chlorine released, as follows:

$$c_{\mathrm{Cl}} = c_{\mathrm{Cl-ATR}} - c_t \qquad \text{(Eq. 13)}$$

where c_{Cl} is content of chlorides bound in atrazine (mg L^{-1}), and c_t is chloride concentration in time determined according to Mohr (mg L^{-1}). The dechlorination efficiency was calculated based on the difference of the chloride content in the atrazine molecule over time:

$$E_{\mathrm{D}} = \left(\frac{c_{\mathrm{Cl-ATR}} - c_{\mathrm{Cl}}}{c_{\mathrm{Cl-ATR}}} \right) 100\,\% \qquad \text{(Eq. 14)}$$

where E_D is dechlorination efficiency (%).

Parameter values of the applied kinetic models were determined by the grid search optimization procedure.[41] To evaluate the quality of the fit of the kinetic models to the experimental data, correlation coefficient between the experimental and calculated data was used:[42]

$$R_{yx} = 1 - \frac{(n-m)S_R^2}{(n-1)S_y^2} \qquad \text{(Eq. 15)}$$

where R_{yx} is correlation coefficient, n is the number of measurements, m is the number of parameters of used kinetic model. S_R^2 is the residual sum square between experimental $y_{i,exp}$ and calculated data $y_{i,cal}$,

$$S_R^2 = \frac{\sum \left(y_{i,exp} - y_{i,\mathrm{cal}} \right)^2}{n - m} \qquad \text{(Eq. 16)}$$

S_y^2 is the dispersion of dependent variable values:[39]

$$S_y^2 = \frac{n \sum y_{i,exp}^2 - \left(\sum y_{i,exp} \right)^2}{n(n-1)} \qquad \text{(Eq. 17)}$$

The dispersion value S_y^2 reflects the variability of the values of the dependent variables (in our case the data of COD, Cl$^-$), and is part of the calculation of the value of the correlation coefficient R_{yx}. However, if different mathematical models are used to evaluate the same set of experimental data, the differences in the values of the R_{yx} correlation coefficient, as well as the quality of the description of the experimental data measurements using the values of these coefficient, depend only on the values of the residual dispersion S_R^2.

Results and discussion

Ozonation experiments and kinetics study

The reaction kinetics study confirmed that the degradation of atrazine showed different behavior depending on pH. The best fit of experimental data in alkaline pH range was obtained with the second order kinetic model (Table 3). Experimental data at neutral pH range (a range of pH values with parallel direct and indirect ozone reaction mechanisms) were best fitted by first order kinetic model. However, there was no significant difference in the correlation coefficient between the experimental and calculated data at neutral pH for applied kinetic models. Using the second-order rate constant, we compared the rate of atrazine degradation in different pH ranges. Higher kinetic constant with value 2.45 · 10^{-3} mg^{-1} L min^{-1} was for ozonation in alkaline pH (Table 3), meaning that the degradation of atrazine and its intermediates was faster in this pH range. This is also evident on the time profile of the COD in Fig. 3. This can be explained by the well-known formation of hydroxyl radicals in an alkaline pH, which are more reactive than ozone itself.

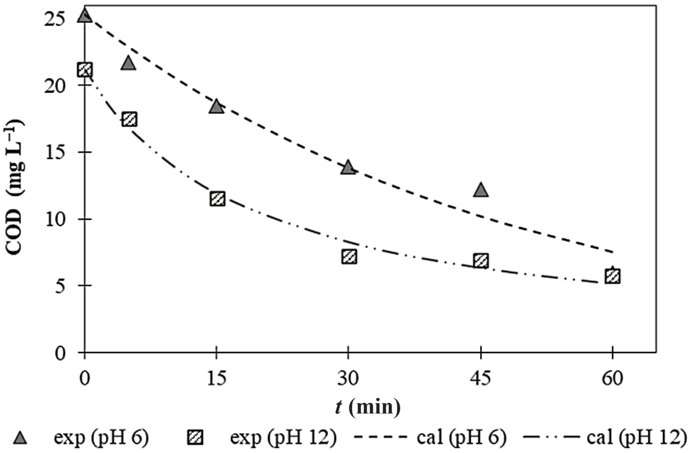

Fig. 3 – *Time profiles of COD in the ozonation process performed at different pH*

