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Application of Ozonation-Based Processes to Reduce Environmental Impact of Waste Antibiotics

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Abstract The aim of the work was to determine the efficiency of direct ozonation, ozonation at elevated pH, ozonation at elevated pH with the addition of hydrogen peroxide, catalytic ozonation, photo-catalytic ozonation, ozonation with Fenton oxidation and ozonation with photo-Fenton oxidation for removal of waste Vancomycin from industrial wastewater. Vancomycin belongs to the glycopeptide antibiotics, preventing cell wall synthesis in susceptible bacteria. Batch oxidation experiments were carried out at room and elevated temperatures in a 300 mL laboratory bubble column. Additional toxicity test with *Vibrio fischeri* was accomplished to determine the environmental toxicity of treated and untreated wastewater. It was confirmed that a two-stage ozonation reaction takes place, more efficient at elevated temperatures. Complete mineralization was not achieved with any type of enhanced ozonation, as the decomposition efficiencies were up to 94%. Based on TOC (Total Organic Carbon) and COD (Chemical Oxygen Demand) determination, ozonation at elevated temperature with photo–Fenton oxidation was the most successful. Toxicity tests revealed significant detoxification of model wastewater in most of the applied oxidation processes. In most of the cases obtained inhibitions that were higher than 10%, while in photo-catalytic ozonation it was reduced below 10%.
Keywords: antibiotics, catalytic processes, ozonation, wastewaters

1. Introduction

Advanced wastewater treatment processes, which are mainly used in tertiary wastewater treatment, are: sand and membrane filtration, reverse osmosis, ion exchange, activated carbon adsorption and advanced oxidation processes (AOPs). Of all these technologies, AOPs has the greatest potential for application, mainly due to its high efficiency. The use of advanced oxidation processes (AOPs) includes processes based on hydroxyl radicals (·OH), superoxide ($\cdot O_2^-$) and ozonide ($\cdot O_3^-$), as well as processes based on other oxidizing species that favor sulfate or chlorine radicals. Various technologies have been investigated for the use of AOPs, in particular ozonation and UV irradiation.

2. Materials and Methods

Ozonation experiments with antibiotic Vancomycin (VM) were performed at constant gas flow and constant nominal ozone concentration in the gas phase, while varying the temperature at which catalytic and non-catalytic ozonation processes was performed. Reactor with a volume of 300 mL was used. Ozonation (O_3), indirect ozonation at elevated pH (O_3/pH=9.5), indirect ozonation at elevated pH with the addition of H_2O_2 (O_3/pH=9.5/H_2O_2), catalytic ozonation (O_3/Fe^{2+}), photo-catalytic ozonation (O_3/Fe^{2+}/UV), ozonation with Fenton oxidation ($O_3/Fe^{2+}/H_2O_2$) and ozonation with photo-Fenton oxidation ($O_3/Fe^{2+}/H_2O_2$/UV) were accomplished. The ozonation processes were carried out at two temperatures (21/50 °C) To determine the treatment efficiency, total organic carbon (TOC) and chemical oxygen demand (COD) were monitored.

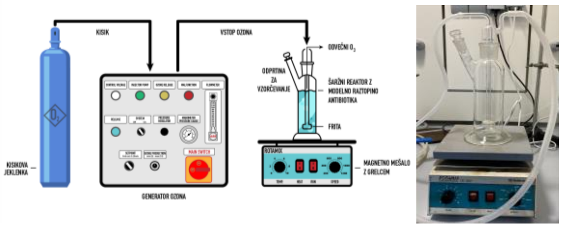
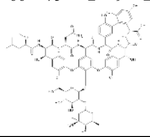


Figure 1. Experimental laboratory system for AOPs (Courtesy of Nina Lekše, 2025).

3. Results

The basic data on investigated antibiotic are presented in Table 1. First thermal stability of the antibiotic Vancomycin was checked to exclude its degradation due to elevated temperature. A solution of the selected antibiotic with a concentration of c = 400 mg L^{-1} was prepared and heated up to 50 °C. TOC and COD measurement confirmed that the degradation of VM does not depend on the elevated temperature but on the treatment processes, since there were no significant changes in measured values (± 3%).

Table 1. Basic data on investigated antibiotic Vancomycin (VM).

