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TESI DI LAUREA

OZONATION OF DOMESTIC WASTEWATER MODEL CONTAINING PHARMACEUTICAL RESIDUAL

RELATORI:
CH.MO PROF. ING.AMEDEO LANCIA

CANDIDATO
CARMEN D'ORSI M67/290

CORRELATORI:

ING. MARCO TAMMARO

ING. ALESSANDRO ERTO

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ABSTRACT

The emission of so-called *emerging* unregulated contaminants has become an environmental problem and there is widespread agreement that this kind of contamination requires a legislative intervention. Emerging pollutants are detected in relevant quantities in wastewater treatment plants effluents, since the wastewater treatment process is usually not or scarcely effective, due to emerging pollutants relatively low concentrations and the associated difficulty in analysis.

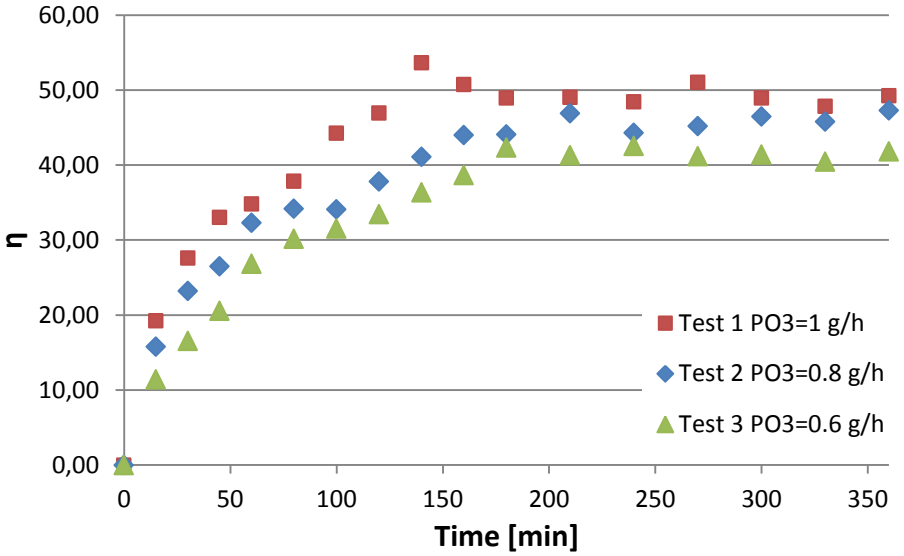
Different classes of pollutants, mainly PPCPs (Pharmaceutical and Personal Care Products) and EDCs (Endocrine Disrupting Compounds), have been traced during wastewater treatment in a conventional urban STP (Sewage Treatment Plant).

The presence of small concentration of PPCP has been associated to chronic toxicity, endocrine disruption and the development of pathogen resistance. The consequences are particularly serious in aquatic organisms as they are subjected to multigenerational exposure [Halling-Sørensen *et al.*, 1998]. Concerning the EDCs, they disturb the endocrine system by mimicking, blocking or also disrupting function of hormones, affecting the health of humans and animals species.

The study, performed in ENEA Centre of Research of Portici (Naples), is focused on the simulation of an on-site ozone treatment, in a continuous system, of emerging pollutants contained in the liquid fraction of blackwater (LFB).The simulated LFB is deionized water, containing four representative pharmaceutical compounds (ofloxacin, atenolol, hydrochlorothiazide and 17-βestradiol).The concentrations of these emerging pollutants are assessed being based on a typical family's hypothesis of pharmaceuticals consumption. The treatment is simulated at different production of ozone and pollutants concentrations. The efficiency of mineralization of the four compounds is evaluated by measuring the TOC (Total Organic Carbon) variation.

Test 1 to Test 3 were carried out to assess the variation of the mineralization efficiency according to the established ozone production. The tests were performed for equal initial TOC concentration (≈9.52 mg/L), but with different ozone production. Test 1 was conducted with a production of ozone of 1 g/h, Test 2 with a production of 0.8 g/h whereas Test 3 with a production of 0.6 g/h, respectively.

In Figure the efficiency patterns for each tests are shown.