Table 3 – *Result of reaction kinetics study*

pH range	Zero order		First order		Second order	
	k_0 (mg L^{-1} min^{-1})	R_{yx}	k_1 (min^{-1})	R_{yx}	k_2 (mg^{-1} L min^{-1})	R_{yx}
neutral	$3.26\cdot10^{-1}$	0.9480	$2.01\cdot10^{-2}$	0.9680	$1.19\cdot10^{-3}$	0.9472
alkaline	$3.18\cdot10^{-1}$	0.7000	$3.005\cdot10^{-2}$	0.9346	$2.45\cdot10^{-3}$	0.9882

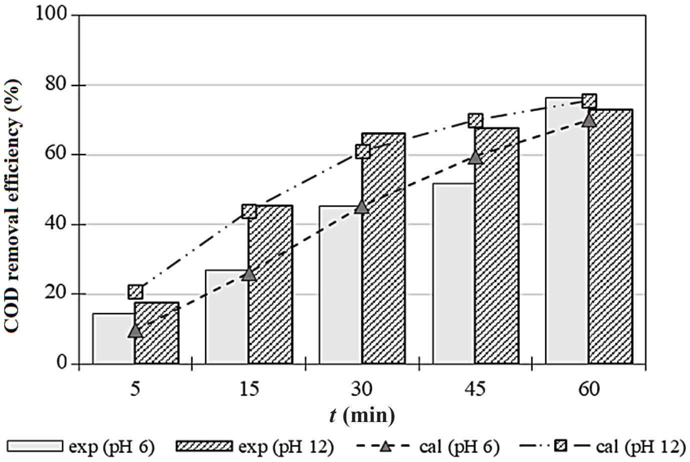

Fig. 4 – *Time dependence of COD removal efficiency*

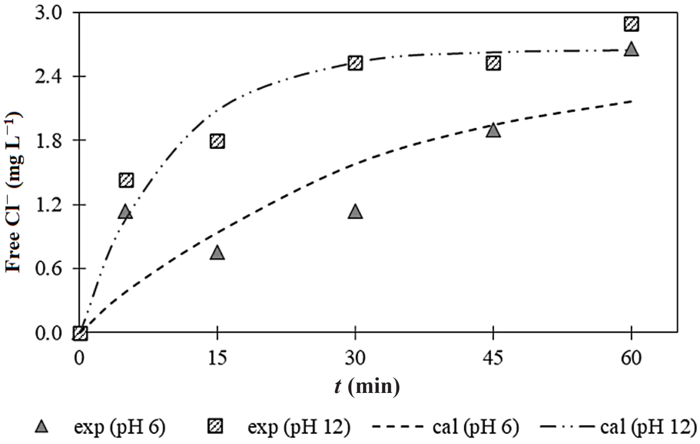

Fig. 5 – *Time profile of free chloride ions determined according to Mohr*

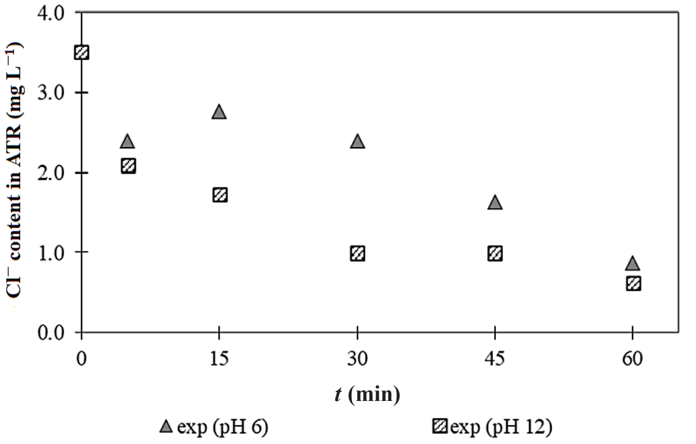

Fig. 6 – *Time profile of chloride content in the wastewater of atrazine at both pH*

