Ozone-based reclamation of a Sewage Treatment Plant effluent

Antonio Rodríguez, Roberto Rosal, María José Gómez, Eloy García-Calvo and Amadeo R. Fernández-Alba. Ozone-based reclamation of a Sewage Treatment Plant effluent. Water Science & Technology Vol 63 No 10 pp 2123–2130, 2011

https://doi.org/doi:10.2166/wst.2011.298

http://www.iwaponline.com/wst/06310/wst063102123.htm

Ozone-based reclamation of an STP effluent

Antonio Rodríguez[1,*], Roberto Rosal[1], María José Gómez[2], Eloy García-Calvo[1] and Amadeo R. Fernández-Alba[2]

[1] Department of Chemical Engineering, University of Alcalá, 28771 Alcalá de Henares, Spain
[2] Department of Analytical Chemistry, University of Almería, 04010 Almería, Spain
* Corresponding author: antonio.rodriguez@uah.es

Abstract

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 25ºC . 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. Removal efficiency ratios in the range of 7–26 mg O_3/mg TOC and 0.24 mg O_3/ng micropollutants at 5 minutes of ozonation were assessed as reference data to reclaim wastewater from STP. The relation between the extent of TOC removed and ozone doses used was related by a second-order kinetic model in which the time-integrated ozone-hydrogen peroxide concentration was included.

Keywords: Advanced oxidation processes, Kinetics, Ozonation, Reclaimed water, Water pollution control

1. Introduction

The aim of EC Water Framework Directive (2000/60/EC) is to achieve good ecological water status in terms of the presence of chemicals from human activity. In this connection, increasing water scarcity enhances wastewater reuse, which is especially geared to the large amount of effluents from Sewage Treatment Plants (STP) that currently are discharged to surface bodies. Possible reuse targets for biotreated municipal wastewater include industrial, agricultural and domestic uses. Any of these reuse options require different water qualities, but in general tertiary treatments must be implemented after the secondary settling of activated sludge treatments to avoid the presence of organic pollutants in treated waters (EPA/625/R-04/108 US). Certain regulations include TOC as quality parameter for practices of indirect drinking water reuse such as spreading basins or injection (van der Graaf et al.2005). Organic compounds, even in very low amounts, severely endanger water reuse in many applications. This is the case of endocrine-disrupting compounds and other emerging pollutants that are only partially removed from waste-water in conventional wastewater treatments in the STPs and whose presence is repeatedly reported in effluents (Ternes, 1998; Carballa et al., 2004; Gagné et al., 2006; Roberts & Thomas, 2006; Al-Rifai et al., 2007).

Technologies based on Advanced Oxidation Processes (AOP) as Fenton, photo-Fenton, photocatalysis on TiO_2, ultraviolet-based oxidation processes (H_2O_2/UV, O_3/UV), and the ozone based O_3/HO^- and O_3/H_2O_2 can be used to reclaim water (Gogate & Pandit, 2004; Ikehata et al., 2006). All of these involve the generation of hydroxyl radicals, a highly reactive and unselective species, in sufficient amounts to oxidize the organics in wastewater. Technologies based on O_3/H_2O_2 system provides a high degree of mineralization (Yang et al., 2005) which ensures the absence of any oxidation intermediates and a reduction in toxicity, as well as the removal of persistent, emerging or any other individual pollutant from the many compounds identified in STP effluents (Gómez et al., 2007). Furthermore, the ozone base technologies are well admitted by society and are easy to combine with others such as UV, biological, electrolysis and membranes to mineralize organic matter or to remove micropollutants from wastewater (Alaton et al., 2004; Agustina et al., 2005; Kishimoto et al., 2005; Lafi & Al-Qodah, 2006; Bennera et al., 2008) and make them an attractive candidate to optimize the reclaim water processes.

