

Ozone-based reclamation of an STP effluent: Ozone Doses

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Introduction

The system ozone and hydrogen peroxide was used to reclaim wastewater from the secondary clarifier from a Sewage Treatment Plant (STP) of Alcalá de Henares (Madrid-Spain). The assays were performed by bubbling a gas mixture of oxygen and ozone, with ~ 24 g Nm⁻³ of ozone concentration, through a volume of wastewater samples for 20 minutes at 25 °C. The removal of dissolved micropollutants such as Pharmaceutical and Personal Care Products (PPCPs) and Organic Carbon (TOC) was enhanced by adding periodic pulses of hydrogen peroxide while keeping pH above 8.0 throughout the runs.

Analysis

Dissolved O₃ (C_{O₃}) was measured using an amperometric Rosemount 499A OZ. O₃ in gas phase was measured using an Anseros Ozomat GM6000 Pro. Total Organic Carbon (TOC) analyses were performed with a Shimadzu TOC-VCSH analyzer. Samples were preconcentrated prior to the chromatographic analysis by SPE with Oasis HLB cartridges, using an automated sample processor ASPEC XL from Gilson. The analysis was performed by a 3200 QTRAP MS/MS system (Applied Biosystems) using a turbo ionspray source in positive and negative modes. Separation was performed in an Agilent Technologies HPLC series 1100, using a ZORBAX SB column (250mm- 3.0mm I.D.; 5 mm).

Results

Table 1 shows the main parameters of three wastewater samples related to three different data of 2008. The results of BOD₅ with non-filtered samples led to COD/BOD₅ values in the range 8 -16, indicating a low biodegradability whose origin could be attributed to the load of industrial wastewater received by the STP.

TABLE 1. Wastewater samples before ozonation

Sample	080212	080311	080506
Total suspended solids (mg/L)	4.01	3.95	6.35
Turbidity (NTU)	4.46	4.93	6.30
Conductivity (µS _{cm} ⁻¹)	838	855	962
pH	7.56	7.08	7.31
Alcalinity (mg/L CaCO ₃)	210	200	270
COD (mg/L)	61	61	58
BOD ₅ (mg/L)	5.40	8.10	3.80
TOC (mg/L)	5.95	6.11	3.56

Tables 2 and 3 show the elimination rates of 15 micropollutants studied. Nine of them are removed at rates equal or higher to 80 % at 15 min of ozonation. Nicotine is eliminated at rate higher than 95 % at 20 min of ozonation but this product is not mineralized because a methabolic by-product such as Cotinine remains in the wastewater throughout the run

TABLE 2 Initial concentration (Co) and removal rates of PHPs from STP wastewater samples

PHPs	Co (ngL ⁻¹)	(%) removed at different times (sec)		
		300	900	1200
CAFFEINE (stimulant)				
U 08 02 12	873.01	73.3	84.7	93.6
U 08 03 11	688.48	50.1	80.1	80.1
U 08 05 06	811.35	36.5	85.7	85.7
CIPROFLOXACIN (antibiotic)				
U 08 02 12	741.02	90.5	94.1	94.1
U 08 03 11	1072.31	>95	>95	>95
U 08 05 06	729.65	88.7	95.1	>95
CLOFIBRIC ACID (lipid regulador)				
U 08 02 12	590.12	19.2	80.4	87.3
NICOTINE (alkaloid)				
U 08 02 12	107.31	20.7	>95	>95
U 08 03 11	251.12	50	>95	>95
SULFAMETHOXAZOLE (antibiotic)				
U 08 02 12	150.15	>95	>95	>95
U 08 03 11	103.25	>95	>95	>95
AZYTHROMYCIN (antibiotic)				
U 08 05 06	1653.84	89.6	>95	>95
COTININE (nicotine methabolic by-product)				
U 08 02 12	66.37	20	30	30
LORATIDINE (antihistamina)				
U 08 05 06	17.05	>95	>95	>95
SALICILIC ACID (analgesic)				
U 08 05 06	36.2	55	60	60

TABLE 3 Initial concentration (Co) and removal rates of PCPs from STP wastewater samples

PCPs	Co (ngL ⁻¹)	(%) remove at different times (sec)		
		300	600	900
BENZOPHENONE (UV-A,B filter)				
U 08 03 11	109	40	50	50
U 08 05 06	95	45	60	60
ETHYLHEXYL METHOXYCINNAMATE (UV-A,B filter)				
U 08 03 11	90	30	30	30
GALAXOLIDE (synthetic fragante)				
U 08 03 11	4343	80	90	90
U 08 05 06	468	90	90	90
TONALIDE (synthetic fragante)				
U 08 03 11	370	80	90	90
U 08 05 06	287	90	90	90
TRICLOSAN (antiseptic)				
U 08 03 11	215	80	90	>95
U 08 05 06	75	80	83	90
MUSK XILENE (synthetic fragante)				
U 08 03 11	113	60	80	>95

