

COD Fluctuations in Ozonation Columns for Wastewater Treatment

Effects of Intermediate Organic Compounds

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Abstract- Experiments on Chemical Oxygen Demand (COD) performed in an ozonation column for wastewater treatment showed fluctuations following irregular time patterns, which could not be explained only by the experimental uncertainties or by stripping, the last being the cause of fluctuations during the first stages of ozonation procedures. Fluctuations observed in more advanced times of the experiments suggest that changes in the oxidation state of the organic matter also affected the COD values. The effect of intermediate compounds was considered in order to quantify this influence. A mathematical model is proposed in this study, which considers the consequences of intermediate compounds formed during oxidation. The different behaviors observed in the COD results of the ozonation column could be explained applying the model with different sets of adjustable constants. The joint analysis of the experimental results and the mathematical model allows suggesting that fluctuations observed in COD results, superposed to the mean decreasing trend and occurring at larger contact times, are forced by organic intermediate compounds.

Keywords- Wastewater Treatment; Water Conservancy; Ozone; Ozonation Columns; COD Fluctuations

I. INTRODUCTION

Water conservancy requires the treatment of wastewaters, so that they can be redispersed in the environment with a minimum of deleterious effects. Different treatment strategies are used to attain this main objective, among them the so called oxidative processes.

The use of oxidative processes for the treatment of wastewaters is usually associated with biological processes, and aims to improve biodegradability through the transformation of recalcitrant compounds into easily biodegradable products^[1]. Oxidative processes are also used as a complement for the treatment itself, through oxidation (and consequent reduction of the Chemical Oxygen Demand - COD) and disinfection, for which ozone is used.

Ozone can be applied to wastewaters using injectors or by bubbling^[2], being transferred from the gaseous phase to the liquid phase through the combined mechanisms of molecular diffusion, turbulent diffusion, and convection, while the bubble moves upwards. In this case, turbulence

and mass transfer is a local phenomenon governed by the flow conditions close to the bubble surface, and depending on the relative velocity between bubble and water, as discussed, for example, by [20], [21] and [22].

As a consequence, bubbling removes organic compounds from the liquid phase through stripping and oxidation; the latter, in this case, usually caused by both ozone and oxygen. During oxidation of organic compounds by ozone, the hydroxyl radicals convert complex organic compounds into byproducts more susceptible to oxygen. For example, [3] studied the oxidation of benzene by the hydroxyl radicals, which generated hydroxycyclohexadienyl radicals that, on their turn, reacted with oxygen and produced endoperoxyalkyl and endoperoxyalkyl radicals. Because these phenomena are simultaneous, it is difficult to quantify the different compounds separately while they are produced, but, as mentioned, stripping removes volatile organic compounds, so that quantification is possible through the analyses of the gas bubbles that cross the liquid phase. In this sense, [4] compared the effects of stripping (using nitrogen) and oxidation (using oxygen and ozone-enriched oxygen) on the odour removal from swine manure slurry, caused by phenol, p-cresol, p-ethylphenol and skatole. The authors showed that stripping was always less efficient than oxidation for the removal of the four compounds (zero to 40%), while oxidation through ozone was always the most efficient (80 to 100%). Oxidation through oxygen removed from 10 to 50% of the analysed compounds, being the efficiency dependent on the compound considered. Thus, in the present study, oxidation through ozone was used.

The reactions of ozone with organic matter are mainly bimolecular reactions, following a second order kinetics, that is:

$$\frac{dM}{dt} = -k[M][O_3] \quad (1)$$

where k is the rate constant (L/mol s); $[M]$ is the organic matter concentration (mol/L) and $[O_3]$ is the ozone concentration (mol/L). However, in situations like the

present study, ozone reacts quickly while transferred to the liquid phase, and the ozone transfer rate generally maintains a constant value along the contact time. In such conditions the residual ozone concentration may be assumed constant, and the reaction is viewed as a pseudo-first order reaction^[5, 6]. That is:

$$\frac{dM}{dt} = -k_M [M] \quad (2)$$

where k_M is the pseudo-first order rate constant (1/s).

It is thus accepted, for the usual work conditions, that the COD values resulting from the reaction between ozone and organic matter obey a monotonic evolution with the contact time, as a consequence of the pseudo first order kinetics. That is, the evolution of the function that relates the remaining COD concentration and the contact time would follow a monotonic decreasing behavior, thus improving also monotonically the efficiency of COD removal with time. However, results found in the literature show fluctuating behaviors of the COD concentration and removal. Such fluctuations are present in experiments conducted either with ozone or oxygen. For example, although evidencing the general mean decreasing of COD values, [19] presented results obtained in a water-sparged aerocyclone reactor for wastewater treatment showing COD fluctuations for large stripping times (contact times). The presented results show large scale fluctuations until about 150 min of the performed experiments. As a further example, although not directed to the study of COD fluctuations, [7] obtained similar oscillations for the inactivation efficiency of *Escherichia coli* during the disinfection of wastewater in a facultative pond through ozonization. Using contact times of 10, 20 and 30 minutes, [7] obtained the lowest inactivation efficiency for the contact time of 20 min (that is, in the middle of the studied time range), for consumed dosages of 6 ± 0.3 , 10 ± 0.65 and 18 ± 1.08 mg O_3/L . One of the reasons of the oscillations in the COD values is the variability of the oxidation state of the organic carbon, leading to a COD removal which is not necessarily a linear function of the consumed ozone mass. In this sense, [8], [9] and [10] pointed that the variability in the oxidation state of organic carbon affects the COD values. A possible consequence is that a larger amount of consumed ozone does not imply necessarily in a higher COD removal. The average oxidation state (AOS) is obtained by Equation (3)^[11].

