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Ozonation of washing concentrates from an ultrafiltration pilot plant treating the secondary effluent of a WWTP

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Abstract

This work studies the result of treating, by ozone, washing concentrates of an ultrafiltration plant, which processes the secondary effluent (biological) of a WWTP. The study is presented as a first stage towards the establishment of an integrated process UF-ozonization. Two types of concentrates and two ozonation intensities: 24.4 and 6.4 mg /L of O3 in gas we studied in this work. The results reveal that an initial increase of total organic carbon is given since oxidizable part of total suspended solids dissolve more quickly than it oxidizes. Once this part has been dissolved completely, the total organic carbon begins to decrease, within the global mineralization process, following a two-series-reaction scheme. Ozonation at low concentrations of ozone improves the efficiency of the process in terms of mineralization. It seems to be associated with a change in the overall degradation scheme (TSS solution followed by mineralization). The effluent turbidity increased in all cases analyzed, following clearly an order-zero kinetic in the cases when the ozone concentration is high. The pH is initially set around 9, first suffering a fall not more than 0.8 in none of the cases. The loss of aromaticity was observed around 51.8% as maximum.

Keywords: ozonation, WWTP, ultrafiltration, total Organic Carbon, turbidity

1. Introduction

Emerging contaminants are increasingly more relevant in today's society, since waters containing them can affect the flora, fauna and human beings, even though they are present in very low concentrations (Deblonde *et al.*, 2011). Within this group of pollutants, various types of substances are covered, which include chemicals such as pesticides, medications, cosmetics, aromatic compounds and surfactants (Heberer, 2002). Waste water treatment plants (WWTP) do not have specific treatments for disposal such kind of compounds, so they are poured to the environment through the treated water streams and activated sludge disposal. Currently, different methods to remove these contaminants are being studied (Shi *et al.*, 2012). Within the different treatments, highlights the ultrafiltration (UF). This technology is to make pouring water through a semipermeable membrane separating suspended solids and high molecular weight of water molecules. As the ultrafiltration process progresses, it increases the pressure difference between the two sides of the membrane since they are getting dirty, so it is necessary to remove the particles which are deposited. As a result of this cleaning process, a water with higher concentration of contaminant is obtained, which must be treated. Advanced chemical oxidation processes can be used to degrade contaminants contained in this washing water (Acero *et al.*, 2015). This work studies the ozonation of the washing water generated in an ultrafiltration system. In the analysis, an estimation of mineralization (TOC), together with other parameters, such as: TSS, turbidity and aromaticity to treat the effluent from a WWTP biological process was carried out. The objective is, firstly, to obtain a greater efficiency in the use of ozone for the destruction of concentrated pollutants, which would include the removal of emerging (not in this work). Secondly, to get the necessary information, so the integration of the ozonation within the process of ultrafiltration can be achieved.

2. Experimental Metodology

A pilot ultrafiltration plant was used to treat the effluent from the biological process of a WWTP. The retained material, through the washing water, was subsequently treated by ozonation to degrade the concentrated contaminants (including emerging) that contains and are not eliminated in the WWTP.

2.1. Ultrafiltration equipment

The pilot plant has a treatment capacity of 3.3 m^3/h and can operate with a certain recirculation ratio or without recirculation (dead end). This second mode was the one selected to operate the plant in this study. The plant has 4 hollow-fiber filtration modules made of polyether sulfone (PES) with a size of pore lower than 0.3 μm. The permeate stream presents an inside out direction across the membrane. The ultrafiltration unit operates in continuous mode (c-UF). A constant flow of permeate was maintained continuously (c-UF), since during filtering the washing periods were programmed in which one by one are cleaned the four modules so that the rest of the modules absorb the flow of the module under cleaning.

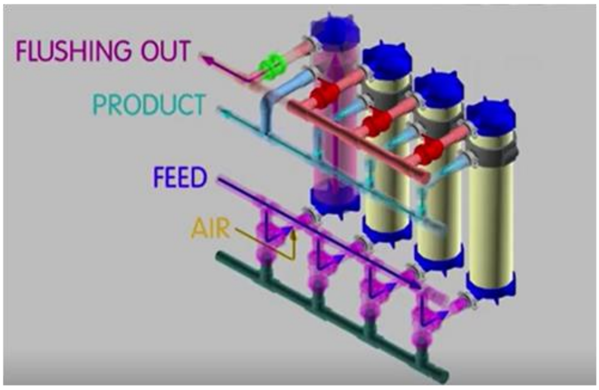

Figure 1. Scheme of the c-UF unit during the flushing stage of washing.

