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PHOTOLYSIS AND ADVANCED OXIDATION TREATMENT OF ESTROGENIC CHEMICALS IN TAP WATER AND TREATED SEWAGE

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ABSTRACT

The removal efficiency by photolysis and advanced oxidation (AOP) of some estrogenic compounds was investigated in tap water and biologically treated sewage. The compounds investigated included parabens, industrial phenols, sunscreen chemicals and steroid estrogens. Treatment experiments were performed using a UV lamp optimized for photochemical treatment in a flow through set-up. The effect of different concentrations of H_2O_2 and difference between tap water and treated sewage was investigated for all compounds.

The treatment effectiveness is evaluated based on the Electrical Energy per Order (EEO) (unit kWh/m^3), which is defined as the electrical energy consumed per unit volume of water treated required for 90 % removal of the investigated compound.

It was found that the removal efficiency was better in tap water than in wastewater which is due to the shadow effect from the inorganic and organic substance in the wastewater. Further, it was found that the removal of all the compounds was dependent of the UV dose for both treatment methods. The energy required for 90% removal of the compounds was between 28 kWh/m^3 ± 2.9 (butylparaben) and 1.2 kWh/m^3 (estrone) for the UV treatment. The AOP results in a more uniform value of EEO, which is between 8.7 kWh/m^3 (bisphenol A and benzophenone-7) and 1.8 kWh/m^3 (17α-ethynyl estradiol).
The removal at different concentration of H_2O_2 was investigated and it was found that removal effectiveness increased with concentration until 60 mg/L, but decreased at 100 mg/L, which may be caused by H_2O_2 scavenging the $HO^•$-radicals.

KEYWORDS

photolysis, estrogens, Electrical Energy per Order, AOP.

1 INTRODUCTION

The presence of estrogenic compounds in the environment has in recent years received considerable attention due to their damaging effects on the aquatic life. The estrogenic compounds influences the endocrine system, resulting in behavior changes, changes in mating

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behavior, feminization of fish and have even been linked to reduced sperm productivity in humans [1].

Degradation of estrogenic compounds by UV photolysis and the advanced oxidation process (AOP) UV/ H_2O_2 in laboratory setups has been reported in literature [2-4]. While degradation by these mechanisms are well known, the present literature does not give the data needed for estimating the real cost of treatment if the techniques were applied as a real treatment since they do not consider realistic flow through conditions, radical scavengers and the shadow effect seen in real wastewater.
Therefore this work has used a setup with realistic dimensions from a UV-treatment plant intended for disinfection of a wastewater treatment plant effluent by medium pressure UV-lamps. With this the removal efficiency by photolysis and advanced oxidation (AOP) of estrogenic compounds was investigated in tap water and biologically treated sewage.

2 METHOD

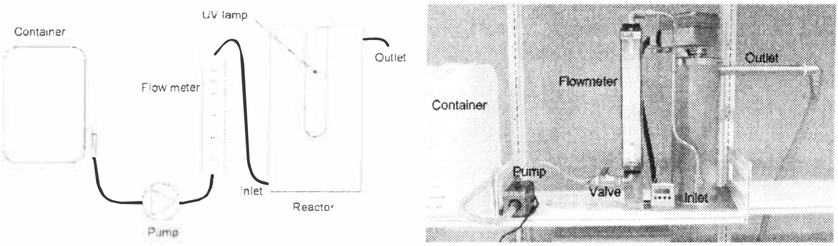
2.1 Regents and materials

All the estrogenic compounds investigated (*See Table 1*) were purchased from Sigma-Aldrich. Methanol, acetone, and heptane together with 35 % hydrogen peroxide, potassium titanium oxide oxalate dihydrate, sodium phosphate monobasic dehydrate and 85 % ortho-phosphoric acid were obtained from Sigma-Aldrich as well. The chemicals for derivatisation of the steroid estrogens (dithioerytrol, trimethylsilyl imidazole, and N-methyl-N-(trimethylsilyl)-tri- fluoroacetamide) were purchased from Sigma-Aldrich. All chemicals were of analytical grade except potassium titanium oxide oxalate dihydrate which was of technical grade.

The water used for experiment was wastewater effluent from Usserød wastewater treatment plant. The effluent was collected 17th and 26th of April together with 14th of May 2007 and 14th of August. The water was stored in the dark at 10 °C. The effluent was used for experiment within 3 days after the collection, however once after 12 days as an exception.
The water was poured into 25 L plastic containers and spiked with the mixed solutions so the concentration of xeno-estrogens and steroid estrogens were 1 µg/L and 400 ng/L, respectively. In the experiment with UV/H_2O_2 the hydrogen peroxide (35% solution) were added so the desired concentration was achieved.