$$AOS = \frac{4(TOC - COD)}{TOC} \quad (3)$$

where TOC is the total organic carbon (mol C/L) and the COD is given in (mol O_2/L).

This study presents and discusses experimental results obtained for COD in an ozonization column using effluents from an Upflow Anaerobic Sludge Blanket (UASB) reactor. The fluctuating behavior of the COD and the COD removal efficiency is presented as dependent of the applied dosages and the contact time. Furthermore, a mathematical model is presented, which takes into account the effect of intermediate organic compounds on the value of the COD

concentration, and which furnishes a conceptual way to describe and explain the observed fluctuations.

As mentioned, the described procedures allow observing the fluctuations of the COD concentration after oxidation with ozone. In other experiments the fluctuations may be caused by other oxidants, allowing us to suggest the use of similar techniques for these oxidants. In the design of wastewater treatment, COD fluctuations can introduce deviations when considering the contact time as main parameter for a given removal efficiency. A mathematical model that considers the interference of intermediate compounds in the removal of COD helps to fill this gap, considering also the needed calibrations.

II. MATERIAL AND METHODS

Experiments were performed in a column with a square transversal section of 19.0 cm and height of 200.0 cm. Two opposite walls of the column were made of glass, while the two remaining walls were made of Perspex, allowing perforations for sampling (Fig. 1). A micropore diffuser was installed at the bottom of the column, with the dimensions shown in Fig. 2. The pores had a mean diameter of 20 μ m, allowing a maximal gas flow rate of 3.0 m^3/h at 25°C and 101,325 Pa.



Fig. 1 Ozonization column made of glass and Perspex [23]

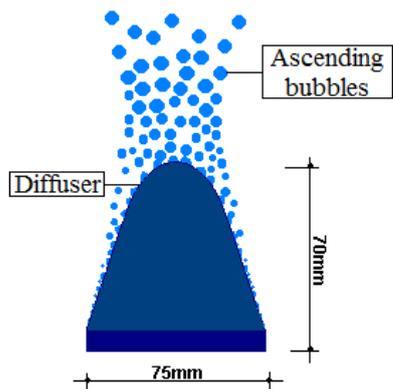


Fig. 2 Dimension of the micropore diffuser used in the column [23]

Measurements of bubble diameters were made using clean water, laser light and a CCD camera (Figs. 3 and 4), see details in [12].

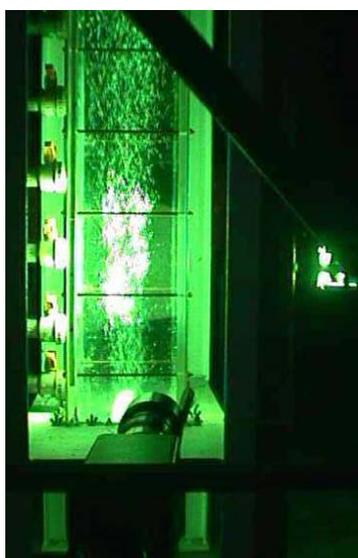


Fig. 3 Experiments of bubble visualization conducted with clean water [23]

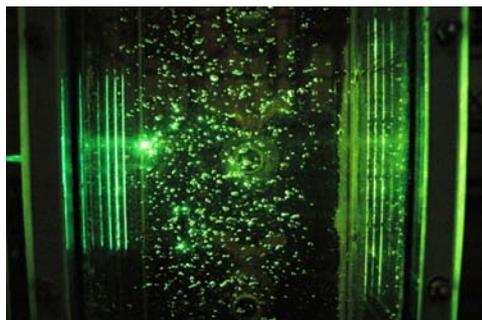


Fig. 4 Ascending bubbles in the column. Experiments with clean water [23]

Water samples were collected at three cross sections of the column, at 15.0, 90.0, and 165.0 cm above the bottom, as shown in Fig. 5. An electronic device was installed to take the samples simultaneously. Fig. 5 presents a sketch of the column, showing the ozone inlet, the micropore diffuser, the three sections where samples were taken, a reservoir to collect foam (municipal wastewater was used), the point where the foam was released, the ozone collector and the oxygen outlet. Fig. 6 shows the laboratory arrangements for the experiments. Descriptions of different aspects of this column may also be found in [12] and [23].

