

OZONE-BASED ADVANCED OXIDATION PROCESS AS PRE-TREATMENT OF WASTEWATER FROM THE WOOD-BASED INDUSTRY

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ABSTRACT

Three ozone-based advanced oxidation treatments (O_3 ; O_3 with initial pH adjustment and; O_3 /UV with initial pH adjustment) were compared for the treatment of a recalcitrant wastewater generated during washing/cleaning of surfaces and equipment used in filling and gluing processes (urea-formaldehyde and phenol-formaldehyde resins) in a wood-floor industry in Sweden. The wastewater (initial COD 3,400-4,000 mg/L) was obtained at the outlet of a sedimentation tank, which receive an inflow with an average COD of 45,000 mg/L. The experiments were performed in a semi-batch microbubble column reactor connected to a UV reactor, where 2.5 L samples of wastewater were submitted to the maximum dose of 2 g of O_3 per gram of initial COD. For the full-factorial design, the independent variables were O_3 concentration ($g O_3/Nm^3$); recirculation flow (L/min); and initial pH (pH_i). The evaluation of the treatment performance was based on COD and TOC reductions (in %), and the effluent obtained was used in respirometric assays with activated sludge obtained at a municipal wastewater treatment plant to assess biodegradability/inhibitory effects. The results showed that ozonation at the original low pH promoted a reduction of 65% and 31% of COD and TOC respectively, but made the effluent less biodegradable. The highest COD and TOC reductions were achieved when O_3 /UV treatment with $pH_i = 9.3$ were applied (93% e 56% reductions for COD and TOC respectively). The results with the respirometry tests suggest that application of O_3 only at higher pH values promoted biodegradability enhancement of the effluent, making it treatable by microbiota obtained with activated sludge from a municipal wastewater treatment plant.

KEYWORDS: Advanced oxidation processes; Industrial wastewater; Respirometry; Ozone; UV.

1 INTRODUCTION

Forestry has always been one of the major industries in Sweden, having registrations of negative impacts to the environment varying from physical alteration of rivers to facilitate logs driving, to runoff of toxic stormwater generated during rain washing of logs in open door

storages [1]. In order to reach the ambitious goals set by the Water Framework Directive (2000/60/EC), great effort has been made to neutralize possible negative effects on water bodies' integrity, especially the ones caused by industrial wastewater discharge. Among forestry industries, water consumption and wastewater generation is diversified. Pulp and paper mills, for example, are known for its large water consumption and generation of toxic wastewater [2,3,4] while wooden furniture and floor industries are characterized as dry-process industries since water is not required in their production processes [5,6]. Yet, wastewater is generated during cleaning and washing procedure of surfaces and equipment used for wood sizing, gluing, filling and surface coating [7], and contains significant amounts of pollutants such as urea- and phenol-formaldehyde, ammonium sulfate, wood filler, lacquer and detergents [8]. Despite the small amount generated ($2.0 - 2.5 \text{ m}^3/\text{week}$) this wastewater contains COD values varying from $3,200 \text{ mg L}^{-1}$ to $50,000 \text{ mg L}^{-1}$ [7,8] and it has been shown to be toxic to microalgae [5], brine shrimp and plant species [9].

Since the construction, operation and maintenance of on-site conventional industrial wastewater treatment plant is not appropriated from economical and operational points of view due to the low volumes of wastewater generated by these "dry industries", the common practice has been dilution with potable water (50 times or more) before discharging this wastewater into the sewage system [6, 8]. To avoid this unsustainable practice, different treatment techniques have been tested at Linnaeus University during recent years. However, [6] and [7] reported unsatisfactory COD removal by anaerobic biological treatment and sorption/filtration process, respectively, whereas [8] observed that efficiency of electrocoagulation treatment decays considerably in the presence of hardener wastewater, which is typically produced by wooden floor and furniture industries.

Advanced Oxidation Processes (AOPs) are based on the generation of highly reactive species of oxidants, mainly hydroxyl radicals, which are capable of unselectively and quickly oxidizing a wide range of recalcitrant, toxic and non-biodegradable compounds into inert or more biodegradable compounds, or even to promote complete mineralization [10,11,12,13]. The literature[14] refers to ozonation as an intrinsic AOP once $^{\circ}\text{OH}$ generation always occurs within ozonation of natural waters or wastewater, as a product of chain reactions initiated by reaction between O_3 and some organic molecules *e.g.* phenols, secondary and tertiary amines. Other ways to generate $^{\circ}\text{OH}$ in aqueous media are ozonation under basic conditions [15] and in the presence of UV-C light [11,14]. Besides oxidation via $^{\circ}\text{OH}$ generation (indirect reaction), O_3 can also react directly with some inorganic and organic groups (*e.g.* double bonds, aromatics, sulfur compounds) [14,16]. Another important characteristic of O_3 is its instability, which makes it impossible to store in tanks, hence demanding *in situ* generation for ozonation processes. On the other hand, this instability imparts O_3 a low residual effect, once unreacted ozone rapidly decomposes to O_2 [17,18].

