EVALUATION OF PERACETIC ACID FOR THE REMOVAL OF PHARMACEUTICALS IN WASTEWATER

E. Sagristà[1], M. Carré[2], L. Sala[3], V. Salvadó[1], M. Hidalgo[1]

[1]Departament of Chemistry, University of Girona, Campus Montilivi, 17071 Girona, Spain
[2]Empresa Mixta d'Aigües de la Costa Brava (EMACBSA)
[3]Consorci de la Costa Brava, Plaça Josep Pla, 4, 3-1, 17001 Girona

INTRODUCTION

Chlorine disinfection is traditionally applied as a tertiary treatment of urban wastewaters. However, it has long been warned that chlorine and their compounds react with organic matter leading to the formation of disinfection by-products (DBPs) that are potentially harmful to humans and aquatic organisms.

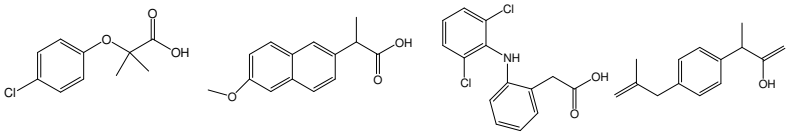
Peracetic acid (PAA), a strong oxidant, is a suitable alternative to NaClO for disinfection of treated wastewaters because of its broad spectrum efficiency against bacteria and viruses and easy application which permits a relatively cheap up-grade of existing wastewater treatment plants (WWTP). The main advantages of PAA application is that no toxic DBPs are generated in disinfection systems for wastewater reclamation when low doses are used.

WWTPs are designed to eliminate organic matter, N and P but wastewaters also contain other products such as pharmaceutical active compounds (PhACs) which are not completely degraded or removed during common biological treatment. Lipid regulators as clofibric acid and anti-inflammatory drugs as diclofenac, naproxen and ibuprofen are detected at µg/L levels in secondary effluents.

OBJECTIVES

1. To study the use of disinfectants (PAA and NaClO) for removing PhACs in wastewater reclamation systems.
2. To evaluate the efficiency of a ternary system consisting of an oxidation agent (PAA or NaClO) and an UV lamp
3. To test the ternary systems described above in the laboratory and in a WWTP (El Port de la Selva, Girona)

TARGET COMPOUNDS



Clofibric acid (CLF) Naproxen (NPX) Diclofenac (DCL) Ibuprofen (IBP)

EXPERIMENTAL

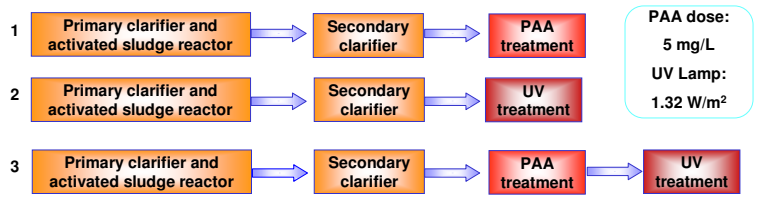
LABORATORY EXPERIMENTS

Spiked ultrapure water at 0.2 mg/L or spiked secondary clarified wastewater at 2 mg/L.

Oxidants → Treatment with different doses (1, 5 and 10 mg/L) of PAA or NaClO during 24 hours. Glass bottles containing the samples were protected from the light.

Oxidants + UV → Treatment with a dose of 5 mg/L of PAA or NaClO and irradiation with UV lamp at 254 nm.

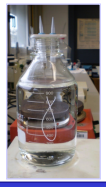
El Port de la Selva WWTP OPERATIONAL SCHEME



ANALYTICAL METHODOLOGY

1. **Preconcentration treatment: Hollow fiber supported liquid membranes**

Hollow fiber	Polypropylene Wall thickness: 200 µm (0.2 µm pore size) Internal diameter: 300 µm Length: 15 cm	Donor phase	0.01 M H_2SO_4 1 L of the sample
		Acceptor phase	0.1 M NaOH 150 µL



2. **Determination:Liquid chromatography (UHPLC-DAD)**

Column	C18 (2.5 µm, 50 x 2 mm)
Mobile phase A	ACN
Mobile phase B	20 mM KH_2PO_4 in water
UV detection	224 nm

RESULTS

LABORATORY EXPERIMENTS

Oxidation treatment

Table 1. Removal (%) of the pharmaceuticals in reagent water spiked at 0.2 mg/L applying different doses of PAA and NaClO after 24 hours.

