A pilot scale comparison of advanced oxidation processes for estrogenic hormone removal from municipal wastewater effluent

Radka Pešoutová, Luboš Stříteský and Petr Hlavínek

ABSTRACT

This study investigates the oxidation of selected endocrine disrupting compounds (estrone, 17β-estradiol, estriol and 17α-ethinylestradiol) during ozonation and advanced oxidation of biologically treated municipal wastewater effluents in a pilot scale. Selected estrogenic substances were spiked in the treated wastewater at levels ranging from 1.65 to 3.59 $\mu g \cdot L^{-1}$. All estrogens were removed by ozonation by more than 99% at ozone doses $\geq$1.8 $mg \cdot L^{-1}$. At a dose of 4.4 $\cdot$ mg L^{-1} ozonation reduced concentrations of estrone, 17β-estradiol, estriol and 17α-ethinylestradiol by 99.8, 99.7, 99.9 and 99.7%, respectively. All tested advanced oxidation processes (AOPs) achieved high removal rates but they were slightly lower compared to ozonation. The lower removal rates for all tested advanced oxidation processes are caused by the presence of naturally occurring hydroxyl radical scavengers – carbonates and bicarbonates.

Key words | advanced oxidation processes, AOPs, estrogenic hormones, ozone, wastewater treatment

Radka Pešoutová (corresponding author)
Luboš Stříteský
Petr Hlavinek
AQUA PROCON s.r.o.,
Palackého tř. 12,
Brno,
Czech Republic
E-mail: *radka.pesoutova@aquaprocon.cz*

Petr Hlavínek
Faculty of Civil Engineering,
Brno University of Technology,
Brno,
Czech Republic

INTRODUCTION

Wastewater treatment plants (WWTPs) have always been one of the major sources of pollution for the aquatic ecosystems. Conventional activated sludge treatment technologies ensure high efficiency of biologically degradable organic pollution and nutrient removal, but are inefficient towards the so-called emerging contaminants: substances such as pharmaceuticals, pesticides, heavy metals, surfactants, burning inhibitors or cosmetic products (Crisp *et al.* 1998).

Prior research proved that concentrations of estrogenic hormones in municipal effluents and in surface water are sufficient to initiate changes in endocrine system resulting in metabolic stress, risk of liver damage, etc. (Purdom *et al.* 1994; Arcand Hoy *et al.* 1998; Kujalová *et al.* 2007). Concentrations of the estrogenic hormones in surface water are in order of units to tens of $ng \cdot L^{-1}$ and major share falls to 17α-ethinylestradiol (Kuch & Ballschmiter 2001; Cargouet *et al.* 2004). As low as 0.1 $ng \cdot L^{-1}$ of 17α-ethinylestradiol is sufficient to alter the endocrine system of fish (Purdom *et al.* 1994).

Despite the demonstrated negative impacts on aquatic fauna, no limits for estrogenic hormones concentrations in the WWTP effluents have been set by legislation to this date. However, the European Union has been encouraging projects focusing on the research on emerging contaminants with the aim of comprehending their impacts on living organisms and to restrict their emissions into the environment.

Tertiary stage of wastewater treatment based on advanced oxidation processes (AOPs) is a promising solution for removal of estrogenic hormones from municipal effluents. A number of studies demonstrated effects of AOPs on degradation of emerging contaminants including estrogenic hormones (Ternes *et al.* 2003; Huber *et al.* 2005; Zhang *et al.* 2006; Larcher *et al.* 2012). The bulk of the previous studies address AOP trials in laboratory conditions. Scale-up and further implementation of emerging contaminants removal to common practice requires trials at pilot scale and on-site comparison of potential AOP technologies.

This study compares ozonation and various AOPs (O_3/H_2O_2; O_3/UV; O_3/UV/H_2O_2) as a tertiary step of treatment of municipal wastewater in a pilot scale on degradation of selected estrogenic hormones. Novelty of this work is the application of ozonation and different AOPs on a pilot scale closely to the real conditions in terms of the treated water quality.