The main objective of this study was to assess the efficiency of ozone-based AOPs on the treatment of process water from a wood-floor industry, applying processes optimization approach, at the same time, assessing the biodegradability enhancement of the treated effluent in view of coupling AOP with biological treatment in the future.

2 MATERIALS AND METHODS

2.1 Studied wastewater

The wastewater studied was supplied by a wood floor factory located in southeastern of Sweden, with a production ranging from 110,000 to 250,000 m^2 of laminate wood floor per

week. For this study, the wastewater samples were collected after on-site primary treatment in a sedimentation tank that receives wastewater generated by machinery washing (gluing, filling and blade sharpening) and cleaning of the factory floor. This primary treatment step delivers wastewater with COD of approx. 5000 mg L⁻¹ and TOC of approx. 1500mg L⁻¹, from which 200 L of sample were collected onsite and transported to the Linnaeus University laboratory where it was stored at 4°C.

2.2 Chemical analyses

Hach Lange kits (Hach Lange, Dusseldorf) were used to analyze Chemical Oxygen Demand (LCK 114), Total Organic Carbon (LCK 386) and Carbonates (LCK 388) using a DR 5000 UV-Vis Spectrophotometer (Hach Lange, Dusseldorf). The pH was measured with pHmeter Mettler Toledo SG2.

2.3 Ozonation system setup

The system (Figure 1) consists of two reactors: one O₃ reactor, built up in stainless steel (diameter = 8.5 cm, height = 59 cm) equipped with stainless steel diffuser with a 20 µm pore size (length = 8 cm, diameter = 1.9 cm) (SD-3; Ozone Solutions, USA); and one UV reactor, glass-jacket immersion-type (diameter = 10 cm, height = 25 cm) equipped with a medium-pressure 150W lamp (TQ150 UV-Consulting Peschl, Germany). Between the two reactors, continuous recirculation flow was kept by two peristaltic pumps (520SN, Watson-Marlow, United Kingdom) countercurrent to gas. The O₃ was generated from 99.5% pressurized oxygen (O₂) by a water-cooled corona discharge ozone generator (ICT-10; Ozone Tech Systems, Sweden), and its concentration in gas phase was measured by an ozone monitor (BMT 964; BMT Messtechnik GMBH, Germany). Unreacted O₃ in the off-gas was destroyed in a catalytic ozone destructor (OD-0100; Ozone Tech Systems).

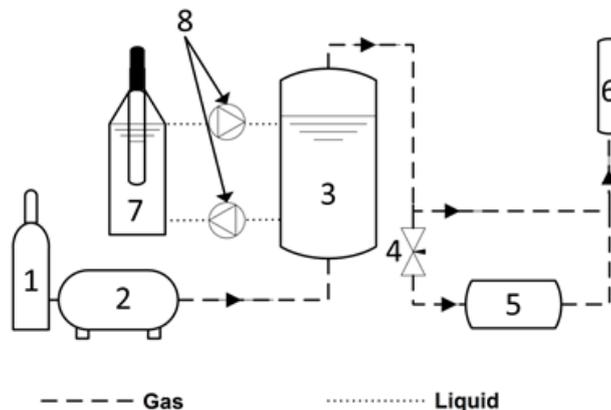


Figure 1. Bench-scale O₃-based AOP System: (1) O₂ pressure tank; (2) O₃ generator; (3) O₃ reactor; (4) needle valve; (5) O₃ monitor; (6) O₃ destructor; (7) UV reactor; (8) peristaltic pumps.

In each experiment the system was filled with 2.5 L of wastewater, with predetermined COD and TOC. Samples were collected once the ratio “O₃ injected (g)/COD of the batch (g)” reached 0.25; 0.5; 1.0; 1.5 and 2.0 to 1.0, and left resting for 24 h at 4°C to avoid interference of residual O₃ over the subsequent analysis.

2.4 Experimental design

Due to the number of independent variables studied, full-factorial Rotational Central Composite Designs were adopted [19]. For the first treatment, ozonation at natural low pH (O_3+pH_{low}), a 2-variables 5-level design was used (Table 1) with a total of 11 runs, whereas for the second and third treatments (O_3+pH_{adj} and $O_3/UV+pH_{adj}$) a 3-variables 5-level design was used (Table 2) with a total of 17 runs. For both designs, triplicate of central point was adopted.