This work is focused on the need to provide adequate information to model the ozonation processes in a real matrix as wastewater from STP in order to optimize the reclaim water technologies based on ozone and to broaden the water reuse practices. This work presents results concerning three water samples taken from the STP of Alcala de Henares (Madrid-Spain) during February, March, and May of 2008. These were treated in alkaline condition by O_3/H_2O_2system for 20 minutes. An accurate monitoring of dissolved ozone as the key measured variable in the system to extent of TOC and PPCPs micropollutants removed at different ozonation times was used. The ozone doses used were related to extent contaminants removed by a kinetic model based in the time-integrated ozone-hydrogen peroxide concentration.

2. Materials and methods

2.1. Materials and ozonation procedure

Wastewater was collected from the secondary clarifier of a STP located in Alcala´ de Henares (Madrid-Spain) that receives a mixture of domestic and industrial wastewater from facilities located around the city. This STP has a capacity of 375000 equivalent inhabitants and is designed to treat a maximum volume of wastewater of 3000 m^3/h. All samples were composites of 1-L aliquots collected on an hourly basis during 24 h sampling periods and they were immediately processed or stored in a refrigerator (4ºC) inside glass bottles. The ozonation runs were performed in batch model in a 5-L glass jacketed reactor at 25ºC. The temperature was controlled by a Huber Polystat cc2 and monitored throughout the experiment by means of a Pt100 Resistance Thermometer Detector (RTD). Ozone was produced by a corona discharge ozonator (Ozomatic, 118 SWO100) fed by an AirSep AS-12 PSA oxygen generation unit. The gas containing ozone was bubbled into the liquid by means of a porous glass disk with a gas flow of 0.36 Nm^3/h. The concentration of ozone in the gas was ~24 g Nm^{-3} and measured immediately before each run. The off-gas was vented to an ozone destruction unit. The reaction vessel was agitated with a Teflon four-blade impeller at 1000 rpm. During the runs, injections of 0.15 mL of H_2O_2 (30% w/v Sigma-Aldrich) were performed every 5 min starting at the beginning of ozone bubbling. This amount was chosen in order to keep the overall H_2O_2/O_3 molar ratio lower than 1, to enhance the production of hydroxyl radicals and to maintain sufficient dissolved ozone throughout the runs to guarantee the chemical step control process. Pulses were intended to avoid a great excess of hydrogen peroxide, well-known radical scavenger of hydroxyl radicals (Beltrán, 2004). During the runs, certain samples were withdrawn for analysis after previously removing ozone by bubbling nitrogen in order to prevent further oxidation reactions. The experiments started at pH 8.5 and were always kept above 8.0 by pumping a diluted solution of sodium hydroxide (Panreac) with a feed-back PID control device. The decomposition of ozone acidified the reaction mixture but the general trend during most of the run was a moderate increase of pH. This effect was attributed to reactions between hydroxyl radicals and carbonate and bicarbonate ions formed during the mineralization process (Chandrakanth & Amy, 1998).

2.2. Analysis

The concentration of dissolved ozone was measured by means of an amperometric Rosemount 499A OZ analyser calibrated against the Indigo Colorimetric Method (SM 4500-O3 B). The signal transmitted by a Rosemount 1055 SoluComp II Dual Input Analyser was recorded by means of a data acquisition unit. The concentration of ozone in gas phase was measured using an Anseros Ozomat GM6000 Pro photo-meter calibrated against a chemical method [21]. The pH of the reaction mixture was measured by means of a CRISON electrode connected to a Eutech alpha-pH100 feed-back control system whose final control element was a LC10AS Shimadzu pump delivering a solution of sodium hydroxide. The signals from the concentration of dissolved ozone, pH and temperature were recorded by means of an Agilent 34970 Data Acquisition Unit connected to a computer with a sampling period of 5 s. Total Organic Carbon (TOC) analyses were performed with the aid of a Shimadzu TOC-VCSH analyzer equipped with ASI-V autosampler. Total suspended solids were determined by the American Public Health Association (APHA) Method 2540 D, 'Total Suspended Solids Dried at 103–105ºC'. The determination of COD followed APHA Method 5220 C. For BOD-5 analysis APHA 5210 B was used with a commercially available nitrification inhibitor (Hach, 2533).