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METHODS

Pilot scale trials of ozonation and other AOP combinations took place at the WWTP Mikulov (municipality of Mikulov, Czech Republic). WWTP Mikulov is a conventional mechanical-biological treatment plant with capacity 24,850 population equivalents. The batch mode pilot plant (Figure 1) installed at the WWTP site was fed by treated wastewater from the secondary clarifier output. Treated effluent parameters were: pH = 7.4 ± 0.1, chemical oxygen demand (COD_{Cr}) = 30 ± 2.3 mg · L^{-1}, biochemical oxygen demand (BOD_5) = 2.5 ± 1.1 mg · L^{-1}, suspended solids = 11 ± 2.2 mg · L^{-1}, dissolved solids = 970 ± 26 mg · L^{-1}, N_{tot} = 8.0 ± 5.1 mg · L^{-1}; P_{tot} = 1.1 ± 0.5 mg · L^{-1}; absorbance$_{436nm}$ = 0.017 ± 0.003; *Escherichia coli* = 3800 ± 1900 CFU · 100 mL^{-1}.

Ozone generator EFFIZON GSO 10 (OZOMATIC) produced ozone from pure compressed oxygen (LINDE GAS) with the actual ozone production rate of 3.15 g $O_3 \cdot h^{-1}$ and concentration of 5% of ozone in the gas mixture. A low pressure mercury lamp with an input of 230 W supplied UV radiation (254 nm) for the UV-based AOP trials. Membrane dosing pump (GRUNDFOS DDI 2–16) fed hydrogen peroxide of technical quality with concentration of 35% (supplied by VIA-REK) into the static mixer. A centrifugal pump (LOWARA, flow rate 4.3 $m^3 \cdot h^{-1}$ at the given conditions) circulated the wastewater within the closed loop during each trial (batch) resulting in gradual increase of ozone (H_2O_2 and UV) dose in reaction tank with time. During trials the pilot plant discharge served as a point for taking samples.

Based on previous studies the ozone dose of approximately a thousand-fold the sum of initial concentrations of estrogenic hormones were set to ensure the estrogenic hormone removal rate is at least 95% at the end of each trial (Irmak *et al.* 2005; Zhang *et al.* 2006). The ozone transfer rate at given ozone generator output and wastewater volume was 0.088 mg $O_3 \cdot L^{-1} \cdot min^{-1}$ and it remained the same for all tested AOPs. The pH value of wastewater in all of the trials was 7.4 ± 0.1 and no further pH adjustments were made during trials. The O_3:H_2O_2 weight ratio of 1:1.6 used in the O_3/H_2O_2 and $O_3/UV/H_2O_2$ trials is in the range suitable according to previous studies, although it is lower than stoichiometric ratio for peroxone process (USEPA 2001; Kurbus *et al.* 2003; Acar & Ozbelge 2006).

Before each trial the wastewater was spiked with concentrated solution of selected estrogenic hormones (17β-estradiol, estrone, estriol and 17α-ethinylestradiol) prepared by solving in DMSO (purity >99.9%). All of these were supplied by SIGMA-ALDRICH in a solid crystalline or powder form with purities: estrone >99%; estriol >97%; 17β-estradiol >97%; and 17α-ethinylestradiol >98%.

Analytical determinations of estrogenic hormones using liquid chromatography-tandem mass spectrometry (LC/MS/MS) were performed at the RECETOX centre of the Masaryk University. Analytical determinations were performed as described by Čechová & Šimek (2012) with formic acid concentration of 5 mM and additional cleaning of eluate using Florisil Strata FL-PR (500 mg, 3 cm^3) and Sep-Pak Vac NH_2, (500 mg, 6 cm^3, 55–105 μm). Limits of quantification for estrone, 17β-estradiol, 17α-ethinylestradiol and estriol were 1.4 ng · l^{-1}, 1.0 ng · l^{-1}, 1.1 ng · l^{-1} and 0.7 ng · l^{-1}, respectively.

All numerical values shown in this paper are mean values of the two duplicates. The differences between these two duplicates for all trials were lower than the differences in performances of the tested AOPs.

