Degradation of Emerging Contaminants (ECs) and Disinfection of Waste Water Treatment Plant Effluents with modified photo-Fenton

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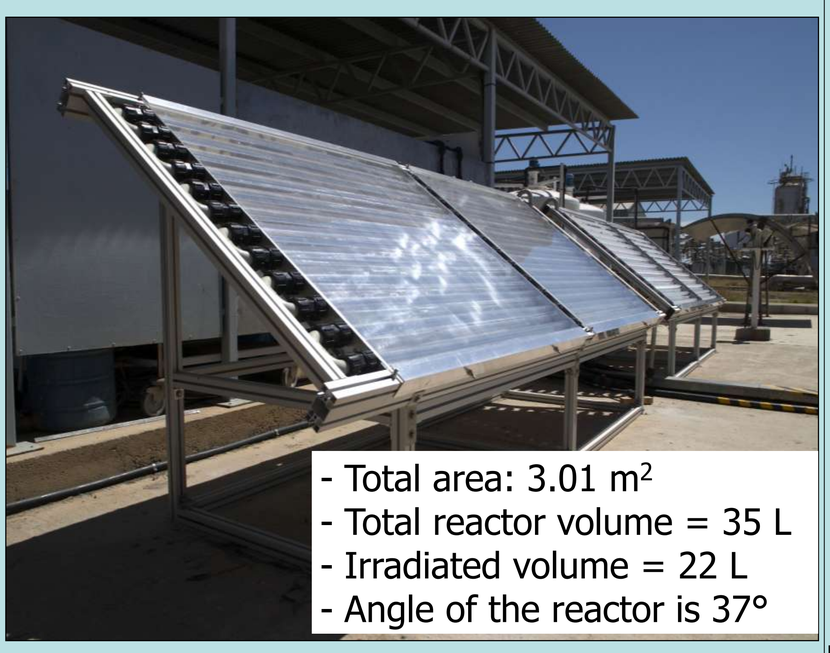
Introduction

In recent years, emerging contaminants (ECs) have been found in treated municipal wastewater. Most of these ECs have xenobiotic, endocrine disrupting, persistent and other non desirable properties. In addition to these organic pollutants, they are also discharged a wide variety of undesirable pathogens. Both matters must be solved prior to the release of the water into the environment or to reuse it . This work focuses on the treatment of real effluents from a municipal wastewater treatment plant (MWTP) with mild and modified solar photo-Fenton for the degradation of emerging contaminants. As MWTPs are biological systems, they are not capable of degrading all substances present in these waste waters, and many “emerging contaminants” [1] leave the MWTP unchanged. Although it is well known that the photo-Fenton process is suitable for the degradation and mineralization of organic contaminants, a typical photo-Fenton process with high Fe concentrations, high H_2O_2 concentrations and pH 2.8 is not suitable as a tertiary treatment for municipal waste water. Therefore the process has to be adapted to lower Fe concentrations and neutral pH values[2].