Fig. 4 shows time dependence of COD removal efficiency during ozonation of model wastewater containing atrazine. It is evident that the removal efficiency was consistently higher at alkaline pH levels. In general, the indirect ozone reaction should be more effective in removing COD compared to the direct ozone reaction. After applying the kinetic model, the theoretical efficiency of degradation was 70 %, while for ozonation at alkaline pH it was 76 %.

Fig. 5 shows the time profiles of chloride ions. The concentration of free chloride ions increased with time. An increase in chloride concentration indicated fragmentation of atrazine in the degradation process, in which chlorides were released from the atrazine molecule – atrazine was dechlorinated by ozonation. Table 4 shows the values of the parameters of dechlorination equation at different pH values of ozonation process. Based on the dechlorination rate constant (R_D), dechlorination in alkaline pH was faster than in neutral pH. Time profile of chloride content in atrazine molecule is shown in Fig. 6. It is evident that the dechlorination of atrazine was faster in alkaline pH.

It is difficult to compare quantitatively our results with those published previously. The principal reason being the significantly different atrazine concentration values used. Most previously published papers mainly focused on micropollutants concentration values, whereas our research centered on examining significantly higher content of atrazine in a model wastewater, i.e., at the macropollutants concentration levels. The main reason was related to the previously mentioned unavailability of the method for direct analysis of atrazine content in the samples, because many available studies directly used concentration of atrazine. Thus, we evaluated the ozonation process of a model wastewater containing atrazine and its intermediates/products as a single contaminant specified by chemical oxygen demand (COD). Another method based on the chlo-

Table 4 – *Kinetics constants of dechlorination*

pH range	c_{eq} (mg L^{-1})	R_D (min^{-1})	R_{yx}
neutral	2.50	$3.33\cdot10^{-2}$	0.7368
alkaline	2.65	$10.3\cdot10^{-2}$	0.9125