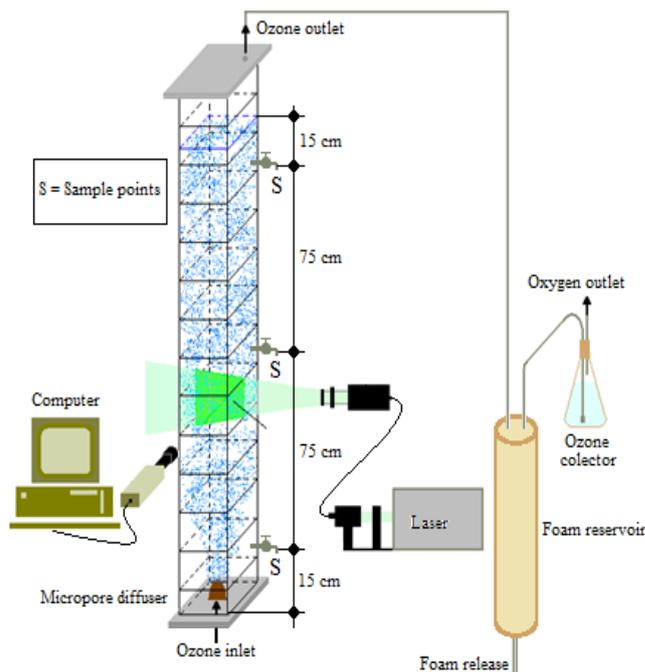


Fig. 5 Sketch of the column for the present ozonization batch experiments. Municipal wastewater was used for the evaluation of COD (adapted from [12])

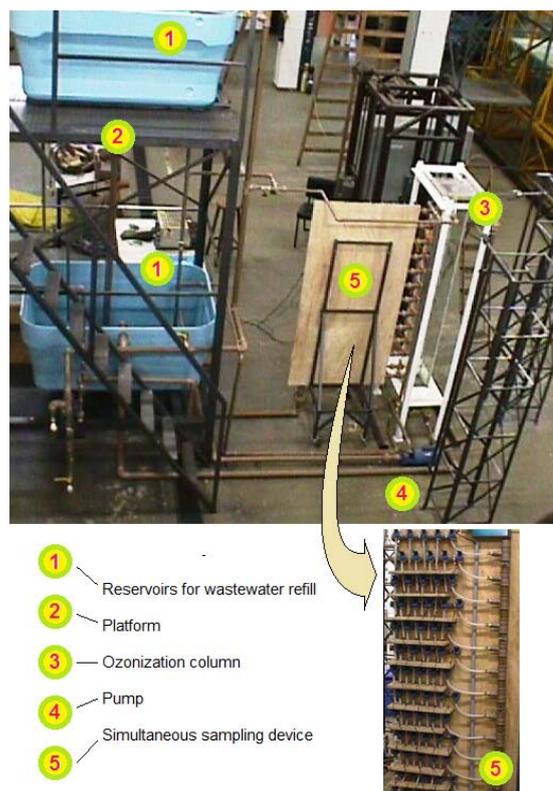


Fig. 6 Equipment used for the COD experiments, as organized in the laboratory

The ozone production was quantified using the iodometric method [13] filling the column with a 2% solution of potassium iodide (KI) (w/w). The ozone production (g/h) and the oxygen discharge (L/min) were used to quantify the ozone dosages. Oxygen was generated in the laboratory using atmospheric air and the PSA method (Pressure Swing Adsorption), attaining a final mass concentration of 98% of

oxygen in the gaseous phase. This oxygen was used directly in the ozone generator adjusting the volumetric rate to attain the dosage of each run. The residual ozone in the liquid phase was quantified using the DPD method (Merck chlortest 1.14803.0001), and the off-gas ozone was captured and quantified using a 2% solution of KI^[14]. The ozone consumed in the column was quantified from the difference between the applied mass and the masses in the liquid phase and in the off-gas. The COD of each sample was measured using the closed reflux, colorimetric method^[14].

As mentioned, municipal wastewater was used in the experiments, collected from the wastewater treatment plant of the University of São Paulo, campus of São Carlos, Brazil. A volume of about 65 L, obtained from a UASB reactor effluent, was used for each batch experiment, which implied a water depth of about 1.80 m in the column. A total of ten runs were conducted, with a total contact time of 20 minutes for each run. Five experiments were run with an ozone dosage of 5.0 mg/L and five were run with an ozone dosage of 15.0 mg/L. Wastewater samples were collected at the beginning of the experiments and at intervals of five minutes.

III. EXPERIMENTAL RESULTS FOR COD AND DISCUSSION

The mixing ability of the column was tested firstly, in order to define the sampling procedures for the experiments. Methylene blue was used, showing that total mixing was always achieved for time intervals lower than 30 seconds; which is short in comparison with the time of 20 minutes of each experiment (Fig. 7). This allowed to use the mean value of the COD measured at the three sampling sections as the representative COD value of the column, and to calculate the uncertainty of each mean value.