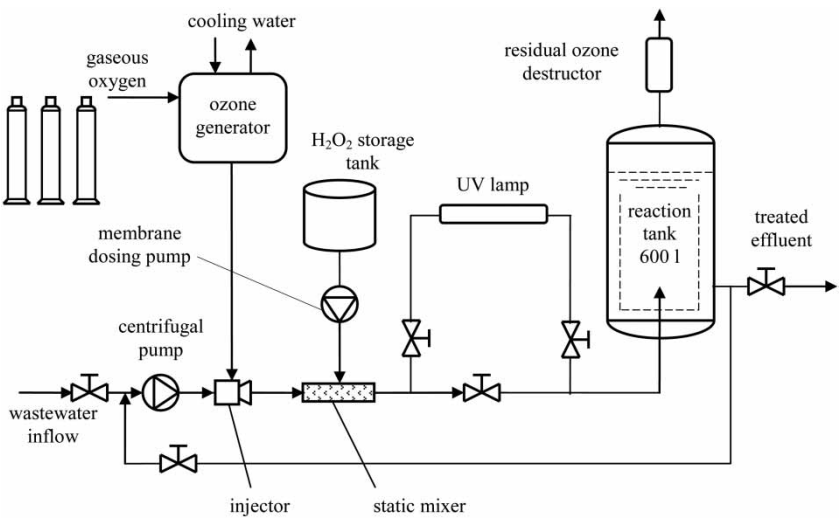

Figure 1 | Scheme of the pilot plant.

RESULTS AND DISCUSSION

Initial hormone concentrations and applied doses of chemicals

The concentrations of selected estrogenic hormones in the municipal effluent were in order of $ng \cdot L^{-1}$. When considering typical limits of quantification of available commercial laboratories it was decided to spike municipal effluent with a mix of concentrated estrogenic hormones. The approximate sum of their concentrations at the beginning of trials was set to be approximately $8\ \mu g \cdot l^{-1}$. The selected estrogenic hormones were spiked to the wastewater to be able to determine 95 to 99% removal.

The initial concentrations of estrogenic hormones for testing of ozonation and for testing of selected combinations of AOPs are presented in the following table (Table 1).

Effect of ozonation on estrogenic hormone degradation

The ozonation trials results demonstrated high degradation efficiency for all of the monitored estrogenic hormones even at low ozone doses. Estrone was the fastest reacting substance; its concentration was reduced by 95.8% at the dose of 0.88 mg $O_3 \cdot L^{-1}$ although its removal in a conventional biological treatment plant is the least of the tested estrogenic hormones (Joss *et al.* 2005). As an intermediate product of 17β-estradiol, 17β-estradiol, estriol and 17α-ethinylestradiol at the end of the ozonation trials (final dose of 4.4 mg $O_3 \cdot L^{-1}$) reached 99.8%, 99.7%, 99.9% and 99.7%, respectively (Figure 2).

The degradation rates acquired in this study are comparable to other studies treating similar wastewaters and hormones with similar initial concentrations (Irmak *et al.* 2005; Zhang *et al.* 2006). Studies on low initial concentration of estrogenic hormones in municipal effluents (units of $ng \cdot L^{-1}$) showed a great variation in removal efficiencies by ozonation (Ternes *et al.* 2003; Nakada *et al.* 2007). The weight ratio of degraded estrogenic hormone to ozone dose is (level of degradation in brackets): 1:560 for estrone (95.8%), 1:2,700 for estrone (99.8%), 1:2,200 for 17-β-estradiol (99.7%), 1:560 for estriol (80.3%) and 1:1,700 for 17α-ethinylestradiol (99.7%).

Table 1 | Initial concentration of estrogenic hormones in spiked wastewater for testing of ozonation and for testing of combinations of selected AOPs

	Estrone [$\mu g \cdot L^{-1}$]	17β-Estradiol [$\mu g \cdot L^{-1}$]	Estriol [$\mu g \cdot L^{-1}$]	17α-Ethinylestradiol [$\mu g \cdot L^{-1}$]
O_3	1.65	2.01	1.97	2.54
O_3/H_2O_2	1.79	1.72	2.06	2.15
O_3/UV	2.13	2.64	2.10	2.97
O_3/H_2O_2/UV	1.95	2.88	2.52	3.59

Effect of UV on estrogenic hormone degradation during O_3 treatment

The results of O_3/UV trials demonstrated no positive effect of UV irradiation on the removal rate of selected estrogenic hormones at given conditions. The removal rate of the ozonation exceeded the removal rate of O_3/UV for all tested estrogenic hormones at all ozone doses (Figure 2). The ozone dose of 0.88 mg $O_3 \cdot L^{-1}$ and the UV dose of 0.07 $Wh \cdot L^{-1}$ resulted in removal rate between 79.9% for estrone and 58.1% for estriol.