2.2 Bench scale reactor

The treatments were carried out in a bench scale, flow through photoreactor (See *Figure 1*). The lamp (700W, Bau47, ScanResearch, Herning, Denmark) is located coaxial in the centre of the reactor. The UV-lamp was placed inside a quarts sleeve which is pumped with an inert gas to avoid ozone production. The distance from the lamp to the inner side of the reactor is 5.7 cm.



(a) (b)

Figure 1: Diagram (a) and photo (b) of the experimental set-up.

Figure 1 shows a photo of the experimental set-up and schematically drawing. The water was pumped from the plastic containers through a flowmeter and into the reactor at the bottom. A valve was used to adjust the flow rate. The samples for analysis were taken from the outlet after one retention time and from the containers (inlet concentration). The blind sample was taken before spiking and addition of hydrogen peroxide.

2.3 Sample preparation

For each experiment three samples of 500 mL each was analysed. The samples were acidified with phosphate buffer (pH 3). Internal standard was added to every sample before solid phase extraction (SPE) to compensate for possible losses during sample preparation and analysis. The extractions were preformed at commercial packed cartridges (500 mg C18 adsorbente/ 6 mL cartridge, Supelco), which were conditioned with 2 x 1.5 mL heptane, 1 x 1.5 mL acetone, 2 x 1.5 mL methanol, and 2 x 1.5 mL acidified water (phosphate buffer, pH=3) before the extraction begins. The water was transmitted to the SPE-column by the means of vacuum with a flow rate at maximum 5 mL per minute. Afterwards the column is dried for approximately 1 hour until completely dryness.
The samples were eluted with acetone until 5 mL eluent was collected in a test tube. Then the eluent was dried under a stream of nitrogen in a thermostat controlled heating block to almost completely dryness. One gram of silica-gel (Silica gel 60, 70-230 mesh from Merck deactivated with 1 % water) was suspended in 3 mL heptane-acetone mixture (65:35) and poured into 3 mL glass cartridge. The almost dried samples was resolved in approximately 0.3 mL heptane acetone mixture (65:35) and transferred to the top of the silica-gel. The test tube was washed with little more of the solvent mixture to minimize the loss of sample. Then glass cartridge containing silica gel and sample, was eluted with heptane acetone mixture (65:35) until approximately 5 mL eluent was collected. Once again the solvent was evaporated under a stream of nitrogen, but this time to completely dryness. The samples were dissolved in 250 µL heptane acetone mixture and transferred to a GC vial (300 µL, Chromacol).

2.4 Analysis of xeno-estrogens

The analysis of the estrogens was performed by gas chromatography using a Varian 3800 GC coupled to Varian Saturn 2000 Iontrap (MS-MS). The column used was a Varian, FactorFour capillary column (VF-5ms, 30mX0.25mm ID DF=0.25) with a gas flow of 1 mL/min. Seven and half µL sample was injected using Varian 8200 Autosampler in split/splitless injection mode with the Varian 1079 injection gate.

The GC oven temperature was maintained at 100 °C for 1 min, then programmed at 20 °C/min to 110 °C, then at 10 °C/min to 250 °C, followed by 25 °C/min to 285 °C, and finally 35 °C/min to 320 °C, which where hold for 7.4 min to ensure most of other organic compounds also came out.

Each compound was quantified based on a characteristic daughter ion of MS-MS spectroscopy and the other daughter ions were used for confirmation of the identity of the detected chemicals.

2.5 Estrogen analysis

After the analysis of xeno-estrogens the remaining extract of the samples was transferred to 3 mL reactival and the GC-vials were washed one or two times with acetone to ensure complete transferring of the sample. The samples were dried under nitrogen to completely dryness. Derivatisation mixture was made by mixing 2 mg dithioerytrol (DTE), 2 µL trimethyl-silylimidazole (TMSI), and 1000 µL N-methyl-N-(trimethylsilyl)-tri-fluoroacetamide (MSTFA). To the derivatisation vials 50 µL of that mixture was added and caped in order to be shaken. The vials were placed in an oven at 60 °C for 60 min. Afterwards, the vials were placed at the thermostat controlled heating block and evaporated to dryness under stream of nitrogen. The samples were dissolved in 250 µL heptane and transferred to GC-vials again.