The washing period was programmed by reintroducing part of the filtered water every 40 min after the transmembrane pressure reaches the value of 0.6 Bar. The feed pressure starts at 1.5 Bar and reaches the value of 2.3 at the end of the filtering period, just before the washing period starts. It has a duration of approximately 9 min and consists of three phases: flushing (F), backwashing (B) and rinsing (R). Figure 1 shows the operation of the flushing phase in which a detail of individualized cleaning of each module can be seen. During the following phases B and R of the washing period, the c-UF unit operates in a similar way to that of F. Phases F and B produces washing water with the greatest concentration of pollutant load, so that this study was conducted on them. However, the rinsing water has low pollutant concentration and it was not treated in this study. Flushing and backwashing waters were collected separately after filtering and then were treated by ozonation. Before introducing F and B waters into the ozone reactor, pH was adjusted to 9.0 in all the cases, by adding NaOH (1.0 M).

2.2 Ozonation equipment

The washing water of the c-UF process were subjected to ozonation in an experimental laboratory equipment (Rodriguez *et al*, 2016), which consists of a generator of ozone (Triogen Lab2B) and a tubular reactor of 30 L capacity (height 79 cm, □22 cm). The ozone generator was powered with a 4.0 L/min stream of pure oxygen and its intensity regulated to operate with two concentrations of ozone gas at the entrance: 24.4 mg/L (+: high concentration) and 6.4 mg O_3/L (-: low concentration). The ozonator was filled with 10 L of washing water and pressurized to 1.5 bar to favor the transfer and absorption of ozone. The reactor was stirred by a recirculation system to enable ozone injection and mixing using a pump of 0.6 kW (Bloch H - 80M) that gives a water flow of about 90 L/min. During the ozonation experiments, and due to the mixing friction, the temperature of the reaction changed from 15º to 40 ºC.

2.3. *Analytical methods*

Dissolved ozone in water (O_3 dissolved, mg/L) and pH were measured with a combined meter model Solu Comp II (Rosemount Analytical) using 390pH Sensor probes for pH and 499AOZ for ozone. Ozone gas (O3 gas, mg/L) was measured with a scanner model Ozone Analyzer BMT 964C (BMT Messtechnik). Total organic carbon (TOC, mg c/l) was measured using a TOC VCSN/CSH-Shimazu Analyzer. Turbidity (NTU) was measured using a turbidimeter (2100N-Hach). The loss of aromaticity (A_{254}, AU) was measured at 254 nm using a spectrophotometer UV/Vis (10-Perkin Elmer Lambda). The solid suspended (TSS, mg / L) was measured with glass fiber filters of 45 μm pore diameter, a muffle DP1-l (Kowell) and a scale handy H110 (Sartorius).

3. Results and discussion

3.1. Ozone efficiency

The concentration of dissolved ozone in the liquid is shown in Figure 2 and the ozone concentration in the gas stream measured at the ozonator outlet is indicated in Figure 3.

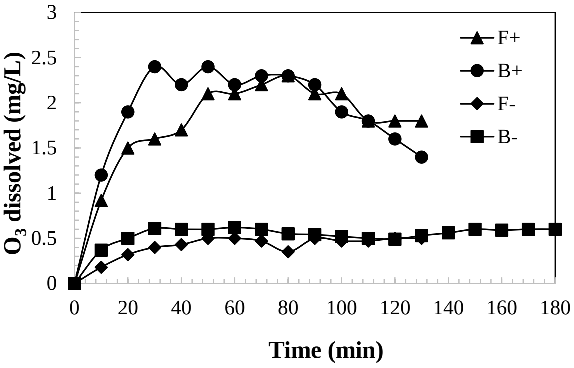

Figure 2. Disolved Ozone during the ozonation of the flushing (F) and backwashing (B) waters operating with low (-) and high (+) ozone concentration. Operation conditions: pH_0= 9.0; P = 1.5 bar; T = 35° C.

The observed ozone concentration either in sample F or B is proportional to the concentration of injected ozone with slight differences depending on the pollutant load of F and B during the first hour.