The weight ratio of degraded estrogenic hormone to ozone dose is (level of degradation in brackets; for UV dose see Figure 2): 1:2,100 for estrone (99.4%), 1:1,700 for 17β-estradiol (98.2%), 1:2,100 for estriol (98.7%) and 1:1,500 for 17α-ethinylestradiol (99.6%). Generally lower removal rates are inconsistent towards other studies (e.g. Irmak *et al.* 2005) and were caused by the presence of radical scavengers (carbonates and bicarbonates) common to real wastewaters as described by von Gunten (2003).

Effect of H_2O_2 on estrogenic hormone degradation during O_3 treatment

The peroxone process (O_3/H_2O_2) resulted in removal rate significantly lower than the ozonation itself (see Figure 2). One potential cause of inhibition of degradation process can be exceeding the steady-state concentration of hydrogen peroxide resulting in the absorption of hydroxyl radicals by H_2O_2 (von Gunten 2003). This was not the case because the actual ratio of O_3:H_2O_2 (1:1.6) was lower than the stoichiometric ratio (1:2.8). Another potential cause is the presence of hydroxyl radical scavengers.

The weight ratio of degraded estrogenic hormone to ozone dose is (level of degradation in brackets; for H_2O_2 dose see Figure 2): 1:2,500 for estrone (99.4%), 1:2,600 for 17β-estradiol (98.2%), 1:2,200 for estriol (98.7%) and 1:2,100 for 17α-ethinylestradiol (99.6%).