Table 1. Variables and levels used in the first treatment: $O_3 + pH_{low}$

Independent Variables	Levels of variables				
	-1.41	-1	0	+1	+1.41
X_1 ($[O_3]$)	40	50.98	77.5	104.02	115
X_2 (RF)	0.3	0.7	1.65	2.6	3.0

$[O_3]$ = O_3 concentration in the feed gas (g/Nm^3); RF = recirculation flow between reactors ($L\ min^{-1}$)

In the first treatment (O_3+pH_{low}) levels were determined according to equipment capacity, while in the second and third treatments $[O_3]$ levels were based on results from the first treatment.

Table 2. Variables and levels used in the second and third treatments (O_3+pH_{adj} and $O_3/UV+pH_{adj}$)

Independent Variables	Levels of variables				
	-1.68	-1	0	+1	+1.68
X_1 ($[O_3]$)	40	50.13	65	79.87	90
X_2 (RF)	0.3	0.85	1.65	2.45	3.0
X_3 (pH_i)	3.0	4.62	7.0	9.38	11

$[O_3]$ = O_3 concentration in the feed gas (g/Nm^3); RF = recirculation flow between reactors ($L\ min^{-1}$); pH_i = initial pH of the batch (adjusted)

Statistica 12 software was used for the experimental design and data analysis. The relationships between independent variables and the targeted responses (% COD and % TOC reduction) were analyzed through a model that follows a quadratic pattern described by the following equation:

$$Y = \beta_0 + \sum_{j=1}^k \beta_j X_j + \sum_{j=1}^k \beta_{jj} X_j^2 + \sum_i \sum_{<j=2}^k \beta_{ij} X_i X_j + e_i$$

Where: Y is the response; X_i and X_j represent coded independent variables; β is the regression coefficient; k is the number of factors studied and; e is the random error.

Analysis of variance (ANOVA) was used to determine the existing interactions between independent and dependent variables and their respective significance within 95% of confidence interval ($p < 0.05$). The fit of the polynomial models was evaluated through the

coefficient of determination (R^2). Statistica 12 software was used for the experimental design and data analysis.

2.5 Respirometry test setup

Respirometry tests were conducted using a pulse-flow headspace respirometer and accompanying software (PF-8000, Respirometer Systems and Applications, Fayetteville, AK, USA) allowing up to 16 simultaneous individual batch tests (Figure 2).

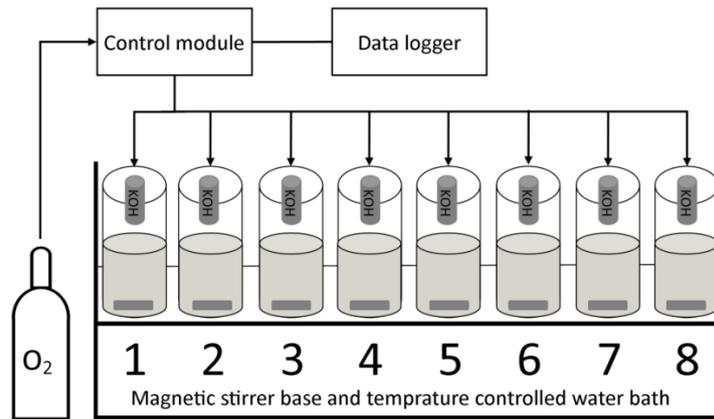


Figure 2. Schematic of respirometer set-up showing eight bottles, instead of the 16 bottles used in the present study. KOH was used as CO_2 scrubber.

For each batch test, activated sludge from a municipal wastewater treatment plant was collected and used as inoculum. Once collected, the sludge was aerated for 48 h prior to use to minimize the amount of substrate that was added by the sludge. For all respirometry experiments, 500 mL bottles were used.

The samples submitted to respirometry tests were the ones with highest reduction of COD and TOC in each treatment. Preparation of samples for respirometry followed pH adjustment to 7.0 and dilution with tap water (free of chlorine) to achieve similar TOC concentration in all samples. Tap-water was chosen as the diluent since it would have less effect on the osmotic pressure and it has showed to work well in previous studies conducted by the authors [20]. Samples of 320 mL were added to each bottle with 90 mL of activated sludge. Minerals and nutrients were then added to each bottle to achieve equal conditions for all experiments, minerals and a buffer solution were added according to [21]. All respirometry studies were conducted for 50 h and the oxygen uptake and the oxygen uptake rate (OUR) were registered. The oxygen uptake is measured over time and when summed up it gives the cumulative oxygen consumption; the slope of the cumulative oxygen uptake curve gives the OUR [21].

