Removal of amoxicillin from processing wastewater by ozonation and UV-aided ozonation: kinetic and economic comparative study

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Abstract. A novel empirical and scaling up simulation study is presented for degradation and mineralization of real residue of amoxicillin (AMX) pharmaceutical formulation in wastewater. A set of UV-ozone-based experiments was used in the kinetics modeling of AMX, considering several chemical/photochemical mechanisms (direct ozonation, radical reactions, and photolysis). Finally, the modeling data was used for scaling up purposes, considering CAPEX and OPEX costs on the US Gulf Coast basis. In terms of experimental results, amoxicillin (AMX) pharmaceutical effluent was successfully degraded by ozone technology in high pH value. The semi-batch ozonation process was effective after 60-min treatment in all experimental conditions, producing degradation intermediates recalcitrant to the ozone oxidative process. From the bench-scale kinetics, scaling up simulations indicate that the smaller gain provided by adding a UV unit does not compensate for the increase in capital and operational costs of adding irradiation equipment, suggesting as the best cost-effective approach the application of direct ozonation.

Keywords: Advanced oxidation processes, ozone, pharmaceutical formulation, kinetic modeling, engineering economics.

1. Introduction

There is a particular concern about the presence and potential hazardous effects of emerging contaminants (EC) in the aquatic environment in the current days. EC are compounds whose presence in different environmental matrices has been not regulated. Pharmaceuticals are the most frequently detected EC in the aquatic environment compared to waste from other industrial areas such as food or metalworking industries (Bolong et al., 2009). From industrial wastewater, pharmaceutical concentration can be g L^{-1} order of magnitude. The use of ozone technology can degrade the structure of EC by attacking pharmaceuticals unsaturated hydrocarbon bonds. Ozone plus UV light produce rich oxidative radicals (•OH and $HO_2^\bullet$) in an aqueous environment, being radicals more effective than ozone itself. Moreover, in alkaline conditions, more O_3 may be transformed into •OH, and indirect oxidation of pharmaceutical compounds is more beneficial in the degradation process than direct oxidation of O_3.

We investigated the ozone application at elevated pH (with and without UV-C) for the degradation and mineralization of amoxicillin molecules in water in a gas-liquid reactor system. Expired amoxicillin formulation was aimed to be used throughout the project to provide the degradation of industrial and household pharmaceutical residues. Kinetics modeling, reactor scaling-up, and economic considerations complete the ozone-based AOP experimental study, providing novelties to the AOP scientific literature.

2. Experimental and Numerical Methods

2.1. Reagents

The water used for chemical analysis and the chemical processes was purified with a Merck Milli-Q Direct 8 system. All the reagents were provided at analytical grade (Sigma-Aldrich). The powder of AMX pharmaceutical formulation used in the effluent was with the expiry date in Jan. 2019. The AMX wastewater was prepared by solubilization of 1.5000 g of amoxicillin pharmaceutical formulation in 3.00 L calibrated flask, completing the volume with Type III water (ASTM D1193-91). The AMX calibration curve was carried out with ultrapure amoxicillin trihydrate VENTRANAL® (Sigma-Aldrich).

2.2. Chemical Analyses

The AMX analysis was performed according to Saleh (1996). The volume of each calibrated flask was completed with 1-propanol. The absorbance was measured at 395 nm against a blank solution with a

Thermo Fisher Genesys 10S UV-Vis spectrophotometer. The blank was carried out with all reagents except AMX. Total Organic Carbon (TOC) analysis was performed according to the combustion catalytic oxidation method (Curiale, 2017), under an O_2 atmosphere (99.9995% synthetic air by IBG Co.). The analyses were performed with a non-dispersive infrared detector (NDIR). Total Nitrogen (TN) analysis was performed according to the chemiluminescence method in a TNM-L Shimadzu equipment coupled with the TOC-L apparatus. Non-Purgeable Organic Carbon (NPOC) was carried out pretreating the samples with HCl solution followed by injection of ultrapure synthetic air before the sample injection into the high-temperature oven.

