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*Publication date:*  
2008

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*Citation (APA):*

Andersen, H. R., Hansen, K. M. S., Kosjek, T., Heath, E., Kaas, P., & Ledin, A. (2008). Photochemical treatment of pharmaceuticals. Abstract from 6th IWA World Water Congress and Exhibition, Vienna, Austria.

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## Photochemical treatment of pharmaceuticals

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**Keywords:** Pharmaceuticals, carbamazepine, clofibric acid, UV, AOP, Electrical Energy per Order.

### INTRODUCTION

Few pharmaceuticals are not removed in conventional sewage treatment, among the most important of these in terms of high consumption volume are carbamazepine [Clara, 2005], clofibric acid [Clara et al., 2005; Kosjek et al., 2007] and diclofenac [Kosjek et al., 2007]. It is known that the above mentioned three stable pharmaceuticals can be photo-degraded in surface waters by sunlight [Doll & Frimmel, 2003, Petrovic & Barceló, 2007]. This is likely the most important ultimate fate of non bio-degradable and non-sorbing pharmaceuticals. The UV-absorption spectra of carbamazepine and clofibric acid [Doll & Frimmel, 2003] shows that carbamazepine absorbs from 320 nm with a local maximum at 280 nm. Clofibric acid absorbs weakly between 300–240 and has a local maximum at 230 nm. Sunlight has very little intensity below 320 nm and even most sunlight below 400 nm is filtered by the atmosphere. UV lamps used e.g. for photo-chemicals reactions and disinfection of water can create a many fold more intensively illumination of water with a higher fractions of light having lower wavelengths thus potentially decreasing half lives of pharmaceuticals to the seconds time scale.

The aim of this study was to investigate the removal efficiency of six pharmaceuticals by photo-degradation and the advanced oxidation process (AOP), UV/H<sub>2</sub>O<sub>2</sub>. The six pharmaceuticals were the four non-steroidal-anti-inflammatory drugs: ibuprofen, diclofenac, naproxen and ketoprofen, the pharmacological active metabolite of the lipid lowering agent, clofibrin, clofibric acid, and the anticonvulsant and mood stabilizing drug, carbamazepine.

### METHOD

Treatment experiments were performed using a UV lamp optimized for photochemical treatment in a flow through set-up. For the AOP experiments 60 mg/L H<sub>2</sub>O<sub>2</sub> was added to the water before treatment. Tap water and treated sewage were spiked with 10 µg/L of each of the pharmaceuticals. The treatment effectiveness is evaluated based on the Electrical Energy per Order (EEO) (unit kWh/m<sup>3</sup>), which is defined as the electrical energy consumed per unit volume of water treated required for 90 % removal of the investigated compound [Bolton et al., 2001].

### RESULTS AND DISCUSSION

It was found that four of the six pharmaceuticals were almost completely removed in tap water both by UV treatment and by the AOP with the lowest treatment dosis of UV applied in the experiment, making it difficult to determine the exact removal efficiency. The exception was ibuprofen and carbamazepine, which exhibited a relationship between UV dose and removal (figure 1). The EEO was determined to 22.7 kWh/m<sup>3</sup> (UV) and 3.7 kWh/m<sup>3</sup> (UV/H<sub>2</sub>O<sub>2</sub>) for carbamazepine and 8.6 kWh/m<sup>3</sup> (UV) and 3.7 kWh/m<sup>3</sup> (UV/H<sub>2</sub>O<sub>2</sub>) for

ibuprofen (Table 1). However, all pharmaceuticals can be removed with UV treatment alone and therefore removal in wastewater was only tested by UV-treatment.

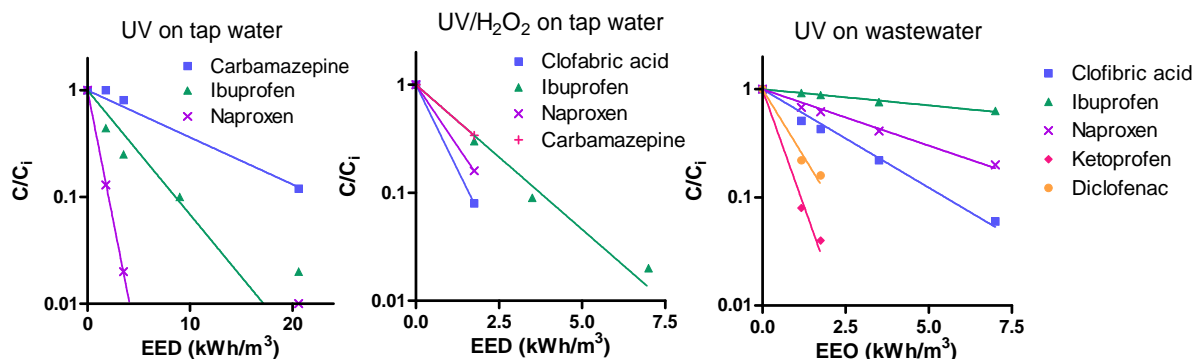


Figure 1: Energy effectiveness of removal of pharmaceuticals.

In the wastewater effluent the removal by UV was almost complete for ketoprofen even at the lowest treatment effect, while the other compounds show dependency of energy/UV dose applied (Table 1, Figure 1).

Table 1: Energy needed for reducing concentrations by one decade.

|                | Tap water          |                                                  | Wastewater effluent |
|----------------|--------------------|--------------------------------------------------|---------------------|
|                | UV<br>EEO ± 95% CI | UV/H <sub>2</sub> O <sub>2</sub><br>EEO ± 95% CI | UV<br>EEO ± 95% CI  |
| Clofibric acid | -                  | 1.6 <sup>a</sup>                                 | 5.5 ± 0.6           |
| Ibuprofen      | 8.6 ± 4.4          | 3.7 ± 0.7                                        | 33.4 ± 3.4          |
| Naproxen       | 2.1 ± 0.9          | 2.2 <sup>a</sup>                                 | 9.6 ± 1.1           |
| Ketoprofen     | -                  | -                                                | 1.2 ± 0.3           |
| Diclofenac     | -                  | -                                                | 2.0 ± 0.6           |
| Carbamazepine  | 22.7 ± 4.1         | 3.7 <sup>a</sup>                                 | -                   |

<sup>a</sup> Regression with only two points.

Ibuprofen is the compound that required the highest UV dose to remove 90 % from wastewater (EEO = 33.4 kWh/m<sup>3</sup>) where naproxen and clofibric acid required 9.6 kWh/m<sup>3</sup> and 5.5 kWh/m<sup>3</sup>, respectively. Ketoprofen and diclofenac needed considerable less energy than clofibric acid. Ibuprofen and naproxen are biodegradable and will be removed in biologically treated wastewater. Therefore the relevant estimate of the needed treatment is the energy use for removal of clofibric acid which required 5.5 kWh/m<sup>3</sup> for 90 % removal.

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