The extent of TOC elimination is in 30 % - 60 % range for 20 minutes of ozonation, as Figure 1 shows

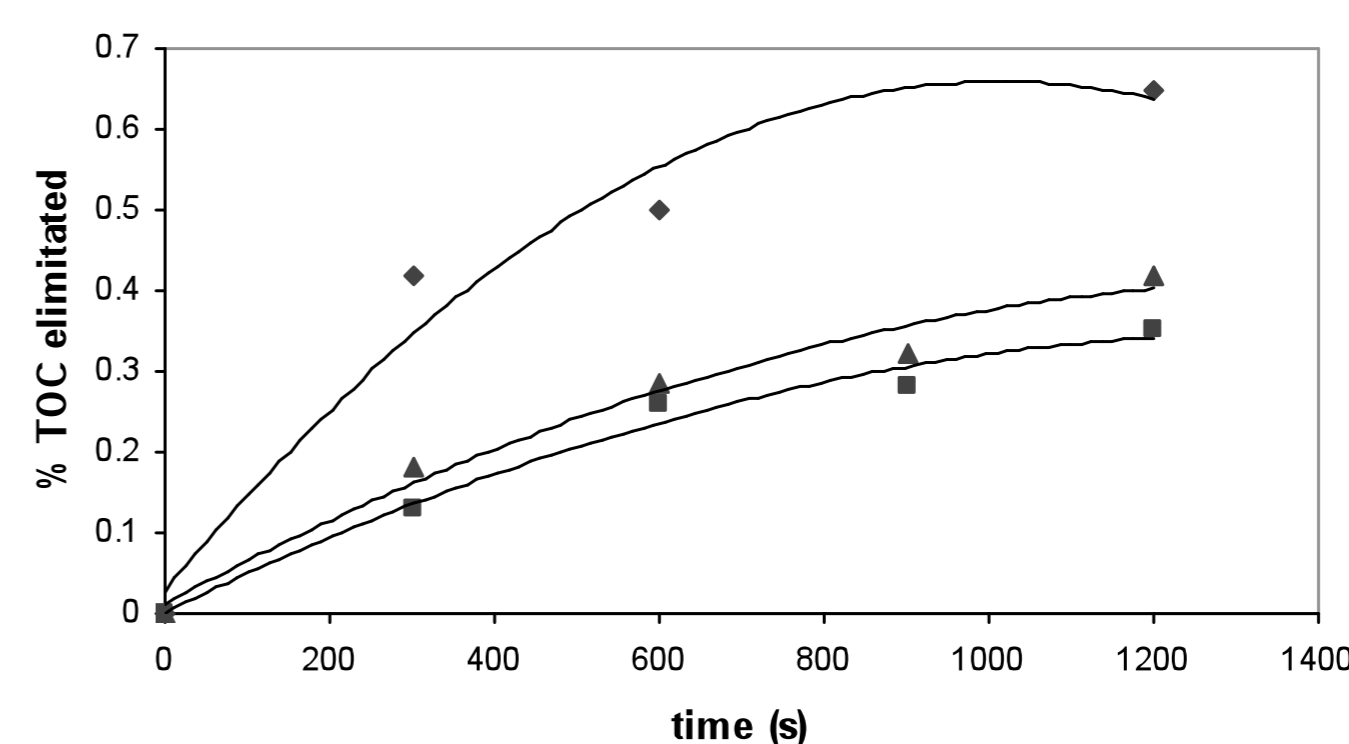


Fig. 1 TOC removed rate at different ozonation times for runs corresponding to (◆) 080212, (■) 080311, (▲) 080511 wastewater samples

The Transferred Ozone Doses (TOD) used to get these removal rates were calculated by integration of ozone absorption rate equation, being C_{O₃}^{*} the equilibrium concentration of ozone in the water (Rosal et al., in press)

$$TOD(t) = k_L a \left(C_{O_3}^* \cdot t - \int_0^t C_{O_3} dt \right)$$

Conclusions

The ozonation treatment of the effluent from the secondary clarifier of a STP was carried out by the simultaneous use of ozone and hydrogen peroxide with the aim to optimize the reclaiming wastewater technologies based on ozone. In this connection, the TOD at 5min, 15 min and 20 min were around 18 mgO₃/L, 56 mgO₃/L and 75 mgO₃/L for the three wastewater samples, respectively and the mg O₃ consumed/ng micropollutants removed ratios were 0.24, 0.63 and 0.83 at the same ozonation times. After 5 min there are no important changes in the removal rates of most refractory micropollutants to ozonation and the removal rates changes observed for the others must be assessed in order to optimize the process. Although the challenges of this work is to remove micropollutants and TOC the ozone dose used at 5 min is in the range of 2 mg/L – 18 mg/L proposed by Pei Xua et al. (2002) for wastewater disinfection