2.3. Bench-scale Wastewater Treatment Apparatus and Experimental Investigation

Three-liter amoxicillin pharmaceutical formulation wastewater was ozonated in a PVC tank column in a semi-batch mode wherein the O_3+O_2 was continuously sparged at a rate of up to 1.0 L min^{-1}. The gas was sparged through a sintered glass dispersion cylinder with a dimension of 15×20 mm. A corona discharge bench-scale ozone generator produced ozone with a maximum capacity of 3.0 g h^{-1} O_3 (O&L3.0 RM Ozone&Life). The O_3 generator was fed with oxygen gas >90% purity. The reaction system temperature was set at (20.0±0.5) °C (thermostatic bath by SL-152 Solab equipment). NaOH and H_2SO_4 were used to adjust the pH. The effluent was recirculated in the system for 120 min. The aliquots were taken in predetermined intervals. No buffer was used to control the reaction pH, but only NaOH and H_2SO_4 (which cause no UV interference in the reaction medium). Figure 1 shows the experimental setup.

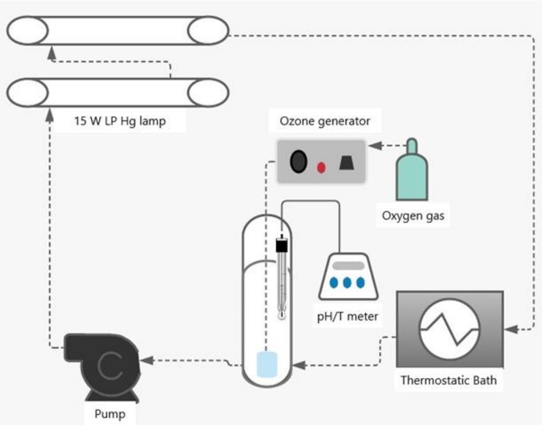

Figure 1. Semi-batch ozone-based advanced oxidation process diagram for the degradation of AMX in pharmaceutical formulation wastewater.

2.4. Kinetic Modelling

The experimentally-measured AMX concentration data were fit numerically to a simplified kinetic model (Equations 1-4) using nonlinear least-squares (LSQ) optimization, considering the experimental arrangement shown in Figure 1 in a data analysis software (Origin 2020, OriginLab Co.).

$$AMX + O_3^* \xrightarrow{k_1} \text{Degradation products} \tag{1}$$

$$AMX + UV \xrightarrow{k_2} \text{Degradation products} \tag{2}$$

$$O_3 + UV \xrightarrow{k_3} PGROS \tag{3}$$

$$AMX + PGROS \xrightarrow{k_4} \text{Degradation products} \tag{4}$$

In this simplified system, O_3^* refers to ozone and the reactive oxygen species that result from its reactions in a high-pH aqueous environment (Gurol and Akata, 1996). PGROS in Equations 3 and 4 refer to photochemically generated reactive oxygen species, i.e., the additional reactive species that were produced in the reaction medium due to the interaction between O_3 and related oxygen species and UV irradiation. Experimental data on the concentration of AMX over time for different reaction conditions (*e.g.*, with ozone feed only, with irradiation only, and with both ozone supply and UV irradiation) were used to extract the relevant apparent kinetic parameters (k_1, k_2, and k_4, respectively). Simulations using extracted kinetic data were carried out in a numerical software package (Matlab 2015a, Mathworks Inc.).

2.5. Scaling-up and economic considerations

The comparison between the three processes (ozonation, UV photolysis, and Ozone/UV) was based on performance evaluation and economic considerations. Equipment sizing was evaluated for three different plant operation regimes: one-, two- and three-shift systems. For estimation purposes, each shift was considered an 8-hour day carried out by a single operator. Thus, in our scenarios, operating in two- or three-shift systems requires adding one or two additional plant operators. Additionally, considering the bench system's typical conversion efficiency, our scenarios simulated the possibilities of carrying out the shift load in one, two, or three batches. According to typical industrial targets and legislation requirements, a target conversion of 80% of the initial antibiotic concentration was set (Martins, 1976). The target processing throughput was fixed at 10 m^3 per day, within small-scale pharmaceutical processing plants (Gadipelly et al., 2014). Capital and operational costs were estimated according to suitable estimation methodologies (Towler and Sinnott 2013). The equipment was sized using suitable estimating methods. Labor costs were calculated from official (BLS) data (BLS, 2019b), and the remaining fixed costs were estimated using factors from ISBL, OSBL, and labor costs, wherever appropriate.