3 RESULTS AND DISCUSSION

3.1 Effects of independent variables on treatment efficiency

The coefficient of determination of the quadratic theoretical models describing the reduction variation as a function of the selected independent variables were as high as 0.88, 0.74, 0.84 for COD and 0.75, 0.70, 0.83 for TOC for each O_3/pH_{low} , O_3/pH_{adj} and O_3/UV respectively suggesting high agreement between experimental and theoretical data. The effect of

independent variables on reduction (in %) of COD and TOC are illustrated through 3D surface plots hereinafter.

The efficiency of ozonation at natural low pH (O_3/pH_{low}) showed to be affected by both concentration of O_3 supplied in the feed gas ($p < 0.05$, effect = -10.8) and recirculation flow between reactors ($p < 0.05$, effect = 8.6), being $[O_3]$ the variable with stronger influence over % COD reduction, and the only variable affecting % TOC reduction.

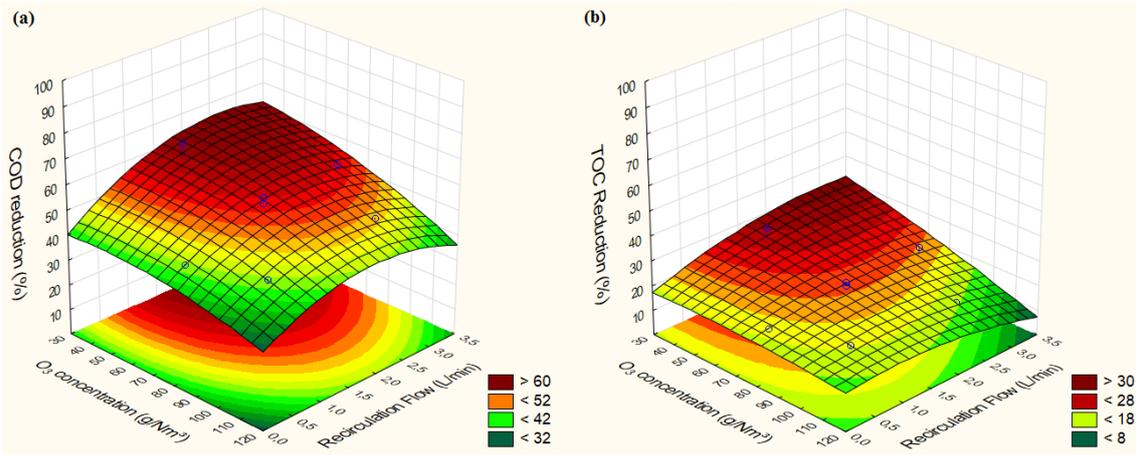


Figure 3. 3D surface plots of COD and TOC reduction (in %) as a function of the independent variables for O_3/pH_{low} .

As can be seen in Figure 3a, the highest reduction of COD was achieved with high recirculation flow (L/min) combined with low concentrations of O_3 (g/Nm^3). This is likely to occur due to lower losses of ozone in the off-gas, as slower feeding of oxidant plus higher mixing (high recirculation flow) results in more efficient consumption of O_3 . This hypothesis is reinforced by specific O_3 consumption models ($R^2 = 0.77$ for both COD and TOC) illustrated in Figure 4, that shows O_3 was more efficiently consumed when it is supplied in lower concentrations with higher mixing, represented by higher RF values.

