

# DEGRADATION OF EMERGING CONTAMINANTS (ECs) IN WASTE WATER TREATMENT PLANT EFFLUENTS WITH MODIFIED PHOTO-FENTON AS A TERTIARY TREATMENT PROCESS FOR WATER REUSE

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## Abstract

Water for reuse has to be free from xenobiotic substances and pathogens like *E. coli*. As normal municipal wastewater treatment plants (MWTP) are not able to entirely degrade these substances and have a high bacterial load, a tertiary treatment has to be found, which disinfects as well as removes these emerging contaminants from the water. This study focuses on modified solar photo-Fenton treatment (5 mg L<sup>-1</sup> Fe, initial pH ≈ 7, 50 mg L<sup>-1</sup> initial peroxide concentration) of a municipal wastewater treatment plant (MWTP) effluent. Various different approaches were investigated to degrade 15 selected emerging contaminants at an initial concentration of 100 µg L<sup>-1</sup> each in real effluent waste water with solar photo-Fenton in a CPC solar plant. Experiments conducted at pH 3 showed that it is possible to degrade ECs at low concentrations as well as disinfect the water. At higher pH, several difficulties have to be overcome, like the necessity of carbonate stripping, and the use of complexing agents to keep the iron available for the photo-Fenton process. The results for disinfection at higher (neutral) pH values showed a poor disinfection rate and even a re growth of bacteria due to the additional organic content which acts as a carbon source.

Keywords: Advanced oxidation process, solar photocatalysis, wastewater reuse

## Introduction

In recent years, emerging contaminants (ECs) [Martinez Bueno et al, 2007] have been found in treated waste water, surface and ground waters and even in drinking water in increasing amounts up to 15 µg L<sup>-1</sup> [Kasprzyk-Hordern et al, 2009]. If treated waste waters are going to be reused for irrigation, it has to be free of ECs, as they could accumulate in soil and crops as well as free of pathogens like *E. coli*. The Spanish "TRAGUA-CONSOLIDER" program, (treatment and reuse of waste waters for sustainable management, <http://www.consolider-tragua.com>) focuses on relieving water stress and on promoting the use of tertiary treatments for the reuse of waste waters. This work focuses on the

treatment of MWTP effluents with solar photo-Fenton at different pH (3, 4, neutral range), low iron concentration ( $5 \text{ mg L}^{-1}$ ) low initial peroxide concentration ( $50 \text{ mg L}^{-1}$ ) and the use of iron complexing agents (oxalic acid, humic acid).

## Methods

All reagents used for chromatographic analyses were HPLC grade. The 15 compounds selected were: Acetaminophen, Antipyrine, Atrazine, Caffeine, Carbamazepine, Diclofenac, Flumequine, Hydroxybiphenyl, Ibuprofen, Isoproturon, Ketorolac, Ofloxacin, Progesterone, Sulfamethoxazole and Triclosan. Photo-Fenton experiments were performed using iron sulfate, reagent grade hydrogen peroxide (30% w/v), sulfuric acid, oxalic acid (OA) and humic acid (HA). The experiments were performed at the Plataforma Solar de Almería in a pilot compound parabolic collector (CPC) solar plant batch reactor with  $3 \text{ m}^2$  illuminated surface, 22 L illuminated volume, 35 L total volume,  $20 \text{ L min}^{-1}$  turbulent flow [Kositzki et al, 2004]. All experiments were done in MWTP effluents taken downstream of the MWTP secondary biological treatment in El Ejido (province of Almería, Spain) and used as received within the next 3 days. pH adjustment and carbonate stripping was done with  $\text{H}_2\text{SO}_4$  (98%) as these species are strong radical scavengers [Klamerth et al, 2009; Vione et al, 2009] and spiked with the abovementioned 15 ECs at  $100 \text{ } \mu\text{g L}^{-1}$  each [Klamerth et al, 2010a]. Although the concentration of  $100 \text{ } \mu\text{g L}^{-1}$  for each compound is quite high compared to the real concentration of these ECs in the low  $\text{ } \mu\text{g L}^{-1}$  range [Unceta et al, 2010], it is still low enough to simulate real conditions and compare the different approaches. The concentration profile of each compound was determined by UPLC-UV (Series 1200 Agilent Technologies, Palo Alto, CA) [Klamerth et al, 2010b].