3. Results and Discussion

Regarding the water matrix, most studies of degradation of pharmaceutical compounds by advanced oxidation processes deal with a standard analytical compound dissolved in ultrapure water, while real effluents or pharmaceutical formulation residues have received less attention. Our work differs substantially from most papers from the literature since it is intended to degrade expired pharmaceutical formulation containing amoxicillin. Moreover, the experimental data of AOP AMX degradation (Figure 2) was used as a base for kinetic modeling and engineering economics for scaling-up purposes. Preliminary studies by the research group were also carried out in an acid medium (pH 3 and 5). However, in a basic medium, amoxicillin is more soluble, and no precipitate was observed. All considerations in the present study are based on experiments at basic-pH values (Figure 2).

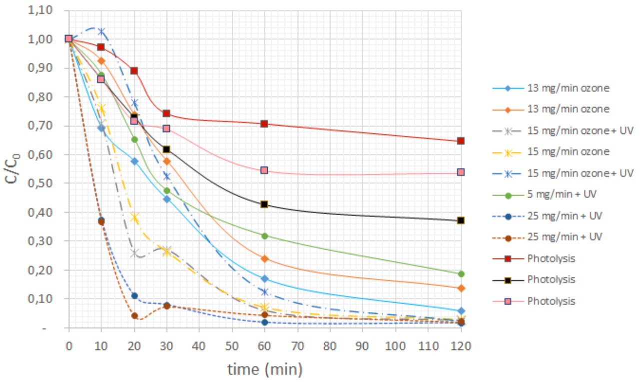

Figure 2. Normalized AMX concentration (C/C_0) abatement kinetics for photolytic (30-watt UV) and non-photolytic processes. pH 13.00 in all experiments. LP-Hg lamps (254 nm). Ozone doses at 5.0, 13.0, 15.0, and 25.0 mg min^{-1}.

Ozone has a high oxidizing ability that can oxidize several recalcitrant organic pollutants. During the production of ozone, hydroxyl radicals, superoxide radicals, and hydroperoxide radicals can be formed by chain reactions (Ma et al., 2005). Among radicals, hydroxyl radicals are the most effective for the degradation of organic pollutants and are more beneficial in the degradation of AMX than direct oxidation of O_3. In alkaline conditions (Figure 2), more O_3 may be transformed into •OH, and indirect oxidation is the main path. The ozone concentration has an important influence on the degradation of AMX. In fact, according to the data shown in Figure 2, ozone concentration is the main parameter of AMX degradation. The mass transfer rate and the volumetric mass transfer coefficient of ozone increase with ozone concentration. More ozone can be absorbed and reacts with AMX molecules, finally improving the decomposition of antibiotics. In terms of chemical mechanisms in the AMX degradation, the UV process (Figure 2) involved in the direct photolysis of AMX molecules and generation of additional •OH by O_3 is marginal. The pharmaceutical formulation contains various inert substances that absorb most of the UV emitted by the LP Hg lamps. In an experiment carried out at pH 13, ozone mass-rate of 15 mg min^{-1}, and C_0=125.10 mg L^{-1} of AMX, there was mineralization of 10% by TOC and 14% by NPOC. TN achieved no mineralization. In another experiment carried out at pH 13, ozone mass-rate of 15 mg min^{-1}, and C_0=95.09 mg L^{-1} of AMX, there was a 3% mineralization by TOC and 16% by NPOC. Again, no mineralization was achieved by TN. With higher ozone mass-rate (25 mg min^{-1}), 30-watt UV emission, and C_0=32.76 mg L^{-1} of AMX, there was mineralization of 46% by TOC and 38% by NPOC. Even with a higher ozone mass-rate, no nitrogen mineralization was observed. The TN measurements indicate no formation of nitrogen (N_2) and ammonium (NH_3). Both N_2 and NH_3 species can escape from the liquid phase as gases, even more, when other gases (O_2 and O_3) are continuously sparged.

3.1. Kinetic modeling

The extracted kinetic data are presented in Table 1, with the respective correlation coefficient. k_1 and k_4 are presented as first-order constants (k_1^* and k_4^*), adopting a pseudo-first-order approximation for both the ozone and the reactive oxygen species concentrations. This approach can be explained by the constant and abundant input of ozone and by the fast reactivity of the radicals, respectively. As can be seen from Table 1, the combination of ozone and UV irradiation promoted a synergistic effect, more than doubling the apparent reaction rate constant at the photochemical reactor ($1.92 \rightarrow 3.21 \times 10^{-1}\ min^{-1}$).