The GC oven temperature was maintained at 80 °C for 1 min, then programmed at 25 °C/min to 230 °C, followed by 1 °C/min to 248 °C, and finally 45 °C/min to 320 °C, which where hold for 3 min to ensure most of other organic compounds also came out.

2.6 Data treatment

The treatment effectiveness is evaluated based on the Electrical Energy per Order (EEO) (unit kWh/m^3), which is defined as the electrical energy consumed per unit volume of water treated required for 90 % removal of the investigated compound [5].

The normalised concentration of the investigated chemicals was plotted against the electrical energy dose. These plots were used for estimation of the electrical energy per order.

The curves were fitted to the data using nonlinear regression.

$$\log\left(\frac{C}{C_i}\right) = \frac{-1}{EEO} \cdot EED \qquad (1)$$

; where C_i and C is the initial and the final concentration, respectively, EED is the electrical energy dose in kWh/m^3 and EEO is the electrical energy per order.

The regression is done by minimizing the sum-of-squares of the vertical distances of the data from the curve. The points were weighted by 1/Y^2 (relative weighting) [6].

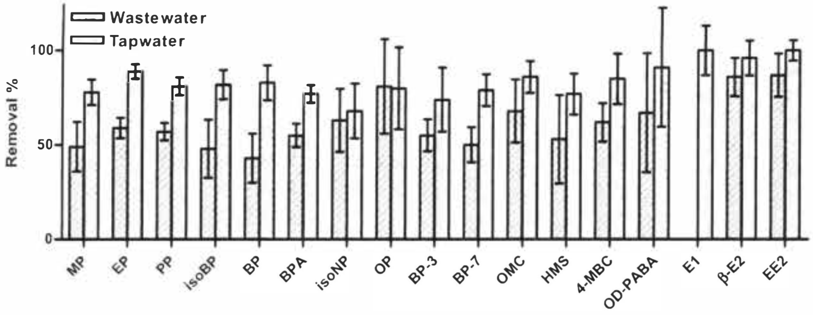


Figure 2: The removal of estrogenic compounds from tapwater and wastewater effluent by UV/H2O2. The electrical energye dose was 1.8 kWh/ m3 and the initial concentration of hydrogen peroxide was 60 mg/L. The error bars present the 95 % confidence interval.

3 RESULTS AND DISCUSSION

3.1 The Effect of water matrixe on the removal by AOP

A single experiment was done in tap water for comparison of the efficiency of UV/ H_2O_2 treatment in different water matrix. *Figure 2* shows the removal of the compound in tap water and wastewater effluent with an initial concentration of hydrogen peroxide of 60 mg/L. It is seen in *Figure 2* that the removal is greater in tap water than in wastewater effluent. This is due to higher contents of other materials than the spiked compound in the wastewater effluent. They can act as scavengers of $^{\bullet}OH$ radicals and/or result in shadow effect, where the compound either block the pathway of the light or adsorb the light.

Furthermore, the activation of hydrogen peroxide was higher in the tap water (21%) than in the wastewater (11%), which may be due to less shadow effect in the tap water resulting in a larger amount of the light being used for photolysis of H_2O_2. These results were in accordance with the literature. Neamtu et al. [4] found the same tendency when they investigated the removal of BPA.

3.2 Removal

At high EED the water thus the compounds, is exposed to a high dose of UV radiation and a high removal is obtained. If the results from UV and UV/H_2O_2 treatment with a electrical energy dose of 2.3 kWh/m^3 is compared, it is seen that a higher removal was obtained at UV/H_2O_2 treatment than only UV irradiation.

In the case of UV/ H_2O_2 treatment the removal seems more similar than when treated with UV. With an EED of 2.3 kWh/m^3 the removal is within the range of 51% to 95 % (51 to 86 without steroid estrogens) while the range is from 20 % to 99 % for UV treatment. This may be due to that the mechanism of the removal with $^{\bullet}OH$ radicals is non selective, while the UV treatment depends upon the absorbance and quantum yield, which varies is a discrete property of each compound. The results of estrone (E1) are missing in *Figure 4* due to analytical error. The increased removal when hydrogen peroxide was added is consistent with results obtained in literature [3, 4]

