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# Evaluation of tertiary treatments for the reduction of refractory micropollutants in wastewater

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## Summary

Some refractory micropollutants remain in treated wastewater after secondary treatments. In order to reduce their concentration in treated water, tertiary treatments can be used such as advanced oxidation processes and activated carbon. The efficiency of granular activated carbon in a long term is not well known and advanced oxidation processes have mostly been studied at laboratory scale. Advanced oxidation processes and granular activated carbon pilots were studied in two different wastewater treatment plants in order to determine their efficiency on numerous micropollutants. Both processes were efficient (>90%) on beta blockers and other drugs. The removal of alkylphenols was not complete with UV and hydrogen peroxide. Activated carbon was still efficient after six months functioning 24/24.

**Keywords:** micropollutants; activated carbon; advanced oxidation processes; pilots

## Introduction

Since several years, scientific studies demonstrated the contamination of natural waters, the presence of micropollutants in wastewater treatment plants outlet water (Pham et al., 1999; Karvelas et al., 2003) and the impact of micropollutants on the aquatic environment and fauna (Gimeno et al., 1997). Conventional wastewater treatment processes, although not initially designed for this purpose, can eliminate part of the micropollutants by adsorption on sludge or biodegradation (Choubert et al., 2010). Nevertheless, some micropollutants called "refractory" because they are not or only partially degraded, remain in treated wastewater at the outlet of the plants.

Tertiary treatments can allow a reduction of concentrations of micropollutants to reach values compatible with a good state of the environment. Processes that seem more efficient to eliminate refractory substances from treated wastewater are advanced technologies similar to the ones used for drinking water production. Among them, advanced oxidation processes (AOPs) rely on the formation of HO° radical witch is less selective than ozone and has higher reaction constants. The removal efficiencies of AOPs were mainly investigated at lab-scale for metals and organic micropollutants (Pereira et al., 2007) but results are lacking at a bigger scale. Granular activated carbon (GAC) seems also interesting but its efficiency is not well known in a long term.

## Material and Methods

### Micropollutants studied

Substances analysed during this study were chosen according to their occurrence in treated wastewater (Martin Ruel et al., 2011), their physicochemical properties

(mostly hydrophilic non biodegradable substances), their toxicity and the legislation but also their limit of quantification (LoQ) and the availability of a reliable analytical technique. The resulting selected substances include alkylphenols, beta blockers, antibiotics, contrast media, drugs, metals, herbicides, pesticides and PAHs.

#### Wastewater treatment plants selection and sampling

Two types of tertiary treatment were studied in three different conditions : an activated carbon pilot was tested in one plant and an advanced oxidation processes pilot was tested in two plants. The activated carbon pilot is a two meters height column filled with GAC and a control board to regulate the water flow in the column. It worked 24/24 during 6 months to evaluate the efficiency of GAC during time. The AOP pilot is a container with two reactors in parallel (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV) and a computing interface. The characteristics of the processes studied are presented in table 1.2.

**Table 1.2** Characteristics and operating conditions of the studied processes

Code	Size (PE)	Upstream treatment	Process type
A	28 000	Low load activated sludge + sand filter + ozone reactor	Granular activated carbon (Filtrisorb 400)
B	60 000	Membrane bioreactor	Advanced oxydation processes (O <sub>3</sub> , UV, H <sub>2</sub> O <sub>2</sub> )
C	28 000	Low load activated sludge + sand filter	Advanced oxydation processes (O <sub>3</sub> , UV, H <sub>2</sub> O <sub>2</sub> )

Water was taken at the inlet and at the outlet during periods of two hours to reconstitute a representative sample. To reduce contamination, the use of plastic elements was avoided during sampling. The samples were then conditioned in glass bottles. Samples arrived at laboratory within 24h after sampling and were treated the same day before analysis.

#### Data processing

Mass balances were performed based on wastewater flow and micro-pollutant concentration data at the inlet and at the outlet of the studied processes. The removal efficiencies (R) were calculated according to specific rules to take into account the variability of concentrations in wastewater and the analytical uncertainties associated to low concentrations of substances in complex matrices.

## **Results and Discussion**

Most of the analysed substances were detected in the treated water after a low load activated sludge or a membrane bioreactor. Concentrations ranged from 1 to 100 ng/L for PAHs, 1 to 1000 ng/L for beta blockers and pesticides, 0.1 ng/L to 10 µg/L for drugs, 0.1 to 10 µg/L for alkylphenols and 0.1 to 1000 µg/L for metals.

The fate of these substances through tertiary treatments was determined. Some significant results are :

- Activated carbon is efficient on beta blockers, other drugs excepted contrast media, herbicides and pesticides (>90%). Metals are not retained on the activated carbon. Removal of alkylphenols can vary. The measurement of the substances at the inlet and the outlet of the activated carbon pilot after 6 months of functioning proved that it was still efficient.

– All advanced oxidation processes tested were efficient on beta blockers and other drugs (>90%). The removal of alkylphenols is not complete with UV and hydrogen peroxide.

## Conclusion

Tertiary treatments can be used to reduce refractory micropollutants concentrations in treated wastewaters in order to improve their quality. The information obtained in this research project will allow Suez Environnement to propose efficient new solutions tested on a pilot scale for wastewater treatment plants.

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