Table 1. Apparent First-order Rate Constants.

Rate constant	Value (min^{-1})	R^2
k_1^*	$(4.63 \pm 0.74) \times 10^{-2}$	0.9556
k_2	$(1.92 \pm 0.25) \times 10^{-1}$	0.9147
k_4^*	$(3.21 \pm 0.34) \times 10^{-1}$	0.9442

3.2. Scaling up

Figure 3 shows the impact of *f(UV)* on the CAPEX and OPEX for the three-shift systems (1S, 2S, 3S) with one to four operation batches (1B, 2B, 3B, 4B) per shift.

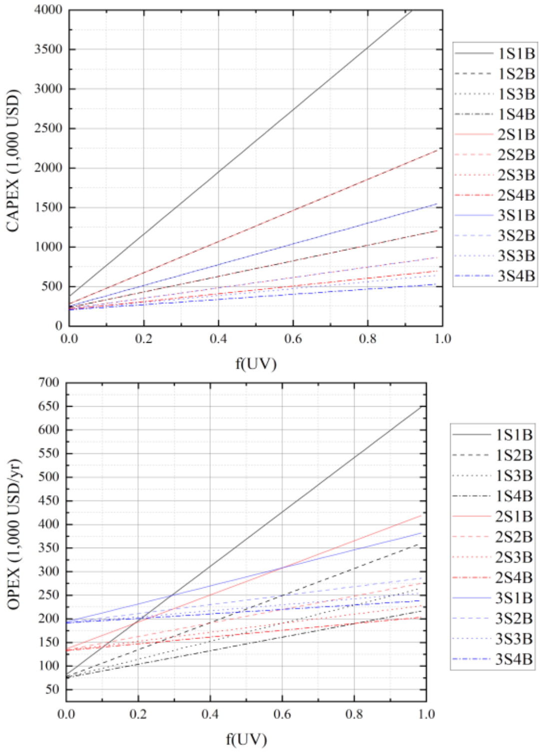

Figure 3. CAPEX (*top*) and OPEX *(bottom)* cost as functions of the weight of the photochemical component of the AOP plant. *S* refers to a shift *system* (one, two, or three 8-hour shifts per day), and *B* refers to the number of batches into which the treatment load is divided per shift.

CAPEX costs can be reduced by 10-fold just by changing the operation system: this results from the possibility of using smaller (and cheaper) equipment when the daily throughput can be processed in more batches. An analysis of CAPEX and OPEX curves (Figure 3) indicates that operation in 4 batches is the most cost-effective. Based on this preliminary cost analysis and supported by our experimental evidence that has shown that ozonation alone (Figure 2) is sufficient to achieve a desirable mineralization degree (~40%), the most cost-effective course of action for scaling up the AMX degradation process is adopting a 4-batch single-shift operation regime without any UV reactor. Table 2 summarizes the costs and equipment sizing required in this condition.

Table 2. Detailed Cost Estimation and Operation Parameters.

Equipment	**Sizing**	**CAPEX**	**OPEX**
Ozone generator	800 g h^{-1}	15,720	934
Ozonation tank	2.5 m^3	17,300	
H_2SO_4 tank	2.0 m^3	7,490	656
NaOH tank	4.5 m^3	11,460	4,080
ISBL factors			
Equipment erection	0.3	15,850	
Piping	0.8	42,230	
I&C	0.3	15,850	
Electrical	0.2	10,560	
Civil	0.3	15,840	
OSBL expenses		15,310	
Engineering costs		50,510	
Contingency reserve		16,840	
Fixed costs			69,570
Variable costs			57,880
Expected batch time		44 min	
Cleaning / Idle time		3 h day^{-1}	

4. Conclusions

From the chemistry point of view, effective degradation of amoxicillin and a high degree of wastewater mineralization were achieved using UV-O_3-based advanced oxidation technology. The mechanistic assessment revealed that organic-nitrogen heteroatom was not mineralized into N_2 and NH_3. CAPEX and OPEX analysis indicated that ~44 min of treatment is necessary to achieve the minimum requirements from the Sao Paulo state legislation (Brazil), considering a 4-batch operation in three labor shift system for 10 m^3 of effluent per day. Considering the efficiency of ozonation at high pH, the energy consumption, and lamp replacement cost, the best option for scaling up is to avoid a system with a UV reactor, relying on an ozone generator.

Acknowledgments

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