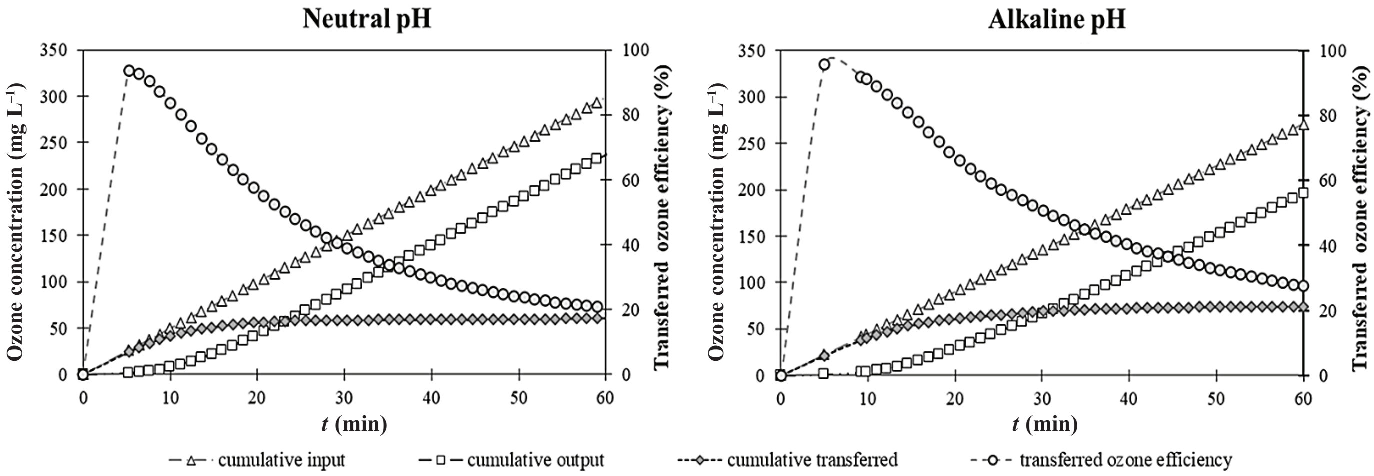

Fig. 7 – *Time dependencies of cumulative input and output, transferred ozone and efficiency of supplied ozone during ozonation of atrazine sample carried out at both pH*

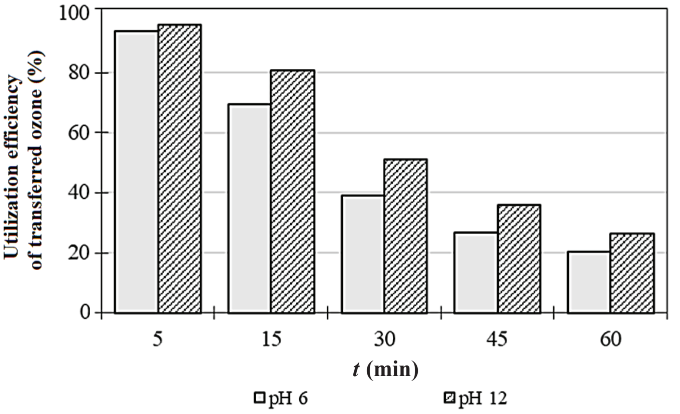

Fig. 8 – *Utilization efficiency of the supplied ozone by time*

ride concentration was used as indirect parameter to determine the atrazine dechlorination in ozonation process. For this determination, argentometric titration according to Mohr[29] was conducted. However, we compared our results directly with at least one available paper.[27] From a practical standpoint, it is of interest to study the kinetics of ozonation of wastewater containing a higher content of atrazine, e.g., in the case of contamination leaks or degradation of stored pesticide.

Teixeira *et al.*[27] studied the degradation of atrazine as the only contaminant characterized by the COD indicator by applying catalytic ozonation. A rotating packed bed with a volume of 200 mL was used. They achieved removal of 41–71 % of COD depending on the pH and catalyst dose in one hour of ozonation. Dissolved ozone in the reaction system was between 1.0–9.0 mg L^{-1}. Compared to this paper, we achieved almost the same COD degradation efficiency without the use of a catalyst. This result suggests that the use of a jet loop ozonation reactor, utilizing a Venturi ejector for the gas phase microbubbles inlet into liquid phase, enhances the process both at neutral and alkaline reaction conditions.

Fig. 7 illustrates the dependencies of the cumulative input and output mass of ozone in the unit volume of the reactor, the transferred ozone, and the efficiency of utilization of the supplied ozone on the reaction time during the ozonization of atrazine carried out at neutral and alkaline pH. The efficiency using the supplied ozone was higher by 17.6 % at a higher pH value of the experiment.

The utilization efficiency of the transferred ozone at different pH over time is shown in Fig. 8. The results show that the higher efficiency was obtained with the alkaline pH throughout the experiment. For ozonation at neutral pH, the value of specific amount of transferred ozone related to removed COD was 3.2 mg O_3 mg^{-1} COD. In the case of ozonation at alkaline pH, the value of specific amount of transferred ozone related to removed COD was 4.8 mg O_3 mg^{-1} COD.

