



Removal of Selected Micropollutants by Ozonation

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Micropollutants are natural and manmade substances, such as pharmaceutical and personal care products, pesticides and industrial chemicals, which have been detected in water and in the environment in very low concentrations. Many of them, raise considerable toxicological concerns, are poorly removable by conventional wastewater treatment technologies. To reduce the release of such substances into the aquatic environment two advanced treatment processes based on ozone utilisation were investigated in laboratory scale. Degradation of two types of micropollutants, i.e. selected organochlorine pesticides and oil compounds have been studied. The results of ozonation and O₃/UV show that the highest removal rates were observed during the first 5 minutes of ozonation for all investigated pollutants. Removal efficiencies of chlorinated pesticides were in the range from 70.2 to 90.7 % after 60 minutes of ozonation. Removal efficiencies of about 90 % were observed for all investigated BTX compounds after 40 minutes of ozonation..

1. Introduction

Adoption of the Water Framework Directive (WFD) (EU, 2000) provides a policy tool that enables sustainable protection of water resources. The EC member countries have extended this list by relevant pollutants for individual countries. Thus, in the supplement of the Water Act (Act No. 364, 2004), altogether 59 relevant substances for SR have been identified. Many of the included substances belong to persistent organic pollutants. They are toxic, slowly biologically degradable and accumulative in organisms, in terrestrial and aquatic ecosystems. Environmental Quality Standards Directive (EU, 2008) defines the good chemical status to be achieved by all Member States in 2015 and it gives, together with the WFD (EU, 2000), the legal basis for the monitoring of priority substances in water, sediment and biota.

This paper focuses on the use of ozone for the elimination of selected dissolved organic pollutants from water and wastewaters. The first group comprised five selected organochlorine pesticides. Heptachlor (HCH) is an organochlorine compound that was used as an insecticide. The compound was designated as a possible human carcinogen by The International Agency for Research on Cancer (IARC, 2007). Hexachlorobenzene (HCHB) is a fungicide formerly used as a seed treatment, especially on wheat to control the fungal disease bunt. It has been classified by the IARC (2007) as possibly carcinogenic to humans. Hexachlorobutadiene (HCB) has been classified by the United States Environmental Protection Agency (U.S. EPA, 1991) as a possible human carcinogen. Pentachlorobenzene (PCHB) is very toxic to aquatic organisms, and it decomposes on heating or burning forming toxic, corrosive fumes including hydrogen chloride. Combustion of PCHB can also result in the formation of polychlorinated dibenzodioxins ("dioxins") and polychlorinated dibenzofurans. Lindane (LIN) is the

gamma isomer of hexachlorocyclohexane ("γ-HCH"). It is relatively long-living and in the environment it is transported long distances by natural processes like global distillation. It is a persistent organic pollutant which can bioaccumulate in food chain, though it is rapidly eliminated when exposure is discontinued (POPRC, 2007). The first four of them are classified as priority hazardous substances (EU, 2001; EU, 2008).

The second group consisted of selected organic petroleum compounds. Many petroleum compounds are believed to be a source of toxicity for the aquatic ecosystem and to create a chronic impact in water environment. The concentration of 60 % of soluble gasoline in water can be created by benzene, toluene, ethylbenzene and xylene (BTEX) compounds. The reasons why the BTX's are created such a serious problem are their acute and long term toxic effects. In addition to the toxicity, benzene is a known carcinogen (Mathur et al., 2007).

The influence of ozone on the degradation of selected organochlorine and organic petroleum compounds present in the water sample was studied.

2. Experimental

Ozonation experiments were carried out in a laboratory scale jet loop ozonation reactor. Synthetic wastewater containing single component standards of investigated compounds and distilled water was used in all experiments.

2.1 Experimental equipment and procedures

A scheme of the jet loop ozonation equipment is shown in Figure 1. The ozonation reactor was 0.08 m in diameter and 1.0 m in height. Effective volume of the reactor was 3.5 dm³. External circulation of the reaction mixture was maintained at 2.5 dm³ min⁻¹ by a membrane pump. A Lifetech ozone generator with maximum ozone production of 5 g h⁻¹ was used. Continuous flow of oxygen of 60 dm³ h⁻¹ was applied for the generation of ozone. Ozonation trials were carried out at 50 % of the maximum of the ozone generator's power.