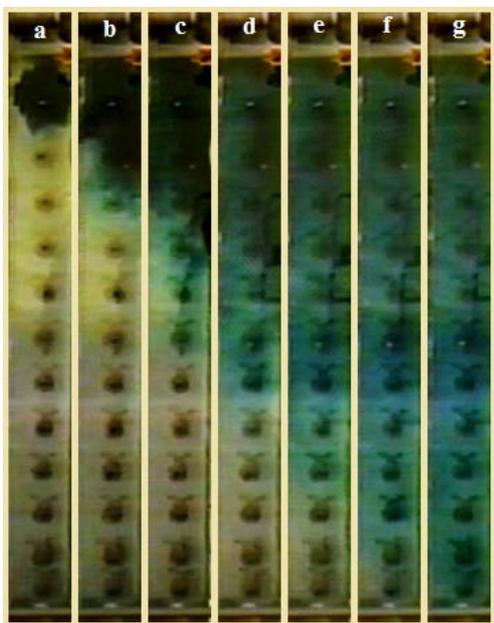


Fig. 7 Mixing ability of the column for batch experiments. Total mixing is obtained for time intervals lower than 30s. The time intervals for the photographs are: a) 1.0s, b) 5.0s, c) 10s, d) 15s, e) 20s, f) 25s, g) 30s

The initial mean COD concentration of the effluent of the UASB reactor was 110.82 mg/L, with a standard deviation of 19.82 mg/L for the different experiments. The final mean COD after the application of ozone was 84.07

mg/L, with a standard deviation of 23.60 mg/L for the different experiments. The observed mean removal was 26.75 mg/L.

The mean value of the experimental uncertainty was obtained from the three simultaneous measurements along the column. The mean uncertainty was 6.2%, and the larger fluctuations were not covered by this uncertainty value. Fig. 8 presents data obtained for the run 8 of the experiments. The bars were not added to Figs. 9 to 15 in order to simplify the visualization of the experimental results.

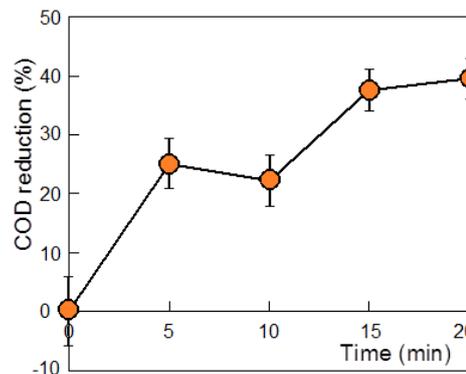


Fig. 8 Observed fluctuations of the mean COD value are larger than the experimental uncertainty. The figure present results of run 8 of the experiments

The residual ozone concentration in the liquid phase and in the off-gas was negligible for all the experiments, showing that the applied ozone was consumed in the column. The ozone transfer rate was 0.97 and 2.92 g/h for dosages of 5 and 15 mg/L, respectively. Consequently, the applied ozone dosages were the same for similar time intervals, allowing expecting monotonic COD removals. Figs. 9 and 10 show the evolution of the COD removal curves along time. The expected monotonic growing was in fact observed for runs 1, 4, and 10, but the whole set of results shows a higher number of runs with fluctuations superposed to the mean growth.

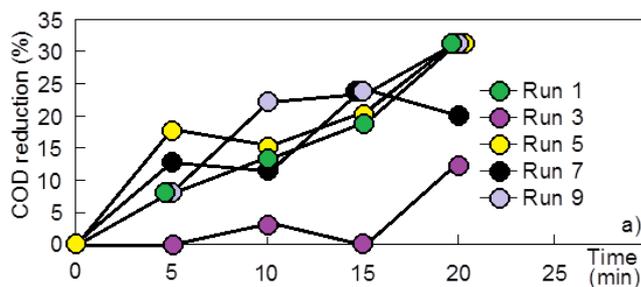


Fig. 9 COD runs with ozone dosage of 5 mg/L. Four runs show fluctuations

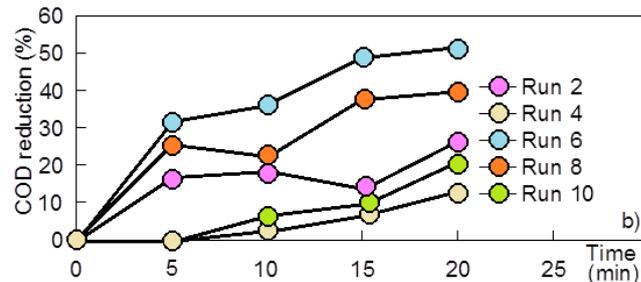


Fig. 10 COD runs with ozone dosage of 15 mg/L. Three runs show fluctuations

The experimental conditions were carefully controlled, allowing concluding that, for most of the present experimental conditions, the removal of COD was affected basically by the following two different mechanisms: 1) stripping of reactants and; 2) the effect of intermediate organic compounds formed from reactions with ozone, which hindered the monotonic increasing of the COD removal. This effect is named here shortly as “inhibition”