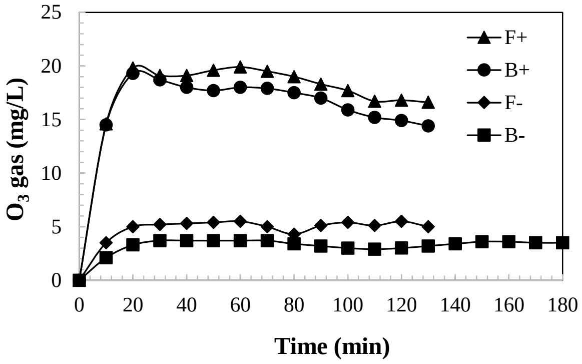

Figure 3. Ozone concentration in the gas outlet during the ozonation of the flushing (F) and backwashing (B) waters operating with low (-) and high (+) ozone concentration.

Operation *c*onditions of: $pH_0 = 9.0$; P = 1.5 bar; T = 35 ° C.

The use of ozone (RO_3, mg C/mg O3) was estimated according to the Eq. 1, to compare the use of ozone to operate with low (B-) and high (F +) concentrations of ozone. The ratio RO_3, expressed as the amount of oxidizable suspended solids (OSS) and the carbon organic total (TOC) that is removed during 130 min for B+ and 180 min for R-, in relation to the transferred O_3 to the liquid.

$$R_{O3} = \frac{(OSS_0 - OSS_f) + (TOC_0 - TOC_f)}{O_3 \text{ transfered}} \qquad (1)$$

being:

OSS_0: initial oxidizable C in solid suspended (mg/L).

OSS_f: Final oxidizable C in suspended solids (mg/L).

TOC_0: Initial total organic carbon in solution (mg/L).

TOC_f: Final total organic carbon in solution (mg/L).

Estimations gave ozone utilization ratios RO_3 between $1.81 \cdot 10^{-3}$ mg C/mg O_3 for B+ and $7.19 \cdot 10^{-3}$ mg C/mg O_3 for R-. Consequently, it is more efficient to operate at low ozone concentrations obtaining mineralization degrees until 4 times higher than at high ozone concentration.

3.2. Turbidity changes and aromaticity loss

Figure 4 shows the aromaticity evolution the ozonation of samples. The results indicate that this loss is produced during the first hour of reaction. Operating with high ozone concentration, reductions less than 30% in the absorbance A_{254} are obtained, while when washing water samples F and B were treated with low concentrations of ozone, higher reductions of the order of 50% in the A_{254} were observed (Table 2). This effect may be because, at low ozone concentration, a greater ozone efficiency leading to more advanced oxidation levels is obtained. Moreover, the aromaticity values present important variations along the ozonation with high concentration. This fact may indicate that in the degradation routes, probably reactions of condensation among the degradation intermediates occur (Villota *et al*., 2016a).

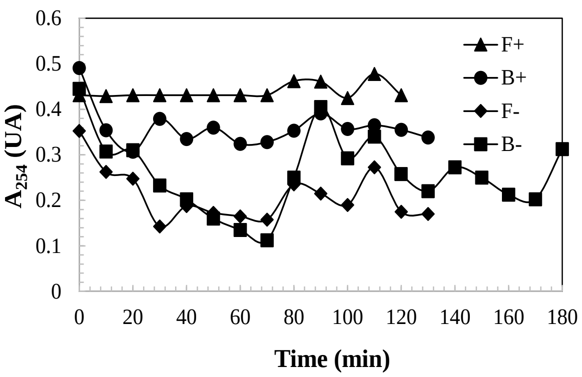

Figure 4. Aromaticity changes (A_{254}) in washing waters F and B using high (+) and low (-) O_3 input. Operation conditions de: pH_0=9.0; P=1.5 bar; T=35ºC.

Table 2. Aromaticity loss (A_{254}) expreseed as percent of the initial value (η_{254}). Operation conditions: pH_0=9.0; P=1.5 bar; T=35ºC.

Washing water	η_{254}, %
F+	0
B+	31.2
F-	51.8
B-	29.8

Figure 5 shows a linear increase in turbidity during the ozonation of the wasing waters. This phenomenon can be due to reactions among the reaction intermediates appearing during the process, that can interact forming links by hydrogen bridge, giving rise to the formation of supramolecular structures of high molecular weight that intercepts the light beam pass (Villota *et al*., 2016a; Villota *et al*., 2016b). Therefore, the increase in turbidity does not show a linear dependency with the loss of aromaticity. The kinetic constant for the turbidity formation adjusting the NTU values to a zero order kinetic, according to Eq. 2. In Table 3, estimated kinetic parameters are displayed.

$$NTU = NTU_0 + k_{NTU}\, t \qquad (2)$$

NTU: turbidity (NTU)

NTU_0: initial turbidity of the efluente (NTU)

Table 1. Estimated parameters to analyze te ozone efficiency using low (-) and high (+) O_3 concentrations. Operation conditions: pH_0=9.0; P=1.5 bar; T=35ºC.