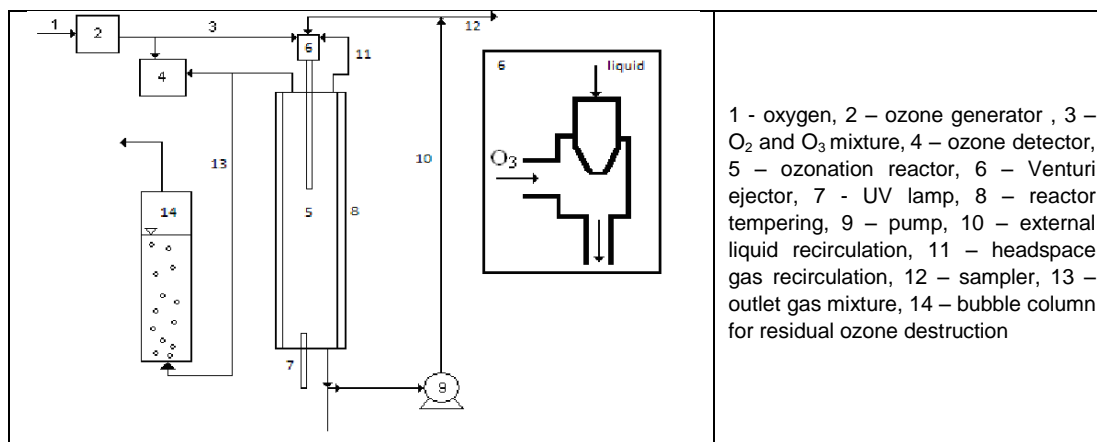


Figure 1: Schematic diagram of the experimental apparatus

The system was operated in batch mode with regard to wastewater samples. The samples were added into the jet loop ozonation reactor at the beginning of the trials. A mixture of O₃ and O₂ was injected into a wastewater sample through a Venturi ejector. At the same time, the ejector sucked the mixture of O₃ and O₂ from the reactor headspace. This, together with the external circulation, should improve the efficiency of ozone utilisation in the ozonation reactor. Pen-Ray UV lamp with the wavelength of 254 nm was used to generate hydroxyl radicals in the reactor. The excess ozone destruction was carried out in a bubble column filled with a solution of potassium iodide.

2.2 Analytical methods

Quantification of the organochlorine pesticides in water was determined by the gas chromatographic method after liquid-liquid extraction into n-Hexane, 96% p.a. for HPLC (Analytika, s r.o.). The extract was analysed by gas-chromatography by a micro electron capture detector (Agilent Technologies 7890A GC Systems). All parent organochlorine compounds used for the preparation of synthetic wastewater and standard stock solutions were purchased from Supelco Co in high quality.

The BTX compounds in water were analysed by the gas chromatographic method after static headspace extraction. The headspace part was analysed by gas chromatography using an MS detector (Agilent Technologies 7890A GC Systems). All compounds used for the preparation of synthetic wastewater and standard stock solutions were purchased from Dr. Ehrenstorfer.

The standard indigo method recommended by APHA, AWWA, WEF (2005) was used for the determination of ozone concentration in the aqueous phase.

2.3 Kinetic data processing

Experimental data were fitted by the zero, first and second order reaction kinetic models. Parameters of the applied kinetic models were calculated by the optimization procedure.

3. Results and discussion

Removal of studied pesticides in dependence on ozonation time is presented in Table 1 and Figure 2 (left).