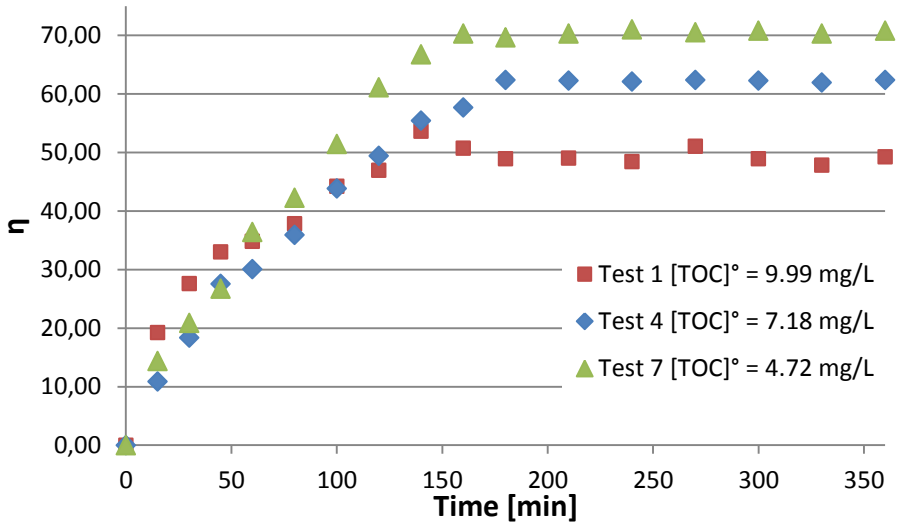
Variation of the efficiency of mineralization at different ozone production. Experimental conditions: $[C]_0$ = 16.4 mg/L, [TOC]≈9.52 mg/L, t = 360 min

It is known that the ozone will initiate a series of reactions in water that are very complex and quite specific according to the water being treated. After the ozone decomposition phase, the oxidative attack of the pharmaceutical molecules begins. Ozone reacts with TOC in water by two different path ways: directly as molecular ozone and indirectly via radicals ($OH^{\cdot}$**),** formed by decomposition of ozone in water. Decomposition of O_3 in water is affected by pH, since it affects the concentration of OH radicals. In fact, at low pH values the formation of $OH^{\cdot}$ radicals decreases and the ozone direct attack is mainly prevalent. By evaluating the initial and final pH, it can be noticed that pH decreases over time. This pH decay is related to the formation of the intermediate molecules (TPs) from oxidative reactions between ozone and pharmaceutical molecules. These intermediates are mainly carboxyl compounds with an acidic behavior. Consequently, as the direct reaction of ozone is slower compared to the attack of radicals $OH^{\cdot}$**,** a lower oxidization/degradation rate of organic compounds occurs, with a relative lower TOC removal. It is evident, thus, that constant pH corresponds with almost constant TOC concentrations.

As shown, the efficiencies of mineralization are lower in the test carried out with a lower production of ozone (0.6 g/h). In fact, increasing the production of ozone from 0.6 g/h to 1 g /h, the efficiency of mineralization increases from 43 to 50 %. This seems to suggest that the system was close the maximum mineralization efficiency for those experimental conditions.

Test 1, Test 4 and Test 7 were carried out to assess the variation of the mineralization efficiency as a function of the initial TOC concentration to be treated. In fact, these tests were performed for equal ozone production (1 g/h), but with different initial TOC concentration. Test 1 was conducted with an initial TOC concentration of 9.99 mg/L, Test 4 with a concentration of 7.18mg/L whereas Test 7 with a concentration of 4.72 mg/L, respectively.

In Figure, the efficiency patterns for each tests are shown.



Variation of the efficiency of mineralization at different initial TOC.

Experimental conditions: PO_3 = 1 g/h, t = 360 min

As can be seen, in the early phases of the treatment process, the efficiencies of mineralization at different initial TOC can be comparable, whereas in a second phase of the tests (after 100 minutes) their patterns show some differences.

As shown, the efficiencies of mineralization are lower in the tests made with higher initial concentration, since ozone had to react with a greater quantity of pollutants. For this reason, conversion rate of TOC increased with the decreasing initial concentration. As can be seen, in the early phases of the treatment process, the efficiencies of mineralization at different initial TOC can be comparable, whereas in a second phase of the tests (after 150 minutes) their patterns show some differences.

The main conclusions reached in this present work are:

- The efficiency of mineralization is highly dependent on the initial concentration of TOC, since results show that, by decreasing TOC concentrations, the efficiencies increased;
- The efficiency of mineralization depends on the ozone production. As expected, a greater ozone production is associated with greater mineralization efficiency.

The results indicate that ozone oxidation did not allow a full mineralization, in the experimental conditions investigated. This could be due to the formation of by-products (B. Carbajo *et al.*, 2015; Borowska *et al.*, 2016) and probable formation of more stable intermediates species. Future research should focus on pharmaceutical removal by coupling ozone with other AOPs, such as photocatalysis and H_2O_2.It would be also useful to improve the working conditions, in order to increase the efficiency of mineralization. To this purpose,it could be considered the use of oxygen for ozone production, so that the rate of ozone production would be higher. Simultaneously, a new sintered steel injection system could allow a better homogenization of the gas in the liquid, so to determine a higher ozone solubilization degree. However, these variations could imply higher construction and management costs.