Fig. 9 shows a graphical evaluation of the ozonation process at neutral and alkaline pH. The effi-

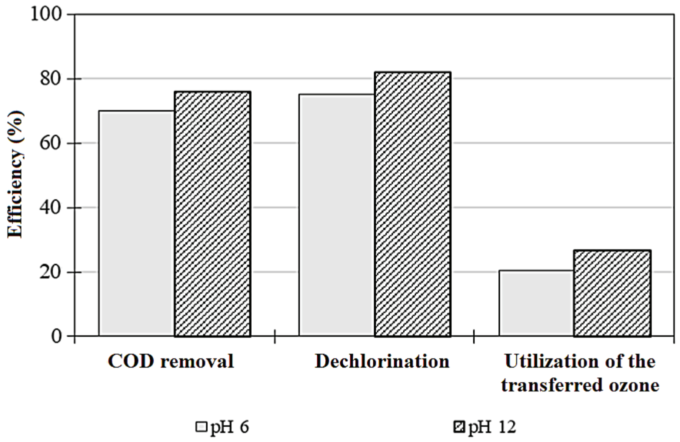

Fig. 9 – *Comparison of the efficiency of the ozonation processes*

ciency of COD degradation, dechlorination, and ozone utilization of supplied ozone were compared. It was evident that ozonation at alkaline pH was more effective for all compared criteria. This indicates the advantage of ozonation at alkaline pH.

Respirometric measurements

Respirometric measurements of a model solution of atrazine before ozonation showed that, as the concentration of atrazine in the respirometric cell increased, the respirometric rate of activated sludge microorganisms decreased (Fig. 10). The inhibitory effect of atrazine on the oxygen consumption of activated sludge microorganisms was observed. Therefore, kinetic equations describing the inhibitory effect of the substrate on the rate of oxygen consumption were used. The values of the kinetic and statistical parameters for the used models are shown in Table 5. The best fit of experimental data was obtained by the Aiba-Edwards model with a correlation coefficient value of 0.918. The Aiba-Edward kinetic model relates product inhibition to the culture's growth rate by introducing an exponential constant K_i.[44] This constant takes into account the presence of the toxic substrate concentration in the bioreactor. The greater the value of the inhibition constant K_i, the inhibition by the substrate occurs at its higher concentration. Based on the K_i value from Aiba-Edwards kinetic model, it was possible to determine that the inhibitory effect on the growth of microorganisms, resp. COD removal occurred at the COD value of atrazine wastewater of 1.62 mg L^{-1}.

The Aiba-Edwards kinetic model provided the best quality description of respirometric measurements even for ozonation products at neutral pH (Table 6). Maximum specific respiration rate was higher, but the value of inhibition constant was ten times lower (0.161 mg L^{-1}) than in the case of atrazine solution before ozonation (1.62 mg L^{-1}). Evaluation of respirometric measurement performed with ozonated model wastewater at neutral pH suggested higher value of inhibition constant K_i = 0.161 mg L^{-1}, meaning that inhibition in this case occurred at lower value COD in comparison to the previous case. For ozonation at alkaline pH, the value of inhibition constant is K_i = 0.842 mg L^{-1}. Thus, it can

Table 5 – *Kinetic and statistics parameters for respirometry measurements of atrazine before ozonation*

Model	$r_{X,max}$ (mg$_{O_2}$ g^{-1} h^{-1})	K_S (mg L^{-1})	K_i (mg L^{-1})	R_{yx}
Haldane	0.530	0.180	0.62	0.8489
Aiba-Edwards	0.425	0.128	1.62	0.9176
Tessier	0.322	0.107	1.98	0.8827