Table 1: Removal efficiency values of organochlorinated compounds by ozonation

t/(min)	HCH/(%)	HCHB/(%)	HCHBD/(%)	LIN/(%)	PCHB/(%)
5	31.3	49.8	67.0	11.8	23.8
20	84.9	56.1	91.8	32.0	50.5
60	90.9	63.2	96.4	58.8	79.9

The highest removal rates were observed during the first 5 minutes of ozonation for all investigated pollutants. The highest removal efficiency was achieved in case of HCHBD. The lowest removal efficiency was obtained in the same reaction time for LIN. Removal efficiencies of chlorinated pollutants increased with the increase of the reaction time. The highest final removal efficiencies were observed for HCHBD and HCH. The best fit of experimental degradation data of all studied pollutants was obtained by the second order kinetic model. The rate constant values and the values of the correlation coefficient, R_{XY}^2 , corresponding to the results of the organochlorinated pesticide removal by ozonation, obtained by this model are given in Table 2.

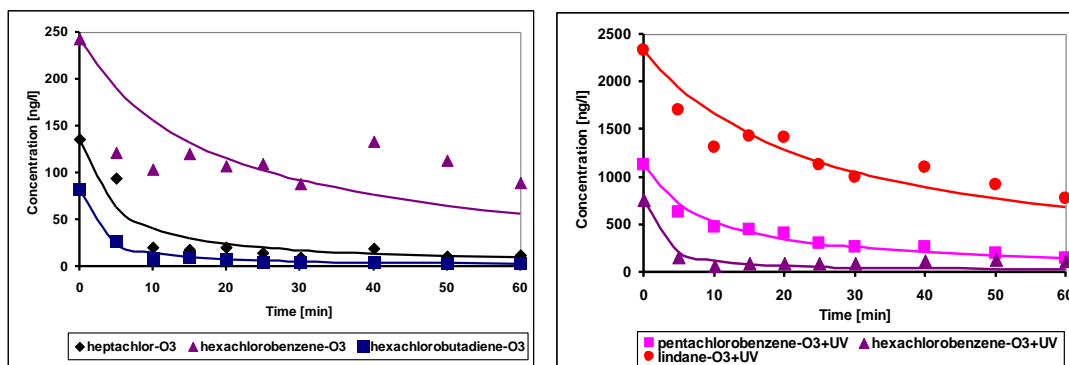


Figure 2: Experimental and calculated (—) pesticides removal during ozonation (left) and O₃/UV (right) treatments of model wastewater

The experimental and calculated degradation of HCH, HCHB and HCHBD with the ozonation time is plotted in Figure 2 (left).

Degradation of studied pesticides with the O₃/UV treatment time is presented in Figure 2 (right). Likewise to trials performed with sole ozonation, the best fit of experimental data was obtained by the second kinetic model. The rate constant values and the values of correlation coefficient r_{xy}^2 corresponding to the results of the organochlorinated pesticide measurements by this model are given in Table 2. The time dependencies of calculated removal of PCHB, HCHB and LIN with O₃/UV are also plotted Figure 2 (right). Kinetic parameter values summarised in Table 1 indicate that higher removal rates for HCH a LIN were observed using the O₃/UV treatment. For HCHBD and PCHB, higher removal rates were achieved by the sole ozone treatment.

Table 2: Kinetic parameter and correlation coefficient values

Pollutants		$k_2 / (\text{g m}^{-3} \text{h}^{-1})$	r_{XY}^2
Heptachlor	O ₃	$1.72 \cdot 10^{-3}$	0.9022
	O ₃ / UV	$1.10 \cdot 10^{-2}$	0.9995
Hexachlorobutadiene	O ₃	$6.09 \cdot 10^{-3}$	0.9924
	O ₃ / UV	$7.66 \cdot 10^{-4}$	0.9821
Lindane	O ₃	$5.43 \cdot 10^{-6}$	0.9031
	O ₃ / UV	$1.75 \cdot 10^{-5}$	0.8532
Pentachlorobenzene	O ₃	$7.59 \cdot 10^{-5}$	0.9517
	O ₃ / UV	$1.00 \cdot 10^{-4}$	0.9716
Hexachlorbenzene	O ₃	$2.27 \cdot 10^{-4}$	0.1782
	O ₃ / UV	$7.07 \cdot 10^{-4}$	0.9043

The time profiles of studied BTX compounds concentration with the ozone and O₃/UV exposure time are presented in Figure 3 (left) and (right) and Tables 3 and 4, respectively. The highest removal rates were observed during the first 5 minutes of both processes for all investigated pollutants.