Preconcentration of the samples prior to the chromatographic analysis was performed by solid phase extraction (SPE) with Oasis HLB cartridges (Waters, 200 mg, 6 cc). An automated sample processor ASPEC XL from Gilson (France) was used for this purpose. The operational procedure has been described elsewhere (Martínez-Bueno et al.2007). Briefly, the cartridges were preconditioned with MeOH (6 ml) and deionized water HPLC-grade (5 ml, pH adjusted to 8 with 20% NH4OH) at a flow rate of 1 ml/min. Aliquots of 400 ml of sample (pH adjusted to 8) were then loaded into the cartridge at a flow rate of 10 ml/min, rinsed with 5 ml of deionized water and finally eluted with 2 x4 ml of MeOH at 1 ml/min. The extracts so obtained were finally evaporated until almost dryness, reconstituted with 1 ml of MeOH : water, 10:90 (v/v), filtered, and diluted 1:1 with MeOH : water (10:90) before the analysis. The analysis of the selected organic compounds 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, equipped with a reversed-phase C-18 analytical column (ZORBAXSB,250mm-3.0 mm I.D.; 5mm). For the analysis in positive mode, the compounds were separated using acetonitrile (mobile phase A) and HPLC-grade water with 0.1% formic acid (mobile phase B) at a flow rate of 0.2 ml/min. A linear gradient progressed from 10% A to 100% A in 40 min, after which the mobile phase composition was maintained at 100% A for 10 min. The re-equilibration time was 15 min. Compounds analyzed in negative mode were separated using acetonitrile (mobile phase A) and HPLC-grade water (mobile phase B) at a flow rate of 0.3 ml/min. LC gradient started with 30% A and was driven to 100%, in 7 min, after which the mobile-phase composition was maintained at 100% A for 8 min. The re-equilibration time was 10 min. The volume of injection was of 20mL in both modes.

3. Results and discussion

3.1. Characterization of wastewater

Table 1shows 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 2 and 3 show the concentration of 15 micropollutants relating to PPCPs such as stimulants, alkaloids, antihistamines, antibiotics, antiseptics, lipid regulator, UV ray filters and synthetics fragrances, usually in surface and wastewater from STP which are recalcitrant compounds to biotreatment.

Table 1 Wastewater parameters 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	7.6	7.1	7.3
Alkalinity (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)	6.0	6.1	3.6

3.2. Removal of micropollutants

The experiments were conducted in semicontinuous mode with periodic pulses of H_2O_2. Consequently, the molar ratio H_2O_2/O_3 changed during the run. The overall H_2O_2/O_3ratio was calculated from the maximum rate of ozone transfer from the gas phase:

$$\frac{NC_{H_2O_2\,o}}{k_L a C_{O_3^*}} \qquad (1)$$

N is the frequency of hydrogen peroxide pulses, CH_2O_{2o} the initial concentration of hydrogen peroxide after every pulse and CO_3^* the equilibrium concentration of ozone in the water, which was calculated from Henry's law yielding a value of 0.125 mM. The mass transfer coefficient was determined in transient runs with pure water yielding a value of $k_La = 0.0107 \pm 0.005\ s^{-1}$ and the correlation of Rischbieteret al. (2000) was used to calculate the adimensional Henry's constant: H = 3.97 at 25ºC (Raknesset al. 1996). For the experimental conditions used in this work CO_3 is less than 8% of CO_3^* throughout the runs. The ratio values of Equation (1) were around 0.7, which are higher than stoichiometric ratio but within the range 0.35–2 given in publications (Kepaet al. 2008). Tables 2 and 3 show the elimination rates of 15 micro-pollutants 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 as the metabolite cotinine remains in the wastewater throughout the run. Cotinine together with a universal analgesic as acetyl salicylic and two UV ray filters as ethylhexyl methoxycinnamate and benzophenone are the more recalcitrant to oxidation with removal rates in the 30% - 50% range after 20 minutes of ozonation. The Transferred Ozone Dose (TOD) used to get these removal rates is shown in Figure 1. These were calculated by integration of ozone absorption rate equation:

$$TOD(t) = k_L a\left(C_{O_3}^* \cdot t - \int_0^t C_{O_3} dt\right) \qquad (2)$$

Table 2 Initial concentration (C_O) and removal rates of several spiking compounds in wastewater matrix.