		Removal (%)			
		CLF	NPX	DCL	IBP
PAA	1 mg/L	1.97	0.64	11.4	0
	5 mg/L	0.7	0	0	3.9
	10 mg/L	0	5.6	9.2	2.6
NaClO	1 mg/L	0	1.4	14.8	5.4
	5 mg/L	3.5	6.7	6.6	1.2
	10 mg/L	0	0.5	9.8	0

UV treatment. Reagent water

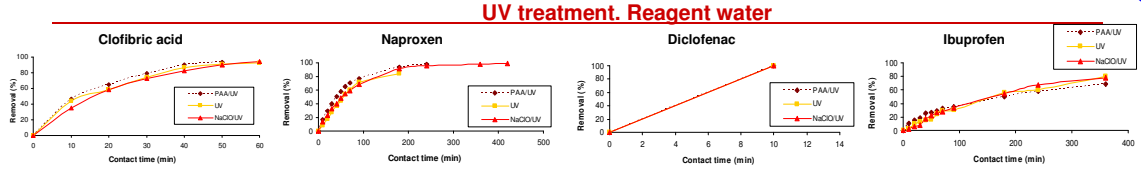


Figure 1. Removal (%) of the compounds in reagent water spiked at 0.2 mg/L by different kind of treatment.

UV treatment. Wastewater

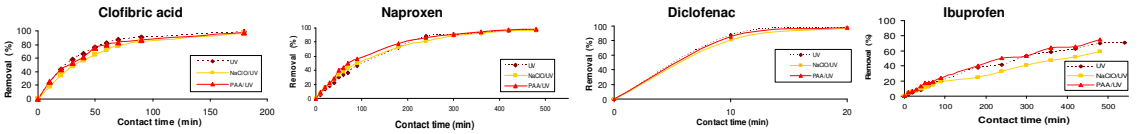


Figure 2. Removal (%) of the compounds in secondary clarifier wastewater spiked at 2 mg/L by different kind of treatment.

WWTP EXPERIMENTS

Occurrence in influent wastewater (after secondary clarifier)

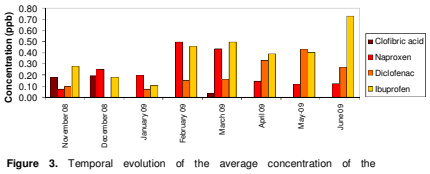


Figure 3. Temporal evolution of the average concentration of the pharmaceuticals detected in secondary clarifier wastewater.

Table 2. Average concentration of the pharmaceuticals detected in secondary clarifier wastewater.

	Average concentration (ng/L)
Clofibric acid	<LOD
Naproxen	150 ± 120
Diclofenac	360 ± 150
Ibuprofen	510 ± 200

Removal (%) after PAA/UV treatment

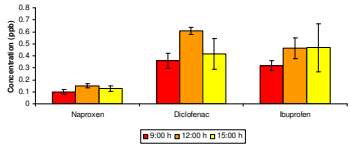


Figure 4. Temporal evolution of the average concentration of the pharmaceuticals detected in secondary clarifier wastewater during along the day.

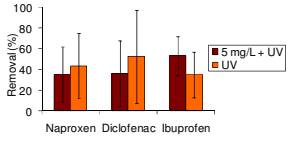


Figure 5. Removal (%) of some PhACs applying UV and PAA/UV PAA with a contact time of 5 minutes.

CONCLUSIONS

- The application of different doses of PAA and NaClO to spiked water samples containing 2 mg/L of CLF, NPX, DCL and IBP did not degraded these compounds.
- The irradiation with an UV lamp of the spiked samples results on an average elimination of 97% for DCL and CLF, 100 % for NPX and a 70% degradation for IBP. The irradiation times required in order to quantitatively eliminated the pharmaceuticals varied from 20 min. (DCL), 90 min. (CLF) and 300 min.(NPX). In the case of IBP only an average removal of 70% was obtained after 8 hours.
- The application of 5 mg/L dose of PAA prior to UV irradiation did not improve the efficiency of the elimination processes.
- The clarified secondary influent of El Port de La Selva WWTP contains few µg/L of NPX, DCL and IBP. Applying UV irradiation for 5 minutes an average removal ranging from 35 to 53 % of these compounds is obtained.

ACKNOWLEDGMENTS

This research was supported by the Spanish National Research Programme (CT;2008-06847-C02-02). E. Sagristà gratefully acknowledges a grant from the Spanish Ministry of Science and Technology (Ref. AP2007-01946).