Table 3: Removal efficiency values of BTX compounds by ozonation.

t/(min)	Benzene/(%)	Toluene/(%)	o-Xylene/(%)	p-Xylene/(%)
5	30.0	36.7	54.6	71.8
20	63.8	79.7	96.6	97.9
40	89.0	96.0	98.8	98.2

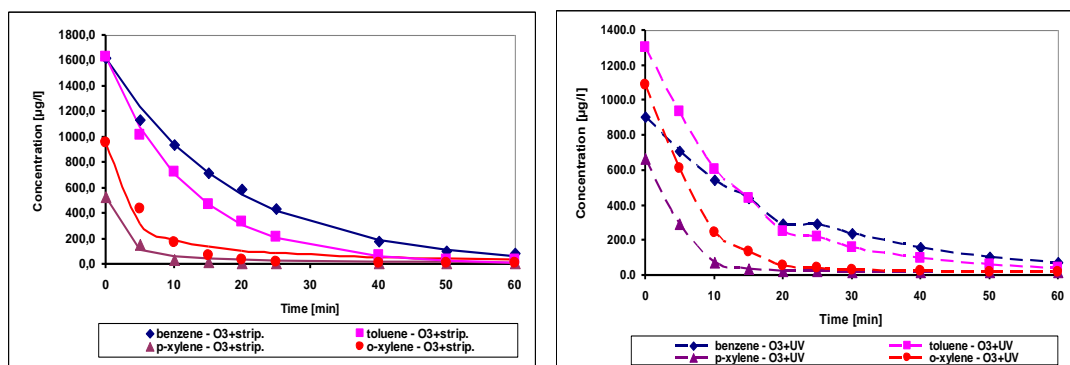


Figure 3: Experimental and calculated (—) BTX removals with O₃ (left) and O₃/UV (right) treatments of model wastewater

The highest removal efficiency was achieved in case of p-Xylene. The lowest removal efficiency in this reaction time was obtained for benzene. The removal efficiencies of BTX components increased with the reaction time. The best fit of experimental degradation data of all studied pollutants was obtained by the first order kinetic model. A comparison of o-Xylene and p-Xylene removal using the ozone and ozone/UV treatment of model wastewater is presented in Figure 4 (left) and Figure 4 (right), respectively. Slightly higher removal rates of these two pollutants were measured when treated with ozone. This is also confirmed by the values of removal rates given in Table 4. On the other hand, a slightly higher reaction rates were achieved for the removal of benzene and toluene (Table 4) with O₃/UV in comparison to the sole ozone treatment.

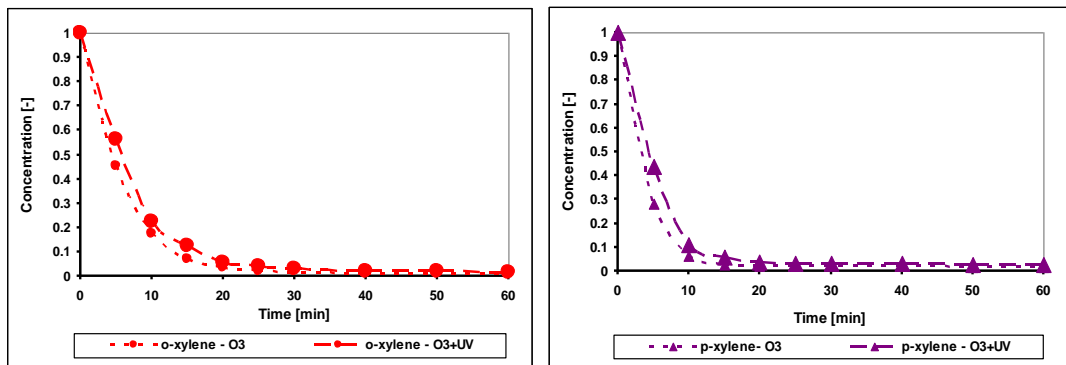


Figure 4: o-Xylene and p-Xylene removals by ozonation and O₃/UV treatments from model wastewater