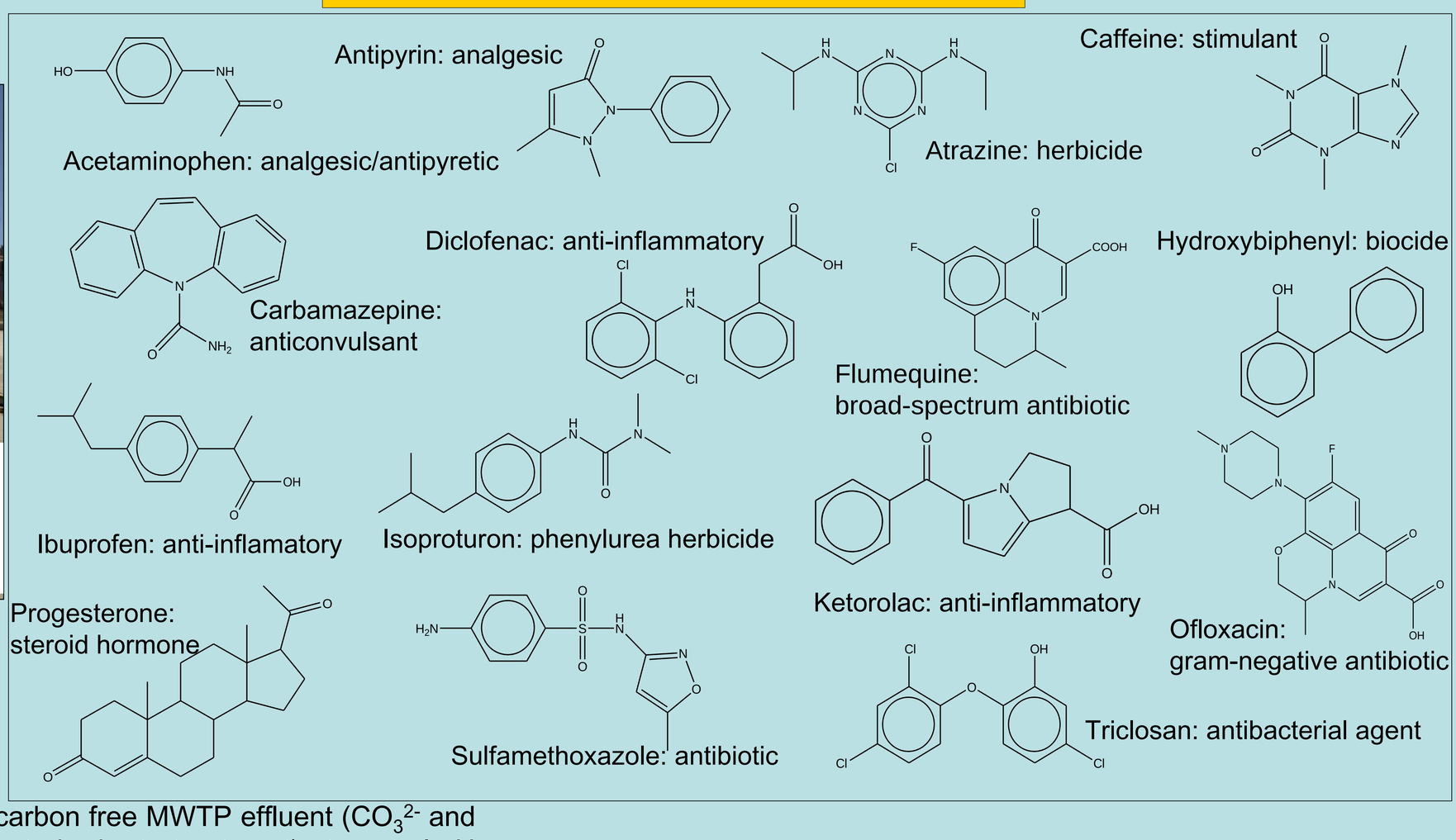
Experimental

Application of photo – Fenton at neutral pH, with 5 mg L^{-1} Fe, 50 mg L^{-1} H_2O_2 initial concentration and different complexing agents (oxalic acid, humic acid) treatment in a solar pilot plant with real effluent water from a MWTP (IC: 95-118 mg L^{-1}, DOC: 12-25 mg L^{-1}, COD: 25-100 mg L^{-1}, pH: 7.5-8.2) which was spiked with 15 ECs (chosen out of hundreds of compounds which can be present in WWTP effluents) at a concentration of 100 µg L^{-1} each or 5 µg L^{-1} each (SPE was performed for the 5 µg L^{-1} samples with a 50 fold concentration prior to injection). The compounds were detected with a UPLC-UV system (Agilent Series 1200). In certain intervals, samples were taken and inoculated on Luri Agar (a medium for total bacteria) and Endo Agar (a medium for total coliformes). The plates were incubated for 24 hours at 37ºC and the colonies counted.