Effluent	**OSS_0** mg C/L	**OSS_f** mg C/L	**TOC_0** mg C/L	**TOC_f** mg C/L	**$O_{3\ total}$** mgO_3/L	**R_{O3}** mg C/mgO_3
B+	20	0	6.79	3.77	12688	$1.81 \cdot 10^{-3}$
R-	24	0	15.9	6.76	4608	$7.19 \cdot 10^{-3}$

k_{NTU}: zero orden kinetic constant for the turbidity formation (NTU/min)

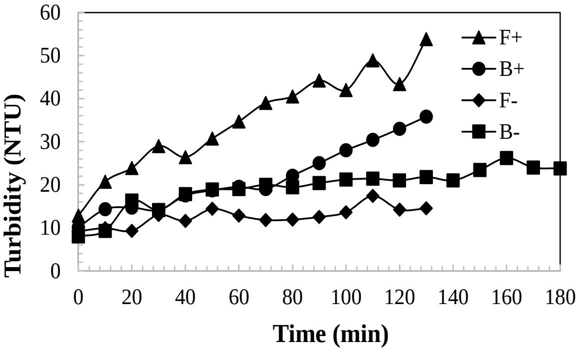

Figure 5. Turbidity (NTU) changes in the flushing (F) and backwashing (B) waters ozonated with high (+) and low (-)ozone concentratio. Operation conditions: pH_0=9.0; P=1.5 bar; T=35ºC.

Table 3. Zero orden kinetic parameters from the observed turbidity changes. Operation Conditions: pH_0=9.0; P=1.5 bar; T=35ºC.

Effluent	**NTU_0** **NTU**	**k_{NTU}** **NTU/min**	**r^2**
F+	17.72	0.280	0.9855
B+	9.79	0.181	0.9510
F-	9.87	0.042	0.6010
B-	12.63	0.074	0.7956

3.3. Mineralization of the washing waters

The waters treated by the ozonation have a great variety of contaminants depending on its origin. Consequently, to estimate the degradation level is necessary to do a global analysis of the organic load that contains the effluent. In Figure 6, the mineralization of the water depending on the analysis of TOC (mg C/L) during the ozonation is shown. The results obtained allow seeing that during the first few minutes of the oxidation an increase in the TOC takes place (60 minutes at low ozone concentration; 25 minutes operating at high ozone concentration). Then, the TOC decreases progressively with time until the steady state is reached. Therefore, this phenomenon can be explained considering that the total suspended solids (TSS) are divided into oxidizable suspended solids (OSS) and non-oxidizable suspended solids (NOSS). As oxidation progresses, the OSS dissolves giving rise to an increase in the solved TOC (Figure 6). Later the TOC reaches a maximum and then begins to decrease due to carbon mineralization process by the ozone action.

3.4. Kinetic modelling of mineralization

The kinetic model proposed to describe mineralization of the washing waters considers two reactions in series, where the OSS dissolves in the liquid, described through the term TOC* that incorporates the soluble oxidizable TOC (Eq. 3). Then, the mineralization of the effluent due to the action of ozone, generated as products of reaction, CO_2 and water would take place. Table 4 shows the kinetic parameters estimated for the collected flushing water oxidized with high ozone concentration. Figure 8 shows the prediction of the model fitted to the experimental results.

$$\mathrm{OSS} \xrightarrow{k1} \mathrm{TOC}^{*} \xrightarrow{k2} \mathrm{CO_2 + H_2O} \qquad (3)$$

k_1: First order kinetic constant for the solution of OSS in TOC^* (1/min).

k_2: First order kinetic constant for the mineralization of TOC^* (1/min).

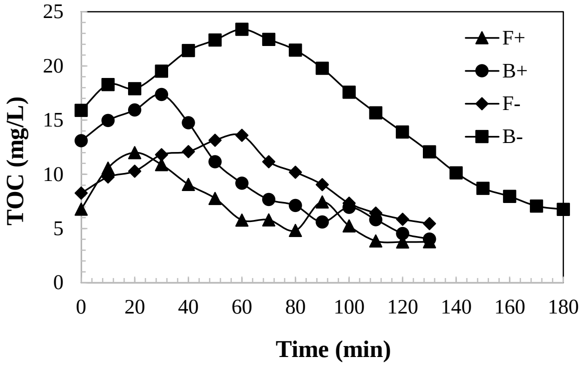

Figure 6. Mineralization of flushing (F) and backwashing (B) waters ozonated with high (+) and low (-) ozone concentration. Operation conditions: pH_0=9.0; P=1.5 bar; T=35ºC.