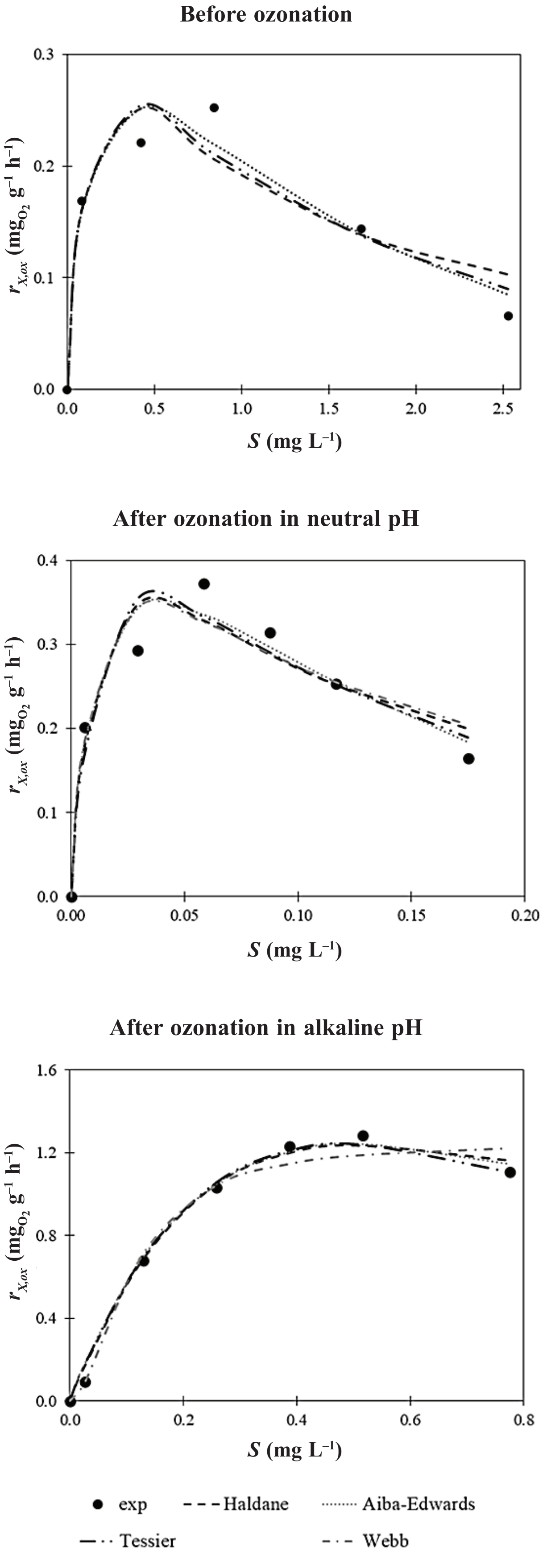

Fig. 10 – *Dependencies of specific oxygen consumption rate on concentration of COD (content of atrazine and its ozonation products) at different pH values*

Table 6 – *Kinetic and statistics parameters for respirometry measurements of atrazine ozone products at neutral pH*

Model	$r_{X,max}$ (mg_{O_2} g^{-1} h^{-1})	K_S (µg L^{-1})	K_i (mg L^{-1})	K_1 (µg L^{-1})	R_{yx}
Haldane	0.654	15.1	0.080	–	0.8913
Aiba-Edwards	0.584	12.3	0.161	–	0.9265
Tessier	0.447	11.3	0.203	–	0.8874
Webb	0.604	13.1	4959.0	92.7	0.8793

Table 7 – *Kinetic and statistics parameters for respirometry measurements of atrazine ozone products at alkaline pH*

Model	$r_{X,max}$ (mg_{O_2} g^{-1} h^{-1})	K_S (mg L^{-1})	K_i (mg L^{-1})	K_1 (mg L^{-1})	R_{yx}
Monod	3.53	1.000	–	–	0.7512
Haldane	4.41	0.660	0.400	–	0.9908
Aiba-Edwards	5.85	0.802	0.842	–	0.9911
Tessier	3.46	0.318	0.884	–	0.9932
Webb	2.27	0.259	481.0	1.27	0.9520

be concluded that ozonated model wastewater containing atrazine performed as a substrate with higher inhibition of activated sludge microorganisms than untreated model wastewater, but lower inhibition than ozonated wastewater at neutral pH.