Compound	C_o (ngL^{-1})	Percent removed at different ozonation times (s)		
		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 regulator)				
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 metabolite)				
U 08 02 12	66.37	20	30	30
Loratidine (antihistamine)				
U 08 05 06	17.05	>95	>95	>95
Salicylic acid (analgesic)				
U 08 05 06	36.2	55	60	60

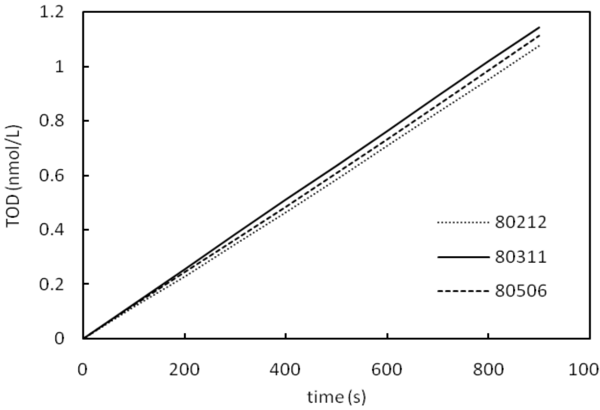

Figure 1. Values of Transferred Ozone Doses (TOD) for three different runs

The time-integrated ozone concentration, $\int_0^t C_{O_3} dt$, was calculated from experimental values of ozone concentration using an integration numerical method. The TOD at 5min, 15 min and 20 min were around 18 mg O_3/L, 56 mgO_3/L and 75 mgO_3/L for the three wastewater samples, respectively and the mg O_3 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 challenge of this work is to remove micropollutants and TOC the ozone dose used al 5 min is in the range of 2 mg/L – 18 mg/L proposed by Pei Xua et al. (2002) for wastewater disinfection.

Table 3 Initial concentration (C_O) and removal rates of Personal Care Products spiking wastewater samples.

Compound	C_o (ng L^{-1})	Percent removed at different ozonation times (s)		
		300	600	900
Benzophenone (UV filter)				
U 08 03 11	109	40	50	50
U 08 05 06	95	45	60	60
Ethylhexyl methoxycinnamate (UV filter)				
U 08 03 11	90	30	30	30
Galazolide (synthetic musk)				
U 08 03 11	4343	80	90	90
U 08 05 06	468	90	90	90
Tonalide (synthetic musk)				
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 xylene (synthetic musk)				
U 08 03 11	113	60	80	>95

3.3. Removal of TOC

The extent of TOC elimination is in 30 %-60 % range for 20 minutes of ozonation, as Figure 2 shows. It is not possible to find a precise answer concerning the differences in elimination rates from global parameters as TOC, COD and BOD5 because these are in relation with the wastewater matrix complexity.

Considering that the chemical stage controls the ozonation process, as the concentration of dissolved ozone different from zero for all the experiments confirms, and assuming from operational conditions that the mineralization of a given organic compound takes place only by means of the hydroxyl radical, the mass balance of TOC to a volume element yields the following expression according to a kinetic model previously developed (Rosal et al., 2009):

$$-\ln\frac{TOC(t)}{TOC_o} = k\,\Gamma \qquad (3)$$

Being the expression of time-integrated ozone-hydrogen peroxide concentration:

$$\Gamma = \int_0^t C_{O_3} C_{H_2O_2} \qquad (4)$$

Γ was calculated from the experimental values of CO_3 and calculated values of CH_2O_2 by an integration numerical method. CH_2O_2 was calculated inside each pulse from the ozone consumed within the liquid phase and that transferred from the gas according to the expression:

$$C_{H_2O_2} = C_{H_2O_2}(0) - \frac{1}{2}\left[C_{O_3}(0) - C_{O_3}(t)\right] - \frac{k_L a}{2}\left[C^*_{O_3} - C_{O_3}(t)\right]t \qquad (5)$$