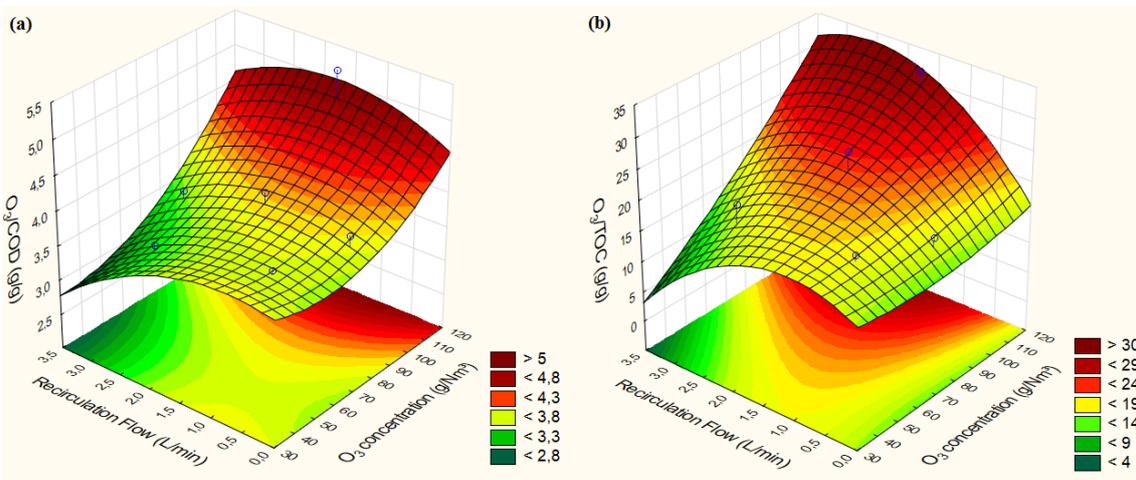


Figure 4. 3D surface plots of specific O_3 consumption per COD and TOC reduced (in gO_3 consumed/ $gCOD$ or g/TOC reduced) as a function of the independent variables for O_3/pH_{low} .

In the treatments with pH adjustment (O_3/pH_{adj} and O_3/UV), the variable $[O_3]$ showed to exert no significant effect on COD and TOC reduction ($p > 0.05$). For this reason, the 3D graphs for these experiments are presented only for the significant independent variables (recirculation flow and pH_0) as shown in Figure 5.

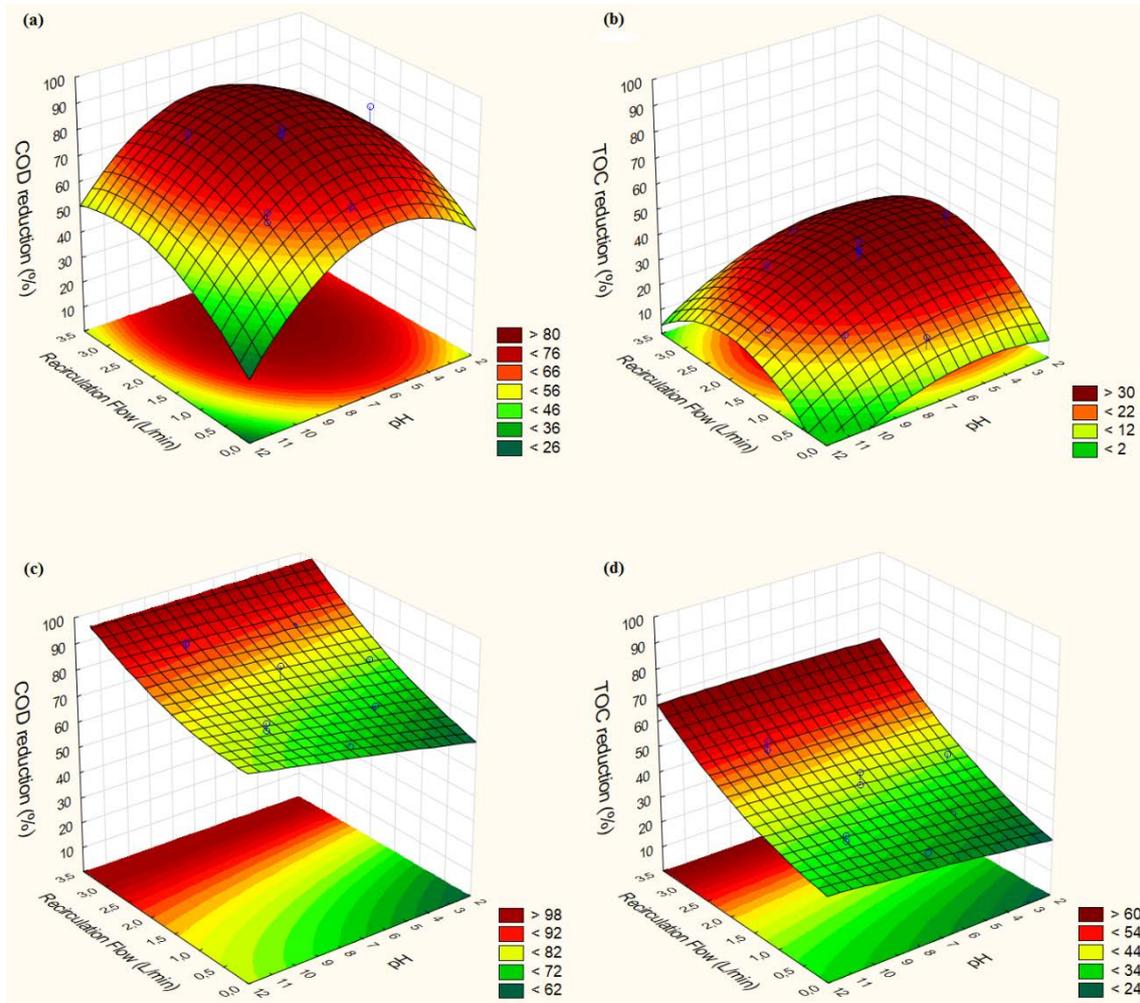


Figure 5. 3D surface plots of COD and TOC reduction (in %), as a function of the independent variables for O_3/pH_{adj} (a, b) and O_3/UV (c,d). Graphs (a) and (c) show % COD reduction, while (b) and (d) show % TOC reduction.