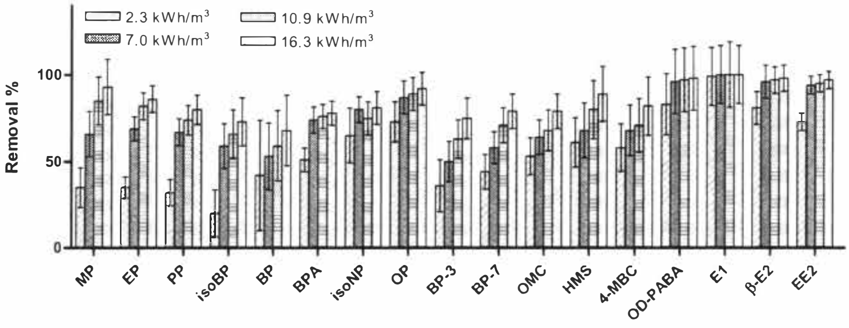


Figure 3: The removal of estrogenic compounds from wastewater effluent by photplysis. The error bars present the 95% confidence interval.

3.3 Electrical energy efficiency

The compounds with low value of EEO are easier to degrade than the one with higher value. In *Table 1* it is seen that the addition of hydrogen peroxide to the UV treatment results in a lower energy consumption (lower EEO values). The compound which value of EEO is between 11.5 and 28 kWh/m^3 for UV treatment, will have a reduction of EEO to approximately 7-8 kWh/m^3 if 60 mg H_2O_2 is added.

The values of EEO for UV treatment are between 1.2 kWh/m^3 and 28.0 kWh/m^3 for estrone (E1) and butylparaben, respectively. For the AOP the value is more uniform. BPA and BP-7 are the ones that require the most energy to be removed one order of magnitude (8.7 kWh/m^3). Estrone (E1) probably would be the one that require smallest amount of energy according to the tendency, but the data is missing due to problem with the analysis. The lowest EEO obtained is 1.8 kWh/m^3 (EE2).

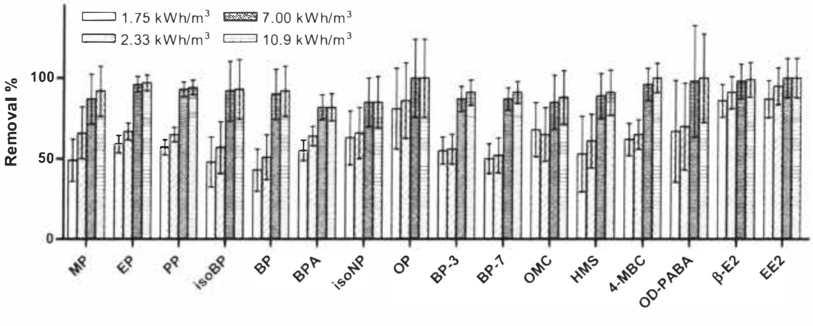


Figure 4: The removal of estrogenic compounds from wastewater effluent by AOP. The initial concentration of H2O2 was 60 mg/L. The error bars present the 95% confidence interval.

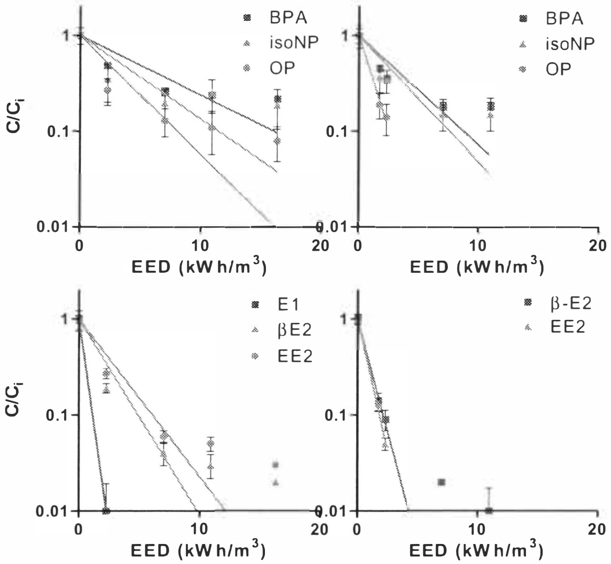


Figure 5. Degradation of selected estrogenic chemicals. Left photo treatment. Right AOP treatment with [H2O2] at 60 mg/L.

Table 1. Electrical energy per order (kWh/ m3) for the investigated compounds by photolysis and advanced oxidation (60 mg H_2O_2/L).