Table 4: Kinetic parameters and statistical characteristics values

Pollutants		$k_1 / (\mu\text{g m}^{-3} \text{h}^{-1})$	r_{XY}^2
Benzene	O ₃	$4.75 \cdot 10^{-2}$	0.9911
	O ₃ / UV	$5.42 \cdot 10^{-2}$	0.9940
Toluene	O ₃	$7.30 \cdot 10^{-2}$	0.9957
	O ₃ / UV	$8.28 \cdot 10^{-2}$	0.9978
o-Xylene	O ₃	$1.66 \cdot 10^{-1}$	0.9988
	O ₃ / UV	$1.34 \cdot 10^{-1}$	0.9946
p-Xylene	O ₃	$1.82 \cdot 10^{-1}$	0.9914
	O ₃ / UV	$8.28 \cdot 10^{-2}$	0.9980

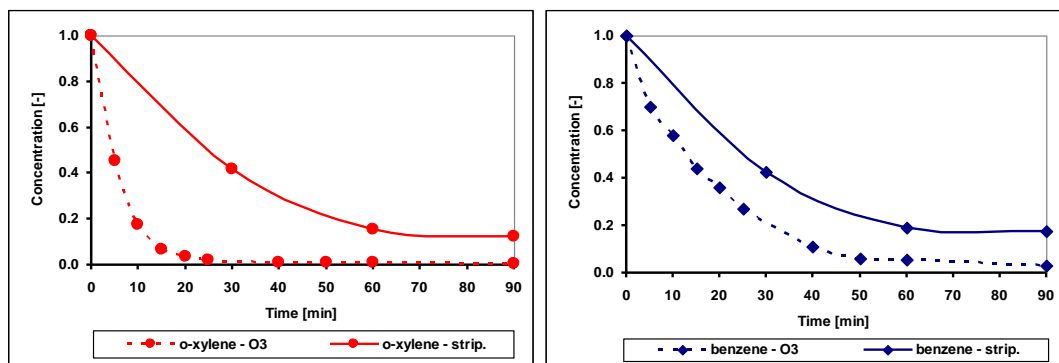


Figure 5: o-Xylene and Benzene removal by stripping and ozonation of model wastewater

The influence of gas stripping of the investigated BTX compounds during ozonation trials was also studied. Comparison of o-Xylene and Benzene removal by stripping and ozonation (including stripping due to O₃+O₂ mixture supply) of model water is presented in Figure 5 (left) and Figure 5 (right), respectively. It is obvious from these Figures that stripping significantly contributes to the removal of these compounds during the ozonation treatment, particularly in case of benzene.

4. Conclusion

Organochlorine pesticides and BTX compounds degradation using ozonation and ozone/UV processing were investigated. The results show that the highest removal rates were observed during the first 5 minutes of ozonation for all investigated pollutants.

The highest final removal efficiency (90.7 %) after 60 minutes of the ozonation of pesticides was observed in the case of HCHBD. The final removal efficiencies of PCHB, LIN and HCHB were 85.2 %, 80.7 % and 70.2 %, respectively. The best fit of the experimental degradation data of all studied pollutants was obtained by the second order kinetic model.

The treatment efficiencies of about 90 % were observed for all investigated BTX pollutants after 40 minutes of ozonation. Reaction time longer than 40 min resulted in very low treatment efficiency enhancement. The best fit of experimental degradation data for all studied petroleum compounds was obtained by the first order reaction kinetic model.

It can be concluded that, except for HCH, ozonation is a promising procedure for the removal of investigated pollutants from aquatic environment. However, further experiments are required in order to improve process efficiency, minimize influence of stripping process and to investigate toxic impact of ozonation intermediates and products on aquatic microorganisms.

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