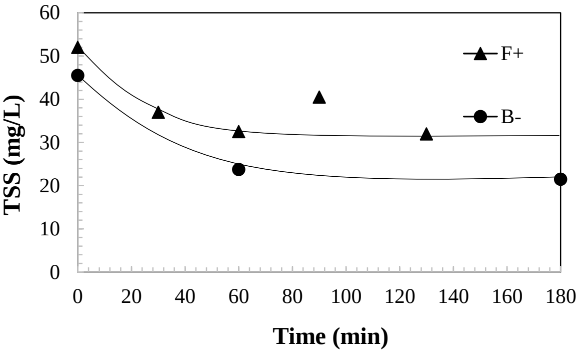

Figure 7. TSS in the flushing (F) and backwashing (B) waters ozonated with high (+) and low (-) O_3 concentration. Operation conditions: pH_0=9.0; P=1.5 bar; T=35ºC.

Table 4. Calculated kinetic parameters for the mineraliztion of flushing water (case F+). Operation conditions: pH_0=9.0; P=1.5 bar; T=35ºC.

Washing W	**OSS_0** **mg C/L**	**TOC_0^*** **mg C/L**	**k_1** **1/min**	**k_2** **1/min**
F+	20	3.036	0.0438	0.0525

The first stage of the system of reactions in series, that corresponds to the OSS solution adjusts to an first order kinetic equation (Eq. 4). The kinetic constant k1 (1/min) has been estimated from experimental data shown in Figure 7, considering that at the end of the reaction the OSS have been consumed entirely, leaving only the NOSS. The second stage of the series reaction, adjusted from experimental data shown in Figure 6, is described by the term TOC^* considering that, at the end of the reaction, all organic carbon TOC* from the OSS has been also consumed, remaining the non-oxidizable organic carbon or observed TOC once the steady-state is reached. TOC_0* is the initial TOC that oxidizes completely at the end of ozonation, so TOC* is the TOC_0* with the addition of TOC from OSS In the ozonation of case B-, operating with low ozone concentration, the fitting of the proposed model to the experiemntal data was not good. This may be due to the considerably slower reaction rate in this case. This sugests the possible existence of a more complex reactions scheme.

$$OSS = OSS_0 \exp(-k_1 t) \quad (4)$$

$$TOC^* = \frac{OSS_0 k_1}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right] + TOC_0^* \exp(-k_2 t) \quad (5)$$

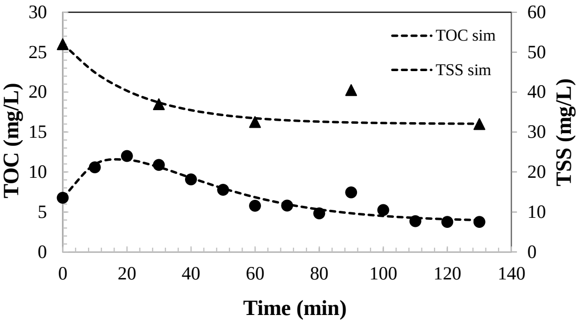

Figure 8. Model prediciton and experimental data in the ozonation of case F+. Operation conditions: F+; O_3=24.4 mg/L; pH_0=9.0; P=1.5 bar; T=35ºC.

4. Conclusions

UF washing waters treated with a lower ozone concentration input (6.4 mg O_3/L of gas) consumed up to 4 waters and from 0.042 to 0.074 NTU/min in the case of backwashing waters. This phenomenon may be due to reactions between the intermediate reactions promoting supramolecular structures that intercept the light passage. During the first minutes of the ozonation takes place an increase of the TOC due to the oxidizable suspended solids (OSS) that contribute to the increase of soluble TOC to decrease later at longer times. This phenomenon seems to respond to a two-series-reactions scheme. The model describes acceptably the experimental results of high O_3 concentration, using kinetic constants: k_1=0.0438 l/min (OSS) and k_2=0.0525 l/min (TOC*). For low O_3 concentration inputs the two-series-reactions is not entirely valid and a more complex reaction seems necessary. times less ozone to mineralize than those treated with high ozone concentration (24.4 mg O_3/L of gas). The loss of aromaticity was also greater (above 50 %) for low ozone concentrations than for high ozone concentrations (no more than 30%) and above 50%. The turbidity increases following a zero order kinetics whose constants varies from 0.181 to 0.280 NTU/min when treating flushing

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