Considering the applied ozone and the consumed oxygen (as COD), a ratio of 1.5 is ideally obtained by stoichiometric equations (mol O₂/mol O₃). For the ratio expressed in mass (removed COD mass/applied ozone mass), an ideal value of 1.0 is attained when all organic matter is completely oxidized. Reference [15] obtained values between 0.4 and 2.5, considering the applied ozone dosage. Higher values of this ratio cannot be explained through direct reactions, being related to mechanisms like the stripping of reactants by the ascending bubbles or by effects of intermediary reactions. Figs. 11 and 12 show the ratio between the accumulated COD removed mass and the accumulated ozone applied mass. Fig. 11 shows a maximum peak of about 12 for run 5, occurring at 5 minutes. Runs 1, 7 and 9 show similar behavior, but with lower peak values. For this initial time intervals, the peaks were caused by stripping. The differences among runs may be related to different physical and chemical characteristics of the wastewater used in each run (the experiments were conducted in different days, and the wastewater was collected from the UASB reactor in each day). The same reason also explains the distinct behavior of run 3, which does not present an initial peak. For higher times, the ratio between the removed COD mass and the applied ozone mass attains mainly lower values.

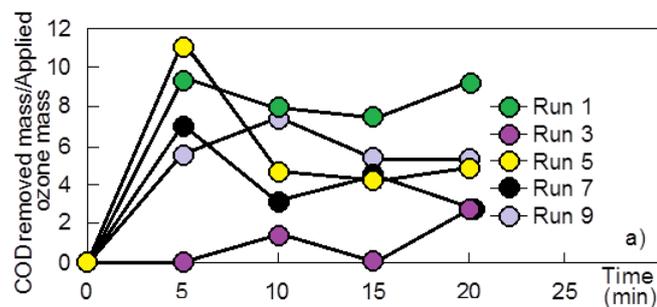


Fig. 11 The ratio between the COD reduced mass and the applied O₃ mass, for experiments with an ozone dosage of 5.0 mg/L and time of 20 minutes

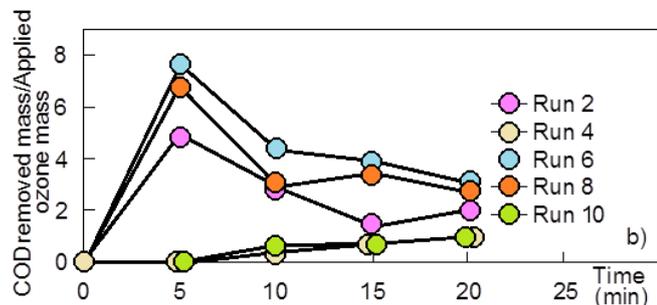


Fig. 12 Ratio between the COD reduced mass and the applied O₃ mass for experiments with an ozone dosage of 15.0 mg/L and time of 20 minutes

Similarly to Fig. 11, Fig. 12 also shows a maximum peak of about 8 for run 6, occurring also at 5 minutes. Runs 2 and 8 show similar behavior, but with lower peaks, while runs 4 and 10 do not show peaks. Also here these peaks at lower times were caused by stripping, and the differences

among runs may be related to distinct characteristics of the wastewater used in each experiment. The mass ratio values of Fig. 12 are in general lower than those of Fig. 11 due to the higher dosage of ozone applied in the experiments of Fig. 12. This is more visible at higher times.

For the analyses of accumulated masses, which used the consumed and the removed ozone masses during all the time of the experiment, the general trend of the ratio “COD removed/COD applied” is to decrease for higher ozonation times. On the other hand, considering the “short time” reduced and applied masses, the peaks do not decrease (see Figs. 13 and 14).

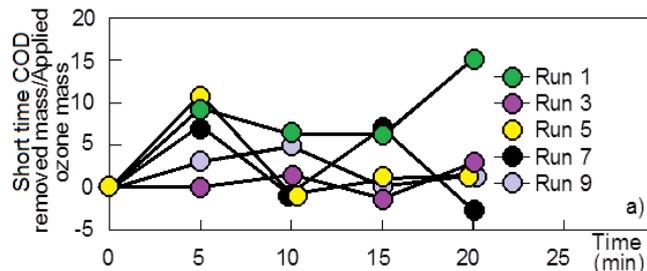


Fig. 13 Ratio between the short time COD reduced mass and the applied O₃ mass, for ozone dosage of 5.0 mg/L and time periods of 5 minutes

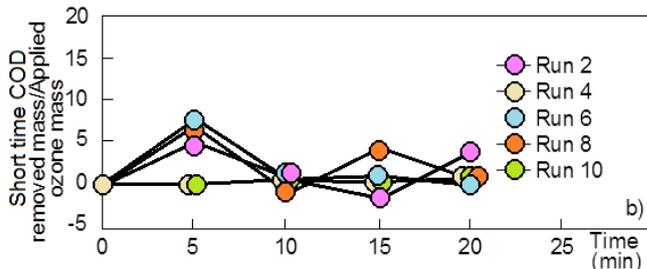


Fig. 14 Ratio between the short time COD reduced mass and the applied O₃ mass, for ozone dosage of 15.0 mg/L and time periods of 5 minutes