Name	Vancomycin
Molecular weight	1,449.3 g mol^{-1}
Molecular formula	$C_{66}H_{75}Cl_2N_9O_{24}$
Chemical structure	

Comparison of the degradation efficiency with respect to TOC for different ozonation processes at room temperature were between 37% and 82%. The most efficient process for degrading the antibiotic was ozonation with photo–Fenton oxidation. Direct ozonation, however, again proved to be the least efficient among the studied ozonation processes, reaching only 37%. At elevated temperature, the degradation efficiencies were between 56% and 85%. Once again, ozonation with photo–Fenton oxidation proved to be the most successful process, while the direct ozonation process was the least successful.

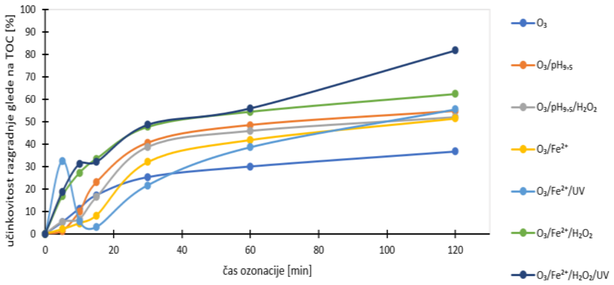


Figure 2. Removal of Vankomycin in different Ozone-based AOPs at 20 ºC according to TOC measurements.

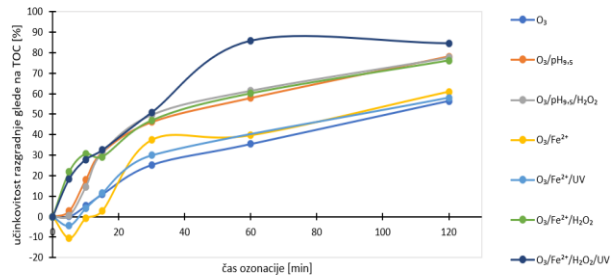


Figure 3. Removal of Vankomycin in different Ozone-based AOPs at 50 ºC according to TOC measurements.

The final COD degradation efficiencies determined in experiments at elevated temperature are in a similar range to those at room temperature; they range between 75% and 99%. Direct ozonation achieved the lowest efficiency, while ozonation with photo-Fenton oxidation and ozonation at elevated pH with H_2O_2 addition were the most efficient. When comparing the COD degradation efficiencies, ozonation processes with elevated process temperature proved to be more efficient.

Table 2. Inhibition of bioluminiscence in *Vibrio fisheri* test before and after AOPs processes at 20 ºC.

AOPs Process	Inhibition (%)
VM (400 mg L^{-1}) – Non-treated.	75 ± 5
Ozonation (O_3)	65 ± 7
Indirect ozonation at elevated pH (O_3/pH=9.5)	35 ± 7
Indirect ozonation at elevated pH and H_2O_2 (O_3/pH=9.5/H_2O_2)	20 ± 4
Catalytic ozonation (O_3/Fe^{2+})	57 ± 4
Photo-catalytic ozonation (O_3/Fe^{2+}/UV)	33 ± 1
Ozonation with Fenton oxidation ($O_3/Fe^{2+}/H_2O_2$)	≤ 10, non-toxic
Ozonation with photo-Fenton oxidation ($O_3/Fe_{2+}/H_2O_2$/UV)	≤ 10, non-toxic

Toxicity test confirmed, that also in terms of toxicity reduction, ozonation with photo-Fenton oxidation ($O_3/Fe^{2+}/H_2O_2$; $O_3/Fe_{2+}/H_2O_2$/UV) and ozonation at elevated pH with H_2O_2 addition (O_3/pH=9.5/H_2O_2) were the most efficient. Toxicity data are important to confirm AOPs efficiency in the case of further biological treatment of wastewaters containing VM.

4. Conclusions

The most successful type of ozonation was ozonation with photo-Fenton oxidation. According to the TOC and COD comparison, we observed that the degradation of the antibiotic into by-products occurred to a greater extent and complete mineralization did not occur. Ozonation itself turned out to be the least effective process, which means that we successfully optimized or upgraded direct ozonation with other combined processes.

5. Acknowledgement

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