With the treatment O_3/pH_{adj} , the COD reduction was significantly affected by both Recirculation Flow (l/min) ($p < 0.05$, effect = 10.1) and pH_0 ($p < 0.05$, effect = -11.2). In the predicted model for %COD reduction, the quadratic term of the variable pH_0 showed to be significant (data not shown) and to have a negative coefficient value (data not shown), meaning that there is a value of pH_0 from which any variation starts to affect the COD reduction, and Figure 5a shows that this value lies around neutral pH. It is known that higher pH leads to higher generation of $^{\circ}OH$ from reaction between O_3 anions OH^- , but in this case

it's possible that this increase in reaction rate is counteracted by the greater ozone requirement due to loss of oxidants by increased self-decomposition [22] and by increased availability of carbonates, which are strong $^{\circ}\text{OH}$ scavengers [14]. On the other hand, lower efficiency at lower pH can be associated to lower oxidation capacity of O_3 direct reactions, since less $^{\circ}\text{OH}$ is generated, O_3 has slower kinetics and attacks selectively specific molecular groups [23, 24] that may not be abundant in the wastewater under investigation.

The TOC reduction achieved with the $\text{O}_3/\text{pH}_{\text{adj}}$ treatment was only significantly affected by the recirculation flow ($p < 0.05$, effect = 8.9), showing that though pH_0 variation caused some decay in oxidation potential of the treatment, it makes no significant difference to mineralization potential of the treatment.

For O_3/UV treatment, % COD and % TOC reductions were significantly affected only by Recirculation Flow ($p < 0.05$, effect = 15.2 and 16.9). Figures 5c and 5d show the clear influence of UV-C exposure (RF) and the way it compensates efficiency decay caused by high and low pH values. It is interesting to notice however, that at neutral pH the amount of O_3 consumed per COD reduced (g/g) in the central points ($\text{pH} = 7$) was practically the same, being $\approx 3,05$ without UV and $\approx 3,06$ with UV (84.2% and 81.43% COD reduction, respectively), showing that at neutral pH, UV-C irradiation caused no enhancement of % COD reduction at all. For TOC reduction the compensation effect of UV at higher and lower pH also happens, but again less efficiency enhancement is observed at $\text{pH}=7$.

3.2 pH variation along treatment

For $\text{O}_3/\text{pH}_{\text{adj}}$ and O_3/UV treatment, pH adjustment showed to cause an average increase in the % COD and % TOC reduction of 24% and 8%. However, it is important to notice that regardless of the wide range tested, there was a clear trend of pH to converge towards an average value with smaller variations. Whereas during the $\text{O}_3/\text{pH}_{\text{low}}$ treatment no variation or convergence towards an average value was observed (see Figure 6), during the $\text{O}_3/\text{pH}_{\text{adj}}$ and O_3/UV treatments, pH_0 of 7.0 ± 2.2 shifted to final pH of 5.7 ± 0.8 and 6.5 ± 0.8 respectively, which corresponded to a shift from 32% of pH_0 variation down to 14% in both cases (see Figure 6).

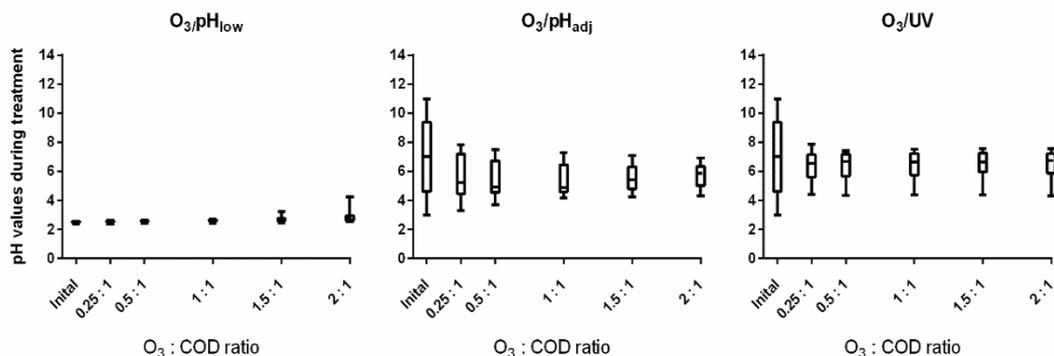


Figure 1. Development of pH during the treatments. Whiskers show max/min values; the horizontal lines within the boxes indicate the median values.