## Results and discussion

Experiments conducted at pH 3 showed a good degradation of the ECs. The degradation of ECs started in the dark (Fenton) and reached within  $t_{30W} = 220 \text{ min}$  a total degradation of over 98.5%. Similar behavior was achieved when working with a pH of 4 ( $t_{30W} = 170 \text{ min}$ , 96%). Working at pH 7, on the other hand, showed degradation in the Fenton phase (50%), and then very slow degradation in the photo-Fenton phase, due to inhibition / precipitation of the iron ( $t_{30W} = 140 \text{ min}$ , 63%). This leads to the conclusion, that complexing agents are necessary to keep the iron available for the photo-Fenton process. Two agents which were tested were oxalic acid and humic acids. The oxalic acid enhanced photo-Fenton showed a huge increase in the degradation rate ( $t_{30W} = 38 \text{ min}$ , 99.5%), but lowered the pH to below 4. The humic acid enhanced photo-Fenton shows pH dependency. Starting at pH 5.5 and ending at pH 4, the degradation is quite similar to the photo-Fenton at pH 4 with a degradation rate ( $t_{30W} = 180 \text{ min}$ , 95%), while starting at pH 7.3 and ending at 5.8 the degradation rate is slower ( $t_{30W} = 200 \text{ min}$ , 78%), but still better than the photo-Fenton at pH 7. Another experiment at pH 7 was conducted to test whether the mixture of waste water and treated waste water provided sufficient complexing agents to keep the iron in solution. The results were quite disillusioning, the degradation rate was very slow ( $t_{30W} = 215 \text{ min}$ , 43%). All experiments are shown in figure 1.

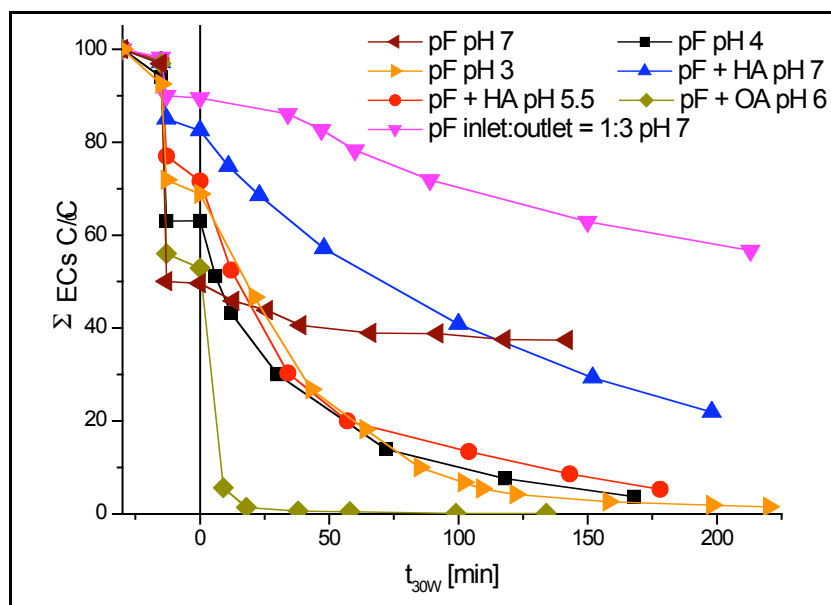


Figure 1. Comparison of different photo-Fenton (pF) experiments with different initial pH and/or different complexing agents, OA – oxalic acid, HA – humic acid.

Disinfection of the treated waste waters showed rather ambiguous results. A low pH favored the disinfection, so photo-Fenton systems with pH 4 and lower have a higher disinfection rate than neutral pH systems. When using humic acid and a neutral pH range there is actually a growth of bacteria population due to the additional carbon source. So the disinfection has to be reevaluated.

## Conclusions

It is possible to degrade emerging contaminants in MWTP effluents with modified photo-Fenton to negligible concentrations, although it strongly depends on pH and the used complexing agent. Disinfection is only effective at low pH values. This means, that the water has to be neutralized (from pH 3 back to pH 7) and therefore will have a higher salinity and therefore may not be useable for all plants. The use of pH range and or complexing agents, as well as the amount of acid for carbonate stripping depends on the particular waste water. Another consideration is the operating costs

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