CPC – solar reactor



Tested Emerging Contaminants



Results and discussion

Photo-Fenton experiments conducted with inorganic carbon free MWTP effluent (CO_3^{2-} and HCO_3^- are potent radical scavengers and were eliminated prior to treatment) at neutral pH showed that the process was not efficient because $[Fe(H_2O)]^{3+}$ concentration was so low at neutral pH. So other ligands have to be found to promote Fe^{2+} regeneration through:

$$Fe^{3+}L + h\nu \rightarrow Fe^{2+} + L^{\bullet}$$

The use of oxalic acid enhances the degradation behavior significantly (faster than photo-Fenton at pH 3), but has the disadvantage that the water had a low pH at the end of treatment (see Fig 2). Using influent and effluent mixture did not enhance the process.

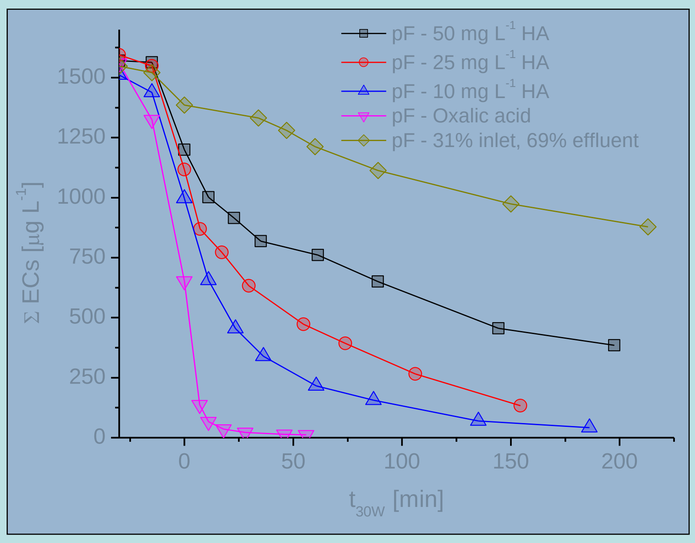


Fig.1 Comparison of photo-Fenton with different experimental setups.

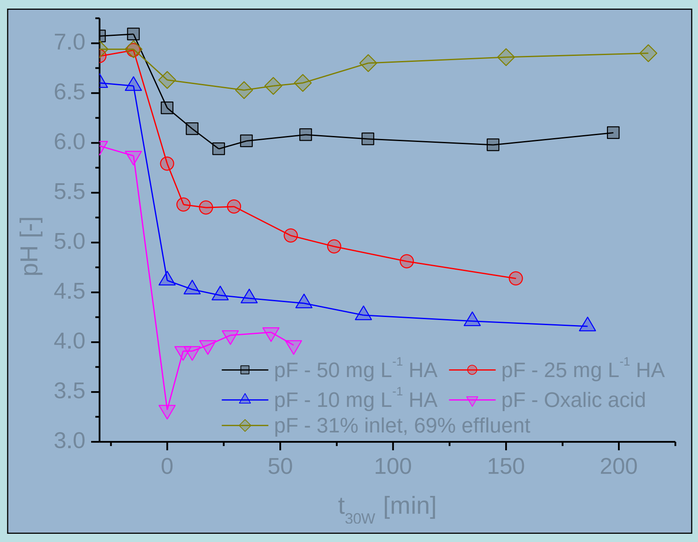


Fig.2 pH behaviour of the different experimental setups.

Adding humic acid (HA) to the stripped water prior to the photo-Fenton process enhanced the degradation significantly, compared to the photo-Fenton process without HA. Processes conducted with HA had a slower degradation rate than with oxalic acid, the pH on the other hand was significantly higher at the end of the process. Higher HA concentrations resulted in a more stable pH but on the other hand a slower degradation of the ECs.