This is likely due to the buffer formed from the carbon dioxide (CO_2) production when the carbon is degraded [25,26], which is confirmed by the fact that it is seen for $\text{O}_3/\text{pH}_{\text{adj}}$ and O_3/UV , the most effective treatments. Figure 7 shows carbonates concentration development along the best treatments of $\text{O}_3/\text{pH}_{\text{adj}}$ and O_3/UV , and confirms that treatment with higher mineralization capacity also promotes higher buffer effect due to carbonate generation.

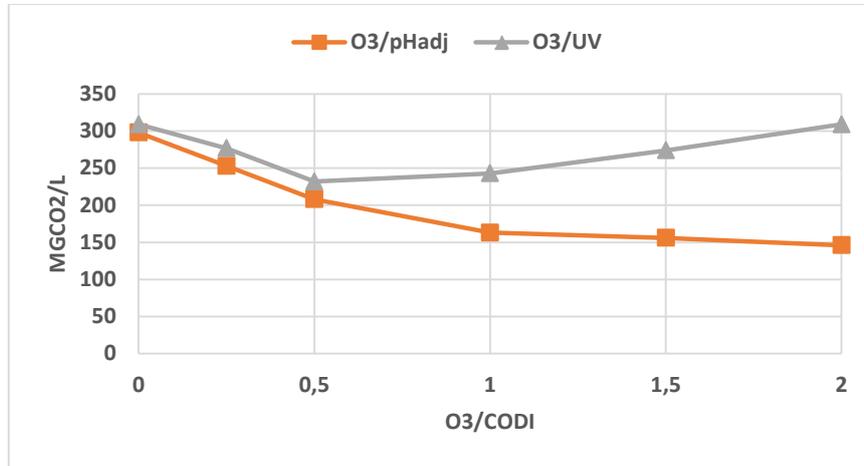


Figure 7. Development carbonates concentration, in mgCO_2/L , during the best runs of $\text{O}_3/\text{pH}_{\text{adj}}$ ($[\text{O}_3] = 50.13 \text{ g/Nm}^3$; $\text{VR} = 2.45 \text{ L/min}$; $\text{pHi} = 9.38$), and O_3/UV ($[\text{O}_3] = 40.0 \text{ g/Nm}^3$; $\text{VR} = 1.65 \text{ L/min}$; $\text{pHi} = 7.0$).

4 RESPIROMETRIC TESTS

In order to verify the possibility of reducing toxic/inhibitory effects after treatment with ozone-based AOPs, activated sludge was exposed to untreated and treated wastewater (effluents from $\text{O}_3/\text{pH}_{\text{low}}$ only, $\text{O}_3/\text{pH}_{\text{adj}}$ and O_3/UV treatments) and the oxygen up-take rate was monitored as an indication of biological aerobic activity. The experimental results have shown that ozonation at low pH ($\text{O}_3/\text{pH}_{\text{low}}$) resulted in increased inhibitory/toxic effects in comparison to the untreated wastewater. This negative effect decreased when higher dose of O_3 was applied (Figure 8). On the other hand, ozonation at neutral pH range ($\text{O}_3/\text{pH}_{\text{adj}}$) and with the use of UV (O_3/UV) the inhibitory/toxicity effects were decreased in comparison to untreated wastewaters, as indicated by the higher oxygen uptake rates (OURs) observed, mainly when considering the lower dose of O_3 (O_3/COD of 1:1). With O_3/UV treatment, inhibitory/toxicity effects were the lowest in comparison to untreated wastewaters, with readily available COD as high as 736 mg/l and 673 mg/l with O_3/COD of 1:1 and 3:1 respectively, in comparison to readily available COD of 419 mg/l before treatment (Figure 8). Even though $\text{O}_3/\text{pH}_{\text{adj}}$ was not as effective as O_3/UV , an increase in the readily available COD was also observed with $\text{O}_3/\text{pH}_{\text{adj}}$, mainly with the O_3/COD ratio of 1:1.

Concerning the period that activated sludge took to achieve the peak of oxygen uptake, a much longer period was observed in samples treated at low pH ($\text{O}_3/\text{pH}_{\text{low}}$) in comparison to those treated with $\text{O}_3/\text{pH}_{\text{adj}}$ or O_3/UV . Whereas the peak of oxygen uptake was reached after 39 h (1:1) and 25 h (3:1) in wastewater treated without pH adjustment, it took less than one hour for the microbial metabolic processes to reach its peak in the effluent of $\text{O}_3/\text{pH}_{\text{adj}}$ or O_3/UV treatment (Figure 8).