In the present runs, the “short time” values were calculated for the time interval between samples, that is, five minutes. The term “short time” was used instead of “instantaneous” values, in order to avoid confusion with the usual definition of “instantaneous” as $\Delta t \rightarrow 0$. As mentioned, in the present case, $\Delta t = 5$ minutes. The high values of the mass ratio for the higher contact times are not explained only by stripping, which affects this ratio mainly during the first minutes of the ozone application, carrying the volatile compounds. Thus, considering the situations where no stripping effects may be associated to the obtained data (higher times), the fluctuating behavior of the measured COD observed in Figs. 13 and 14 suggests that the aforementioned more subtle mechanism of intermediate compounds affected these results. That is, the intermediate compounds “forced” the observed fluctuations.

Ozone consumption is a result of the oxidation of organic matter present as intermediate compounds in the water, and which were formed by the decomposition of the original compounds of the wastewater. Although it is generally verified that this environment is mainly oxidizing, intermediate compounds formed during the ozone decomposition may be reductants [16, 17, 18]. Of course, the general mean trend of increasing COD removal with time is maintained, but the detailed behavior along time may present fluctuations, which, on their turn, may have relative

large amplitudes (occurring around the mean values). So, superposed to the general mean trend, COD may incidentally fluctuate, increasing as a consequence of the de-oxygenation of some compounds (the organic carbon AOS decreases), and decreasing with the oxidation of compounds by ozone (the organic carbon AOS increases). Such fluctuations were observed by different authors [6, 7]. As an example, [10] applied ozone to pulp mill effluent and mentioned that the observed COD variations resulted from variations in the oxidation state of the organic carbon and in the concentration of organic matter in the wastewater. The oxidation state is related to the presence of intermediate compounds, and the reactions with ozone or oxidant radicals modify the oxidation state of organic matter by modifying its chemical structure, or by adding/subtracting oxygen to/from its molecules. Reference [10] applied ozone to organic matter with high values of molecular mass, inducing its transformation into organic matter with lower values of molecular mass. It was shown that organic compounds with low molecular mass usually need more oxygen for its total oxidation, implying in higher COD values. From Equation (1) it is seen that, for a constant TOC value, higher AOS implies lower COD, and vice versa. The description of [10] agrees with the observations of the present study, so that a mathematical form to present these conclusions was searched. As already mentioned, stripping prevailed as the cause of COD removal during the first few minutes of the present experiments, with no significant observable contribution of oxidation by oxygen and ozone. Furthermore, a relationship between increasing AOS and decreasing COD was observed, and the fluctuating AOS values of runs 1, 7 and 8 are presented in Fig. 15.

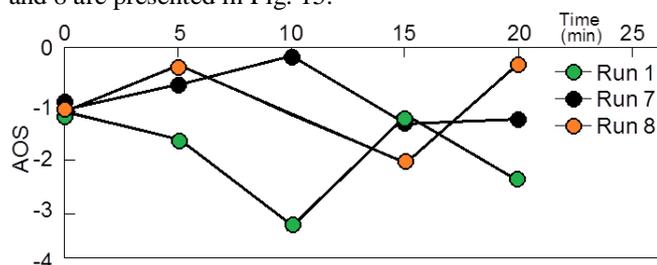


Fig. 15 Examples of AOS values calculated in the present study

Although the observed general fluctuating behavior occurs in different oxidation experiments, the literature does not furnish conclusive conceptual discussions or mathematical models that reproduce such oscillations. In this sense, a mathematical model that produces either monotonic or oscillating COD values along time, by the presence of intermediate organic compounds, is presented in the sequence.

IV. MATHEMATICAL MODEL

The fluctuating behavior of the normalized COD (represented by P and given in %) was analyzed considering the proposal of dependence between the COD and intermediate compounds. As concluded from the experimental observations, these compounds can “inhibit” the expected COD monotonic response along the contact time (Figs. 9 and 10), eventually forcing oscillations. As usual, restrictive hypotheses were introduced to simplify the analysis. As a first approximation, homogeneity of

concentrations is assumed, based on the experimental evidence that complete mixture is achieved quickly when compared to the total time of the experiments. In this case, the movement of the fluid is not relevant.

A number of intermediate organic compounds may inhibit the expected growing of the COD removal [23]. In this study, the effect of the compounds was considered as a whole, and the concentration of all of the compounds together was represented by I . (In this study I is taken as “mass of compounds/mass of the solution”, so that it is dimensionless).

The maximal theoretical efficiency of COD reduction (represented by $R=1-P$) is 100%, or $R=1$. In this case, no COD is measured, and $P=0$.

Two limiting conditions are initially considered: the absence of inhibitory intermediate compounds ($I=0$) and the absence of COD ($P=0$). These limiting conditions are then corrected to take I and P (different from zero) into account. Three main steps are detailed in the sequence, to clarify theoretical approaches.