Figure 3 shows the disinfection rate of the different systems. If the pH is changed to 7 and humic acid (either 10 mg L^{-1} or 2 mg L^{-1}) is used as a complexing agent, the CFU count does not reach the limit of detection (1 CFU mL^{-1}), although the decline is at least 3 log scales (between $4*10^7$ to $4*10^4$ and $3*10^7$ to $3*10^3$) for all bacteria and 10^6 to 10^3 for coliformes

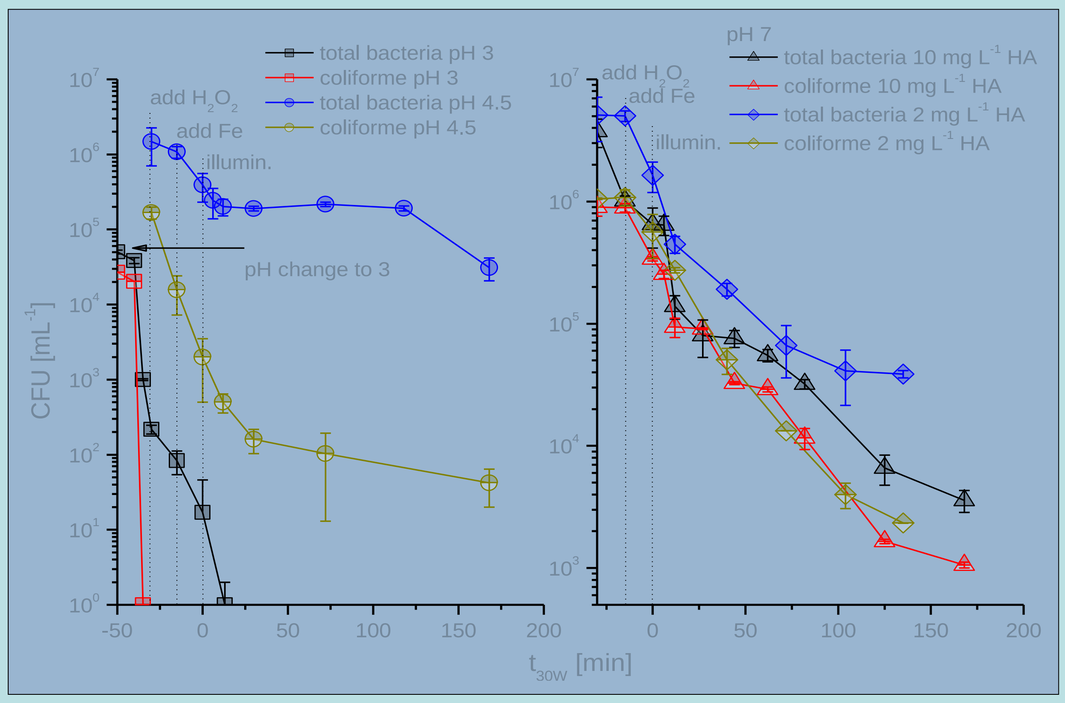


Fig.3 Disinfection of real waste water treatment plant effluents with different modified photo-Fenton systems

Conclusions

The experiments showed that contaminants at low concentrations (100 µg L^{-1} and 5 µg L^{-1}) can be successfully degraded with photo – Fenton at low Fe^{2+} (5 mg L^{-1}) and low H_2O_2 load (50 mg L^{-1} initial concentration).

The well known limitation of photo–Fenton (pH 2.8) is not so critic when using complexing agents such as oxalic acid or humic acid for the elimination of emerging contaminants at low concentration.

Disinfection on the other hand proves to be more difficult. Total disinfection only takes place when using typical photo-Fenton at pH 3, but when raising the pH to 7 and using humic acid, the CFU count does not reach the detection limit.

[1] Richardson S.D., Environmental Mass Spectrometry: Emerging Contaminants and Current Issues, Analytical Chemistry, 2008, 80, 4373-4402

[2] Klamerth N., Malato S., Maldonado M.I., Agüera A., Fernandez-Alba A., Application of photo-Fenton as a Tertiary Treatment of Emerging Contaminants in Municipal Wastewater, Environ. Sci. Technol. 2010, 44, 1792–1798

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