	Compound	UV EEOe± 95% CI	UV/H_2O_2 EEO ± 95% CI
MP	Methylparaben	13.9 ± 0.2	8.1 ± 0.6
EP	Ethylparaben	15.9 ± 0.7	5.3 ± 0.3
PP	Propylparaben	19.đ ± 1.1	6.4 ± 0.4
isoBP	Isobutylparaben	14.2e± 1.6	7.0 ± 0.4
BP	Butylparaben	28.0 ± 2.9	7.9 ± 0.4
BPA	Bisphenol A	16.1 ± 1.9	8.7 ± 1.2
isoNP	isoNonylphenol	11.5 ± 2.6	7.6 ± 1.2
OP	Octylphenol	8.đ ± 1.6	2.6 ± 0.1
BP-3	Benzophenone-3	25.4 ± 1.3	8.5 ± 0.6
BP-7	Benzophenone-7	21.1 ± đ.4	8.7 ± 0.5
OMC	Octyl methoxycinnamate	19.8 ± 2.2	7.đ ± 1.2
HMS	Homosalate	15.0 ± 1.6	7.7 ± 0.6
4-MBC	3-(4-Methylbenzyliden)camphor	17.3e± 2.2	5.0 ± 0.đ
OD-PABA	Octyl Dimethylaminobenzoate	4.2 ± 0.7	4.1 ± 0.đ
E1	Estrone	1.2[a]	-
β-E2	17-β-Estradiol	4.9 ± 0.8	2.2 ± 0.2
EE2	Ethynyl estradiol	6.đ ± 0.7	1.8 ± 0.03

[a] Regression with only two points.

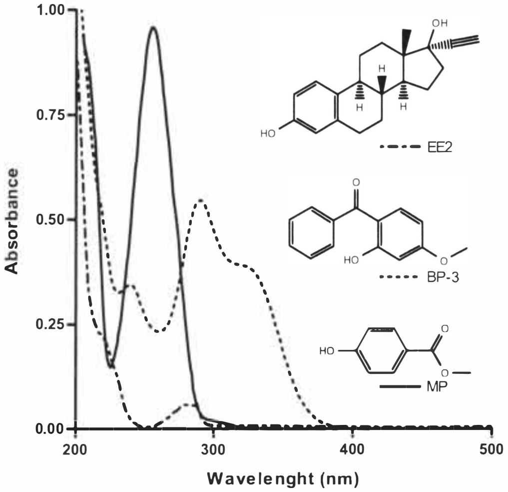


Figure 6: The absorption spectra and molecule structure of methylparaben (MP), benzophenone-3 (BP-3) and ethynyl estradiol (EE2).

3.4 Absorption

In *Figure 6* it is seen that methylparaben (MP) has local absorption maximum at 255 nm, benzophenone-3 (BP-3) has at 240 and 301 nm while ethynel estadiol (EE2) has at 280 nm. It also seems that MP and BP-3 is absorbing more light in the UV-range than EE2. There is no apparent relationship between the absorption spectra and the degradation with UV or UV-H_2O_2 of the compounds. A high absorbant in the UV-range does not make the compound easier to degrade and it is therefore not enough to have high absorption in the UV-range, but the quantum yield should also be high e.g., EE2 is degraded much easier than BP-3 even though it has a much lower absorbent in the UV-range.

CONCLUSIONS

It was found that the water matrix had influence at the removal of the investigated compounds. The organic and inorganic substances in wastewater acted as scavenger compound for the $^{\bullet}OH$ radicals and block the pathway of the UV light. Furthermore it was found that it is important to find the optimum of the concentration of hydrogen peroxide, since to low concentration results in decreased removal and to high also may results in decreased degradation due to formation of the less reactive $HO_2^{\bullet}$ radical.

It was found that all estrogenic chemicals could be removed by photolysis with very varied energy effectiveness and that AOP reduced the spread between the energy effectiveness of removing the chemicals and lowered the electrical energy dose.

In general it was found that the parabens, the industrial phenols, and the sunscreen chemicals required much higher energy dose than the steroid estrogens. BP was the estrogenic compound that required the highest energy dose to be degraded by direct photolysis, while by AOP (UV/H_2O_2) it was BPA and BP-7.

Addition of an optimal concentration of H_2O_2 reduced the energy consumption by 2-3-fold, which would be economical considering the price of energy and the chemical in Denmark. However, the energy use by the treatment is excessive compared to the energy described to be needed for the same efficiency of removal by ozone treatment [7].

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