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Ozone-based reclamation of an STP effluent: Kinetic

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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 ºC .The removal of Organic Carbon (TOC) was enhanced by adding periodic pulses of hydrogen peroxide while keeping pH above 8.0 throughout the runs.

Analysis

Dissolved O3 was measured using an amperometric Rosemount 499A OZ analyser calibrated against the Indigo Colorimetric Method (SM 4500-O3 B). O3 in gas phase was measured using an Anseros Ozomat GM6000 Pro photometer calibrated against a chemical method. Total Organic Carbon (TOC) analyses were performed with a Shimadzu TOC-VCSH analyzer equipped with ASI-V autosampler.

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

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 (μScm^{-1})	838	855	962
pH	7.56	7.08	7.31
Alcalinity (mg/L CaCO3)	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

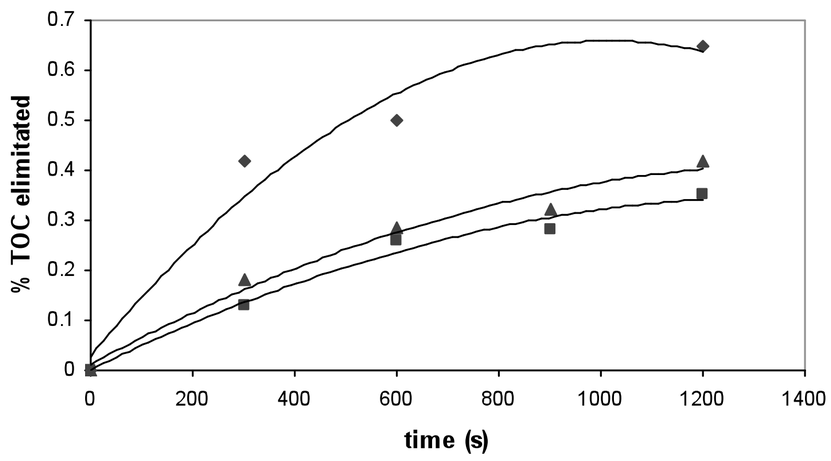

Fig. 1 TOC removed rate at different ozonation times for runs corresponding to (♦) 080212, (■) 080311, (▲) 080511 wastewater samples

The mass balance of TOC to a volume element yields the following expression according to a kinetic model previously developed (Rosal et al., in press)

$$-\ln\frac{TOC(t)}{TOC_o} = k\Gamma \qquad (1)$$

Being Γ the expression of time-integrated ozone-hydrogen peroxide concentration. It was calculated from the experimental values of C_{O_3} and calculated values of $C_{H_2O_2}$ by an integration numerical method.

$$\Gamma = \int_0^t C_{O_3} C_{H_2O_2} \qquad (2)$$

Fig. 3 shows the least square fitting of the experimental results by Eq. 3 for the three experiments. The kinetic constant experimental values of Eq. 3 are shown in Table 4

TABLE 4 Kinetic parameters for runs corresponding to 080212, 080311, 080511 wastewater samples

Exp.	080212	080311	080506
k ($mM^{-2}s^{-1}$)	0.6814	0.5421	0.6113
dTOD/dt (mMs^{-1})	0.0012	0.0013	0.0013

The efficiency of the ozonation system to remove TOC can be determined from the model given by Eq. 1 and the Transferred Ozone Doses (TOD) (Rosal et al., in press)

$$-\frac{dTOC}{dTOD} = \frac{kTOC_o e^{-k\Gamma}\dfrac{d\Gamma}{dt}}{k_L a\left(C^*_{O_3} - C_{O_3}\right)} \qquad (3)$$

The theoretical number of moles of TOC removed per mole of ozone consumed is shown in Fig. 4.

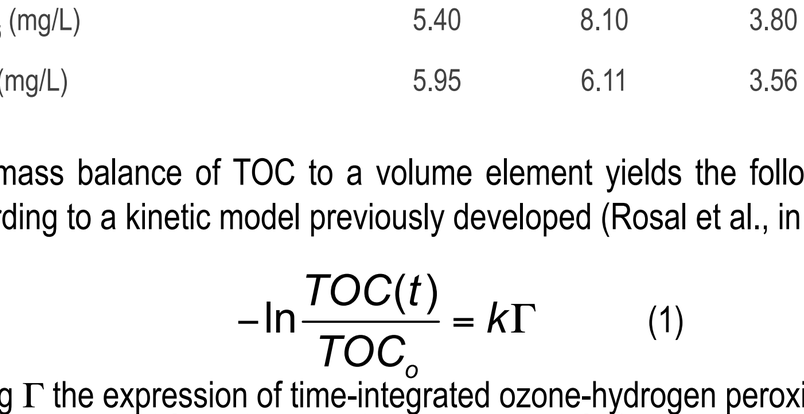

Fig. 3 Logarithmic decay of TOC for runs corresponding to (♦) 080212, (■) 080311, (▲) 080511 samples as a function of Γ defined in Eq. (3).

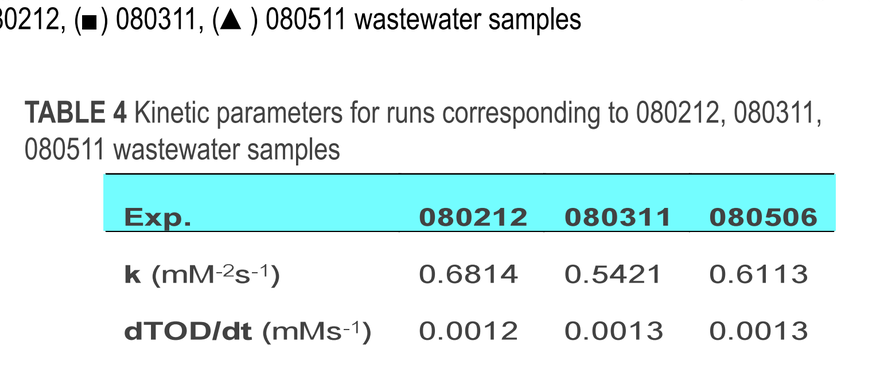

Fig. 4 Moles of carbon eliminated by unit mole of ozone consumed at different ozonation times for runs corresponding to (♦) 080212, (■) 080311, (▲) 080511 wastewater samples. The symbols correspond to experimental values and the continuous lines correspond to estimated values by the kinetic model

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. The removal efficiency ratios at different ozonation times were estimated from a model that take the time-integrated ozone-hydrogen peroxide concentration into account and is borne out by an accurate monitoring of dissolved ozone as the key measured variable. The results show a maximum around 5 min of ozonation with a TOC removal efficiencies ratios in the range of 7 – 13 mg O_3/mg TOC. These figures are around seven times higher than the 1–2 mgO_3/mg TOC efficiencies ratios usually used in surface water ozonation (Larson, 1989; Bozena et al., 2005), but they can be used as a reference range when the challenge is to reclaim wastewater