1) When intermediate compounds are absent, the rate of temporal variation of R is proportional to P ; that is, the COD reduction efficiency is higher for higher values of the COD itself. In mathematical form:

$$dR/dt = K_1 P \quad (2)$$

or:

$$dP/dt = -K_1 P \quad (3)$$

K_1 is a positive coefficient which depends on the experimental conditions and t is the contact time.

2) If no COD is present ($P=0$), all oxidizable material is in fact oxidized by the ozone, eventually generating inhibitory compounds which accumulate in the liquid. Using the compound concentration I as an indicator of these reactions, a general way to express the rate of change of I is:

$$dI/dt = Z_1 I^n \quad (4)$$

Z_1 is a positive coefficient for increasing concentrations of the compounds. For a more general case, different oxidizable compounds may vanish during the reactions, showing that the value of Z_1 may change (that is Z_1 may be a function of time). The exponent n allows to vary the influence of I on its own generation rate, and in the simplest case I does not affect dI/dt , so that $n=0$. This was the situation considered here.

3) To correctly represent the inhibitory effects, Equation (3) (for P) and Equation (4) (for I) must be completed by adding to each of them a function involving the remaining variable (I and P , respectively). The effect must be opposite to the trend of the original equation (the signs of the added functions must be opposite to the original signs). Considering the isolated variables (I and P alone), it results in:

$$dP/dt = -K_1 P + K_2 I \quad (5)$$

$$dI/dt = Z_1 I^n - Z_2 P \quad (6)$$

K_2 and Z_2 are positive coefficients depending on the

experimental conditions. Equations. (5) and (6) form a set of coupled differential equations, which relate the normalized COD and the inhibitory compounds.

Using $n=0$, the following governing equations are obtained for I and P , respectively:

$$\frac{d^2 I}{dt^2} + K_1 \frac{dI}{dt} + K_2 Z_2 I = Z_1 K_1 + \frac{dZ_1}{dt} \quad (7)$$

$$\frac{d^2 P}{dt^2} + K_1 \frac{dP}{dt} + K_2 Z_2 P = Z_1 K_2 \quad (8)$$

Equations (7) and (8) show that Z_1 , which describes the formation of the intermediate compounds, generates forcing functions for I and P (given by the nonzero second member of the equations). The general solutions of Equations (6) and (7) are given, respectively, by:

$$I = C_1 \exp\left(\frac{-K_1 + \sqrt{K_1^2 - 4K_2 Z_2}}{2}\right)t + C_2 \exp\left(\frac{-K_1 - \sqrt{K_1^2 - 4K_2 Z_2}}{2}\right)t + I \text{ particular solution} \quad (9)$$

$$P = D_1 \exp\left(\frac{-K_1 + \sqrt{K_1^2 - 4K_2 Z_2}}{2}\right)t + D_2 \exp\left(\frac{-K_1 - \sqrt{K_1^2 - 4K_2 Z_2}}{2}\right)t + P \text{ particular solution} \quad (10)$$

C_1 and D_1 are integration constants. A monotonic growth, tending asymptotically to a constant value, would be the usual expected behavior of $R=1-P$. This is the case predicted by Equation (10) for $K_1^2 \geq 4K_2 Z_2$ and a convenient particular solution. Additionally, independently of the particular solutions, I and P present oscillations for $K_1^2 < 4K_2 Z_2$ (complex values of the square root); showing that the model contains the necessary information to reproduce the different observed behaviors. The particular solutions for I and P in Equations (9) and (10) depend on how Z_1 evolves with time, and are superimposed by the oscillations.

As an example, a situation with $K_1^2 < 4K_2 Z_2$ and $Z_1 = \alpha e^{-\lambda t}$ was considered. In this case, the following solution for $R=1-P$ is obtained:

$$R = 1 - e^{-\frac{K_1 t}{2}} [E_1 \sin(\lambda_1 t) + E_2 \cos(\lambda_1 t)] - \frac{K_2 \alpha}{\lambda^2 - K_1 \lambda + K_2 Z_2} e^{-\lambda t} \quad (11)$$

E_1 are integration constants and $\lambda_1 = \frac{\sqrt{4K_2 Z_2 - K_1^2}}{2}$. α and λ depend on experimental conditions. In any case, $R=0$ at $t=0$, so that $\frac{K_2 \alpha}{\lambda^2 - K_1 \lambda + K_2 Z_2} = 1 - E_2$, leading to:

$$R = 1 - e^{-\frac{K_1 t}{2}} [E_1 \sin(\lambda_1 t) + E_2 \cos(\lambda_1 t)] - (1 - E_2) e^{-\lambda t} \quad (12)$$