These results suggest the generation of toxic and/or hardly biodegradable oxidation by-products during O_3/pH_{low} treatment, a common effect reported in the literature when applying O_3 treatment at acid pH [27,28,29,30]. On the other hand, the O_2 consumption peaks reached in the initial stages of the biological treatment of the effluent generated by O_3/pH_{adj} and O_3/UV treatments indicate the potential use of these treatment configurations before sending these wastewaters to the MWWTP, since a substantial part of the pollutants in the wastewater could be readily available for microorganisms.

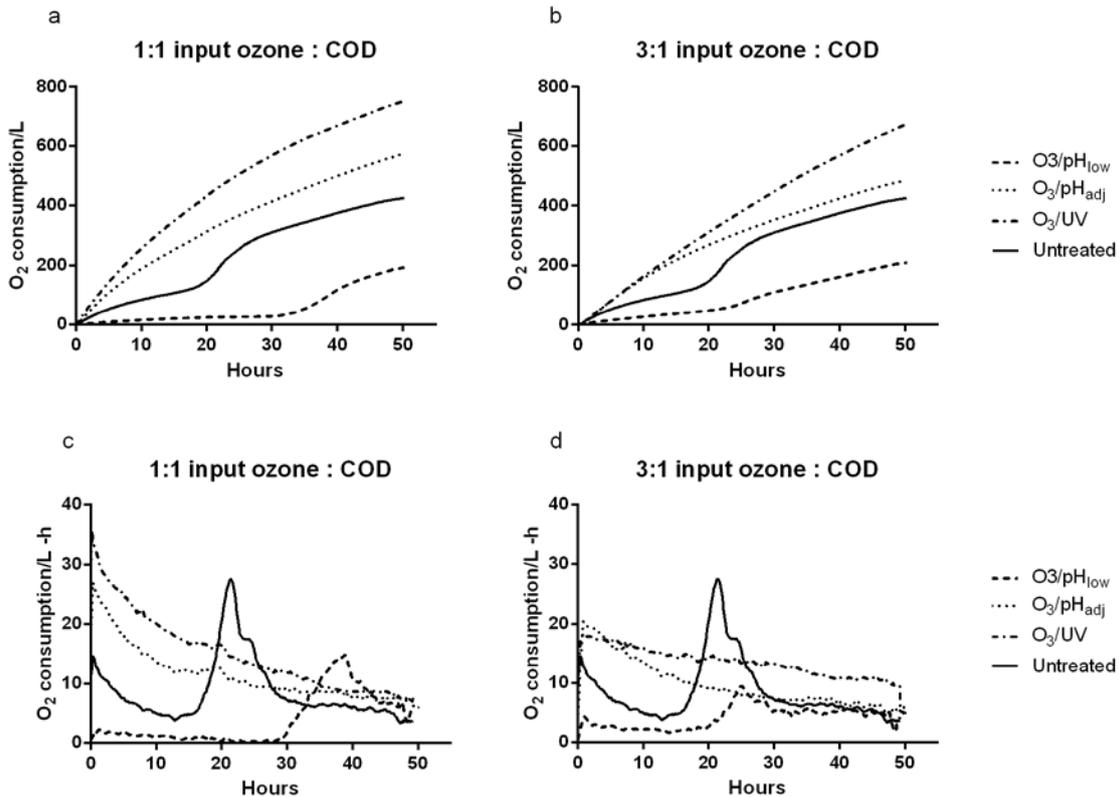


Figure 8. Cumulative oxygen consumption (a, b) and oxygen uptake rate (c, d) per liter of untreated and treated wastewater by O_3/pH_{low} , O_3/pH_{adj} and O_3/UV [31].

5 CONCLUSIONS

Though ozonation at low pH (O_3/pH_{low}) resulted in reductions of 65% and 31% of COD and TOC respectively, respirometry tests showed that this is not a proper pre-treatment before discharge to municipal WWTP once increased effluent toxicity could affect the WWTP efficiency. However, results showed that simple pH adjustment to neutral range could make ozonation a feasible pre-treatment, reaching even higher reduction rates (85% for COD and 31% for TOC) and biodegradability enhancement.

It is true that ozonation with pH adjusted and UV irradiation resulted in most effective treatment (93% of COD and 43% of TOC reduction) and that this technique is much less sensitive to possible pH variation of the wastewater, but it is important to realize that enhancements caused by UV, both in biodegradability enhancement and COD and TOC

reduction, may not justify the electricity consumption of UV lamps. Under these circumstances, it is likely that for this wastewater the better pre-treatment option would be single ozonation under neutral pH.

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