The Monod equation was applied to describe the experimental data gathered during the ozonation of atrazine wastewater at alkaline pH because because it initially appeared to fit this kinetics model (Fig. 7). According to the correlation coefficient values, the experimental data were better fitted by the kinetic models describing oxygen consumption inhibition (Table 7). Although the Haldane, Aiba-Edwards and Tessier kinetic models provided almost the same quality of description of respirometric measurements, the values of the kinetic constants ($r_{X,max}$, K_S, K_i) were different. To compare the respirometric measurements of all samples, it was convenient to use the biokinetic constants according to Aiba-Edward model, because this kinetic model provided good description of inhibition effect of the samples before and after ozonation at neutral pH range. The comparison is shown in Fig. 11. The highest maximum specific oxygen consumption rate and saturation constant were for degradation products formed at alkaline pH range. It indicated that it was a faster biodegradable substance compared to the model solution of atrazine before ozonation and atrazine products formed by ozonation at neutral pH. According to the inhibition constant ($K_i = 0.842$ mg L^{-1}), even during ozonation at alkaline pH range, products were formed that had an inhibitory effect on activated sludge microorganisms even at lower concentrations characterized by the COD value. The inhibitory effect occurred at COD value 0.842 mg L^{-1}, while the inhibitory effect of atrazine before ozonation occurred at a COD value of 1.62 mg L^{-1}.

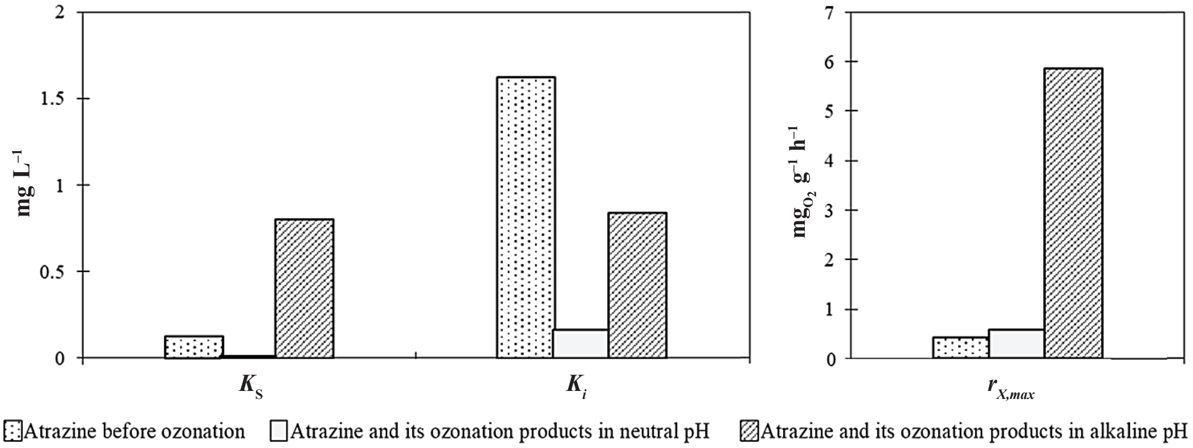

Fig. 11 – *Comparison of Aiba-Edwards kinetics constant values for atrazine model wastewater*

According to the values of $r_{X,max}$, results showed that ozonation of atrazine model wastewater formed faster biodegradable substances compared to the model wastewater of atrazine before ozonation. However, they also showed that ozonation products have an inhibitory effect on microorganisms of activated sludge to a higher degree than atrazine itself.

Conclusion

The results of this work show that the degradation of atrazine is more efficient at alkaline pH for all compared criteria (efficiency of COD degradation, dechlorination, utilization of transferred ozone). After ozonation at alkaline pH, atrazine with its ozonation products were more rapidly biodegradable and exhibited less inhibition on activated sludge microorganisms compared to ozonation at neutral pH. However, after ozonation, inhibition was observed at lower COD doses compared to before ozonation when only atrazine was present in the solution.

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