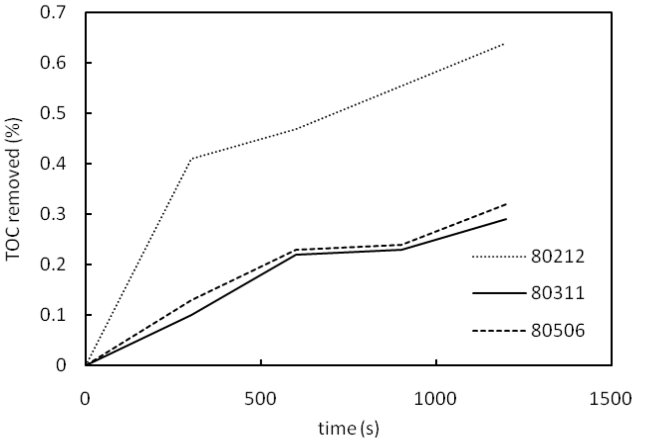

Figure 3. TOC removed at different ozonation times.

where $CH_2O_2(0)$, $CO_3(0)$ and $CO_3(t)$ are the concentrations of dissolved hydrogen peroxide and ozone at the beginning of each pulse of hydrogen peroxide and at any time between pulses. This computation probably overestimates the instantaneous concentration of hydrogen peroxide and it only takes the reaction with ozone into account.

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

Run	080212	080311	080506
k ($mM^{-2}\,s^{-1}$)	0.681	0.542	0.611
dTOD/dt (mM s^{-1})	0.0012	0.0013	0.0013

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. In run 080311 an initial rapid TOC decay period was observed, this was not considered when the kinetic constant of the model was computed. Fig 1 shows that TOD rates are constant throughout the runs which are in relation with the low CO_3 values with respect to CO_3^* detected during the ozonation. Table 4 shows the kinetic constants of the model and the average ozone dosages for t > 300 s).

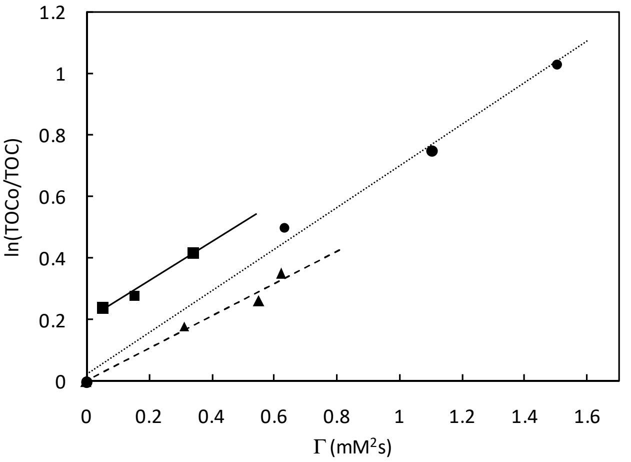

Figure 4. Logarithmic decay of TOC for different samples as a function of *Γ* defined in Eq. (3).

The efficiency of the ozonation system to remove TOC can be determined from the model given by Eq. 3 using only information about the concentration of dissolved ozone and the amount of hydrogen peroxide being injected by the expression (Rosal et al., 2009):

$$-\frac{dTOC}{dTOD}=\frac{kTOC_o e^{-k\Gamma}\frac{d\Gamma}{dt}}{k_L a\left(C^*_{O_3}-C_{O_3}\right)} \qquad (6)$$

A precise evaluation of Γ function is possibly due to the accurate measuring of ozone concentration performed with a sampling period of 5 s throughout the run. The theoretical number of moles of TOC removed per mole of ozone consumed is shown in Fig. 4. The symbols correspond to experimental TOC values. The good agreement between experimental and theoretical ozone efficiency is notable, especially considering that the theoretical profile can be calculated from a relatively simple measure such as dissolved ozone concentration.