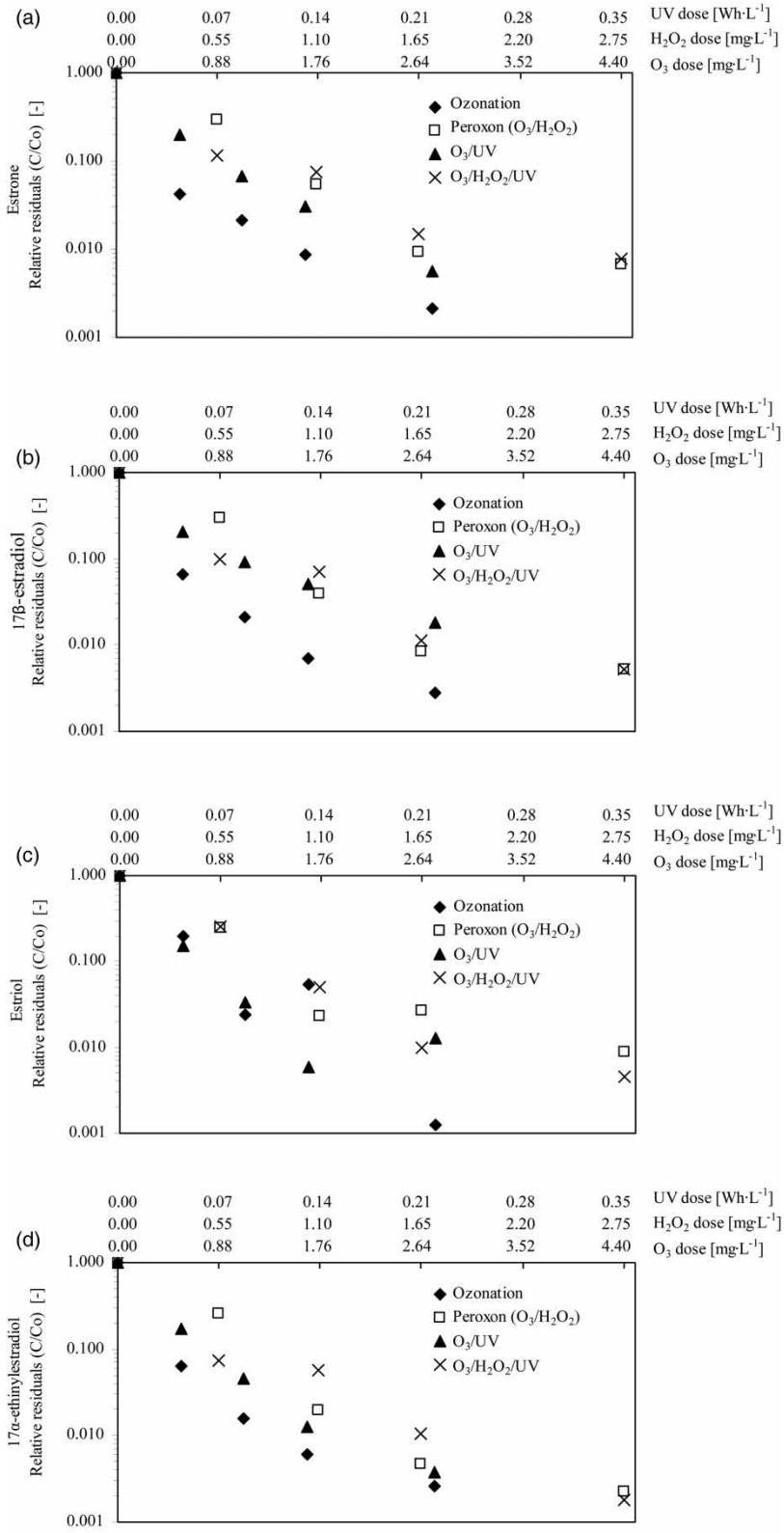

Figure 2 | Comparison of ozonation and different AOP combinations for estrogenic hormone degradation in dependence on O_3, H_2O_2 and UV doses: (a) estrone, (b) 17β-estradiol, (c) estriol, (d) 17α-ethinylestradiol.

Effect of H_2O_2 and UV on estrogenic hormone degradation during O_3 treatment

In theory combination of O_3/H_2O_2/UV supports spontaneous ozone decomposition, thus improves the removal rate (Ultrox International 1998). In comparison to ozonation, the removal rate of O_3/H_2O_2/UV trials decreased. The removal rate using this AOP is the worst of all for 17α-ethinylestradiol and estrone. The total removal rate at the end of the trials was comparable to other processes (removal rate exceeded 99%). Similarly to the peroxone (O_3/H_2O_2) AOP an excessive amount of H_2O_2 may result in process inhibition (Ultrox International 1998). The actual ratio of O_3:H_2O_2 was the same as in the O_3/H_2O_2 trials hence the probable reason for inhibition was the presence of hydroxyl radical scavengers (carbonates and bicarbonates) and not exceeding the steady-state ratio of O_3:H_2O_2.

The weight ratio of degraded estrogenic hormone to ozone dose is as follows (level of degradation in brackets; for H_2O_2 and UV dose see Figure 2): 1:2,300 for estrone (99.4%), 1:1,500 for 17β-estradiol (98.2%), 1:1,800 for estriol (98.7%) and 1:1,200 for 17α-ethinylestradiol (99.6%).

CONCLUSIONS

The effect of ozonation and three AOPs tested on the removal of estrogenic hormones from biologically treated municipal wastewater on pilot scale was investigated in this study. The following conclusions were made from the data obtained:

- Estrogenic hormones are generally easily removed by oxidation.
- In contrast to other studies, the most efficient process was ozonation.
- Disagreement with other studies was caused by presence of hydroxyl radicals scavengers (in this case the carbonates and bicarbonates).
- The presence of scavengers in real wastewaters results in AOPs being ineffective for removal of pollutants easily oxidised by ozonation (i.e. estrogenic hormones).
- The least resistant estrogenic hormone in all trials was synthetic 17α-ethinylestradiol.
- Natural hormone estrone was the most resistant estrogenic hormone tested.
- The lower the estrogenic hormone concentration the higher the required ratio of ozone to estrogenic hormone. For example when reducing estrone from 1.65 $\mu g \cdot L^{-1}$ to 0.07 $\mu g \cdot L^{-1}$ (i.e. reduction by 96%) the needed ratio is 1:560. When reducing estrone from 0.07 $\mu g \cdot L^{-1}$ to 0.003 $\mu g \cdot L^{-1}$ (i.e. reduction by 96%) the needed ratio is 1:56,000.
- The conclusion above could make real-life estrogenic hormone removal by ozonation ozone ineffective and/or cost ineffective as shown in Nakada *et al.* (2007) and Ternes *et al.* (2003).
- Further research on this topic with focus on treatment of real-life municipal effluents without spiking the wastewater is required in order to confirm or disprove if ozonation is sufficient and economic solution for removal of estrogenic hormones from municipal effluents.

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