Equation (12) produces $R \rightarrow 1$ for $t \rightarrow \infty$ and $K_1 > 0$, being composed by a monotonic growing function (following the mean observed results, thus filling the usual expected behavior) superposed by an oscillatory movement (see Fig. 16). Equation (12) was generated to show the ability of the proposed model (Equations (9) and (10)) to reproduce the different behaviors observed in COD results of ozonization experiments. As illustration, Fig. 16 shows comparisons between observed and predicted values of the COD reduction for the runs 2 and 10, in which the mentioned ability is apparent. Although simple, the model involves a large number of constants (Equation (12), for example, involves 5 unknown constants). The predicted values of Figs. 16 and 17 were based on adjusted sets of constants, naturally dependent on experimental conditions. The constants may depend, for example, on parameters like alkalinity, pH, ozone dosage, molecular weight, the distribution of organic compounds, concentration of organic compounds, intermediate organic compounds, oxidizing radicals, contact time, mixing, gas transfer efficiency, radical scavengers, among others. So, the calculation of exact values of R as a function of t is still difficult. However, the exact values of the constants are not relevant in the present discussion, because, as already stressed, the objective was to link the fluctuating behavior of COD to the presence of intermediate compounds in the liquid through a mathematical model, and this objective was effectively attained. In this sense, Figs. 16 and 17 show that substantially different COD evolutions with time may be obtained using the same equation and different adjusted sets of constants.

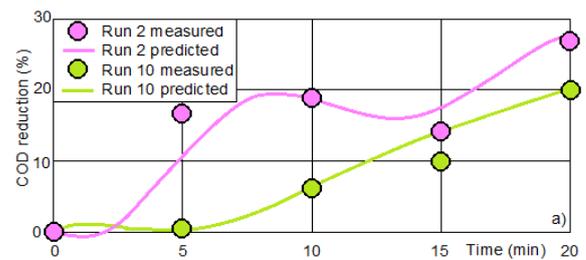


Fig. 16 Comparisons between measured and predicted values of the COD reduction (removal) as function of time. Run 2 shows fluctuations, while run 10 is monotonic. In both cases, the model follows the observed evolutions

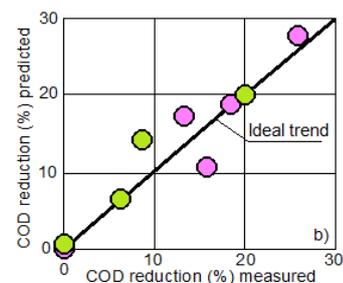


Fig. 17 Predicted values plotted versus measured values. The sets of adjusted constants are " $\lambda=0.012, K_1=0.12, E_1=0.07, E_2=0.05, \lambda_1=0.5$ ", and " $\lambda=0.015, K_1=0.46, E_1=-0.05, E_2=-0.08, \lambda_1=0.4$ ", for runs 2 and 10, respectively

Equation (10) shows that the values of the different constants (K_1 , K_2 and Z_2) determine if the behavior of P (and R) is monotonic or oscillatory. Also the damping of the fluctuations with time depends on these constants. The variety of behaviors observed in the present set of experiments, involving monotonic growth of R and fluctuations (Figs. 9 and 10) could be explained by the proposed model, based on inhibitory effects of intermediate compounds, suggesting its use. But, how to establish *a priori* values of the constants, in order to control the response of the column, is still an open question.

Fig. 18 shows the same data of Fig. 17, but taken as a whole to obtain the best regression equation and the related adjusting parameters. In the example, the regression equation is given by

$$COD R_{\text{Predicted}} = 1.04 COD R_{\text{Measured}} \quad (13)$$

presenting a proportionality coefficient of 1.04 (the ideal value is 1.0) and $R^2=0,91$, and providing a quantitative evaluation of the adequacy of the obtained predictions. R represents the reduction of COD, as defined in the mathematical model.

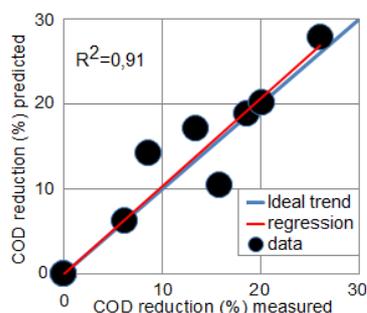


Fig. 18 Predicted and measured values showing the ideal trend and the obtained best adjusted equation

The high value of R^2 points to the adequacy of the prediction

V. CONCLUSIONS

Experimental fluctuating results obtained for the COD in an ozonization column were affected by different phenomena. In agreement with previous studies, stripping affected the measured removal of COD mainly during the initial times of the experiments. In this sense, the results showed peaks of COD removal caused by stripping that occurred 5 minutes after the beginning of the runs. The stripping is not evident for larger times, but fluctuations still occurred, suggesting that intermediate compounds interfered in the measured COD evolution. A theoretical discussion led to the proposition of a mathematical model linking the COD to the concentration of intermediate compounds. The results of the proposed model show that the predicted behavior of the COD with time may follow either monotonic or fluctuating patterns, in agreement with the experimental data. The mathematical model shows that the occurrence of different behaviors depends on values of constants included in this model, which are related to experimental conditions. The good agreement between predicted and observed trends for COD in wastewater treatment through oxidative procedures points to the adequacy of the present discussion and model, about the

effect of intermediate organic compounds on the COD results.

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