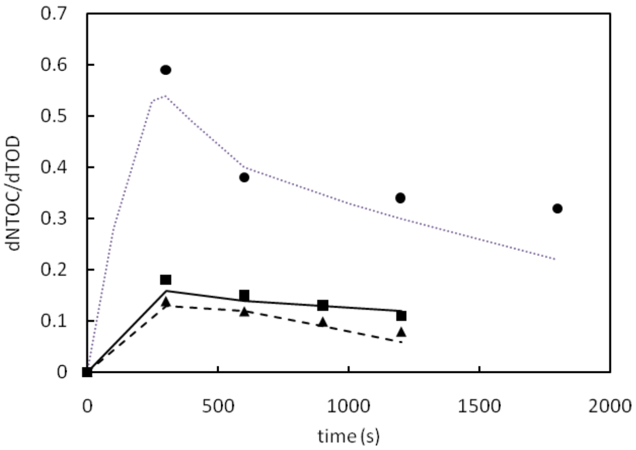

Figure 5. Moles of carbon eliminated by unit mole of ozone consumed at different ozonation times for runs 080212 (●) 080311 (■) and 080511 (▲). The symbols correspond to experimental values and the lines to calculated values.

The results show a maximum around 5 min of ozonation with TOC removal efficiencies ratio in the range of 7 – 13 mg O_3/mg TOC. These figures are around seven times higher than the 1–2 mg O_3/mg TOC efficiencies ratios usually used in surface water ozonation (Larson, 1989; Bozena & Morawsky, 2005), but they can be used as a reference range when the challenge is to reclaim wastewater

4. 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 and to broaden the water reuse practices. In this connection ozone doses to remove recalcitrant compounds/PPCPs to biotreatmennt and TOC around 18 mg O_3/L was determined, being 7–26 mg O_3/mg TOC a removal ratio range that could be used to reclaim these wastewaters. These figures are in the same order that the proposed to wastewater disinfection. 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 composition change in wastewater is a difficult variable to asses and to relate with global parameters as TOC, COD or BOD for that an exhaustive monitoring of wastewater in the aim to determine the more recalcitrant compounds/PPCPs to biological treatment which can be used as reference to determine ozone doses will be necessary.

Acknowledgements

The authors wish to express their gratitude to the Ministry of Education of Spain (Contracts CTM2005-03080/TECNO, CTM2004-0 6265-C03-03 and CONSOLIDER-INGENIO 2010 CSD2006-00044), the Dirección General de Universidades e Investigación de la Comunidad de Madrid under Contract No. PAMB-000395-0505 and the research network from Comunidad de Madrid REMTAVARES Ref. P2009/AMB-1588.

References

Agustina, T. E., Ang, H. M. & Vareek, V. K. 2005. A review of synergistic effect of photocatalysis and ozonation on wastewater treatment. J. Photochem. Photobiol. C: Photochem. 6, 264–273.

Alaton, A., Dogruel, S., Baykal, E. & Gerone, G. 2004. Combined chemical and biological oxidation of penicillin formulation effluent. J. Environ. Manage. 73, 155–163.

Al-Rifai, J. H., Gabelish, C. L. & Schäfer, A.I. 2007. Occurrence of pharmaceutically active and non-steroidal estrogenic compounds in three different wastewater recycling schemes in Australia. Chemosphere 69, 803–815.

Beltrán, F. J. 2004. Ozone reaction kinetics for water and wastewater systems. CRC Press, Boca Raton, pp 178–179.

Benner, J., Salhi, E. & Ternes, T. 2008. Urs von Gunten. Ozonation of reverse osmosis concentrate: Kinetics and efficiency of beta blocker oxidation. Water Res. 42, 3003–3012.

Bozena M. T. & Morawsky, A.W. 2005. Removal of micropollutants from water by ozonation/biofiltration process. Desalination 182, 151–157.

Carballa, M., Omil, F., Lema, J. M., Llompart, M., García-Jares, C., Rodríguez, I., Gómez, M. & Ternes, T. 2004. Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. Water Res. 38, 2918–2926.

Chandrakanth, M. S. & Amy, G. L. 1998. Effects of NOM source variations and calcium complexation capacity on ozone-induced particle destabilization. Water Res. 32, 115–124. 653.

EC, Directive of the European Parliament and of the Council 2000/60/ EC establishing a framework for community action in the field of water policy, Official Journal, 2000, C513, 23/10/2000.

Environmental Protection Agency, US EPA, Guidelines for Water Reuse, EPA/625/R-04/108 U.S., Agency for International Devel-opment Washington, DC, 2004.

Gagné, F., Blaise, C. & André, C. 2006. Occurrence of pharmaceutical products in a municipal effluent and toxicity to rainbow trout (*Oncorhynchus mykiss*) hepatocytes, Ecotoxicol. Environ.Saf. 64, 329–336.

Gogate, P. R. & Pandit, A. B. 2004. A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. Adv. Environ. Res. 8, 501–551.

Gómez, M. L., Martínez, M. J., Lacorte, S., Fernández-Alba, A. R. & Agüera, A. 2007. Pilot survey monitoring pharmaceuticals and related compounds in a sewage treatment plant located on the Mediterranean coast. Chemosphere 66, 993–1002.

Ikehata, K., Naghashkar, N. J. & El-Din, M. G. 2006. Degradation of aqueous pharmaceuticals by ozonation and advanced ozonation processes: A review. Ozone: Sci. Eng. 28, 353–414.

Kepa, U., Stanczyk-Mazanek, E. & Stepniak, L. 2008. The use of the advanced oxidation process in the ozone-hydrogen peroxide system for the removal of cyanide from water. Desalination 223, 187–193.

Kishimoto, N., Morita, Y., Tsuno, H., Oomura, T. & Mizutani, H. 2005. Advanced oxidation effect of ozonation combined with electrolysis. Water Res. 39, 4661 –4672.

Lafi, W. K. & Al-Qodah, Z. 2006. Combined advanced oxidation and biological treatment processes for the removal of pesticides from aqueous solutions. J. Hazard. Mater. 137, 489–497.

Larson, R.A. 1989. Biohazards of Drinking Water Treatment. Lewis Publishers/CRC Press, Boca Rarton, p. 176.

Martínez-Bueno, M. J., Agüera, A., Gómez, M. J., Hernando, M. D., García, J. F. & Fernández-Alba, A.R. 2007. Application of Liquid Chromatography/Quadrupole-Linear Ion Trap Mass Spectrometry and Time-of-Flight Mass Spectrometry to the determination of pharmaceuticals and related contaminants in wastewater. Anal. Chem. 79, 9372–9384.

Rakness, K. L., Demers, L. D., Blank, B. D. & Henry, D. J. 1996. Gas phase ozone concentration comparisons from a commercial UV meter and KI wet-chemistry tests, Ozone: sci. Eng. 18, 231–249.

Rischbieter, E., Stein, H. & Shumpe, A. 2000. Ozone Solubilities in Water and Aqueous Salt. J. Chem. Eng. Data 45, 338–340.

Roberts, P. H. & Thomas & K. V.2006. The occurrence of selected pharmaceuticals in wastewaters effluent and surface waters of lower Tyne catchment. Sci. Total Environ. 356, 143–153.

Rosal, R., Rodríguez, A., Perdigón-Melón, J. A., Petre, A. & García-Calvo, E. 2009. Oxidation of dissolved organic matter in the effluent of a sewage treatment plant using ozone combined with hydrogen peroxide (O_3/H_2O_2). Chem. Eng. J. 149, 311–318.

Ternes, T.A.1998. Occurrence of drugs in German sewage treatment plants and rivers. Water Res. 32, 3245–3260.

Van der Graaf, J.H.J.M., de Koning, J., Ravazzini, A.M. & Miska, V. 2005. Treatment matrix for reuse of upgraded wastewater. Water Sci. Technol. Water Supply 5, 87–94.

Xu P, Janex ML, Savoye P, Cockx A. & Lazarova V. 2002Lazarova, Waste-water disinfection by ozone: main parameters for process design. Water Res.36, 1043–1055.

Yang, C., Xu, Y. R., Teo, K. C., Goh, N. K., Chia, L. S. & Xie, R. J. 2005. Destruction of organic pollutants in reusable wastewater using advanced oxidation technology. Chemosphere 59, 441–445.