Applied Chemical Engineering (2022) Volume 5 Issue 2
doi:10.24294/ace.v5i2.1646

CASE REPORT

Reduction of COD and TOC concentration in pharmaceutical wastewater using Fe^{2+} catalyzed ozone: Full-scale case study

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ABSTRACT

This work was carried out to improve the performance of an ozonation system used for wastewater treatment in a pharmaceutical industry. In order to improve the mineralization of organic matter, ferrous sulfate was applied as a catalyst to the reaction system. After this, the pH of the water was adjusted to 8.5–10, so that the process is carried out under alkaline conditions. Finally, O_3 was injected through a Venturi tube in order to improve the mass exchange between gas and water. Preliminary operating data indicate that the treatment system achieves chemical oxygen demand (COD) removals of less than 10%. The tests were conducted at full scale and the water quality variables were analyzed at different reaction times. It was determined that for an ozone dose equal to 10 g/h and 10 mg/L Fe^{2+} and an initial water pH equal to 9, 4.5 hours were required to achieve a reduction of 30.73% COD and 36.85% total organic carbon (TOC). The results obtained with an initial pH higher than 9.5 indicate that the effectiveness of the process is reduced, a fact that may be caused by the rapid formation of insoluble $Fe(OH)_3$, which decreases the availability of the catalyst for the formation of OH^* radicals in the water.

Keywords: Ozone; Advanced Oxidation Processes; Catalyst; COD; TOC; Pharmaceutical Wastewater

ARTICLE INFO

Received: 20 August 2022
Accepted: 9 October 2022
Available online: 16 October 2022

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1. Introduction

The pollution of freshwater, coupled with the increasing demand for clean water, gives rise to serious problems for humanity. In turn, population growth is the cause of the increasing contamination of freshwater. Moreover, the consumption of water without adequate treatment causes the death of thousands of people worldwide[1]. There are multiple sources of water pollution, among them we can point out domestic, industrial, agricultural and livestock wastewater, in addition to the increase in industrial production.

The development of new product categories has transformed industrial production processes, thereby the condition of wastewater generated by industry is more complex[2]. Within the category of new products, we can mention pharmaceutical compounds, which play an important role in the quality and life expectancy of mankind[3]. The release of pharmaceuticals into the environment is an ecotoxicological issue, since they are substances designed to induce biological reactions[4]. The presence of these compounds in water has two main sources, the manufacture of pharmaceuticals and their common use, which is reflected in domestic, agricultural, livestock and hospital wastewater[3].

Pharmaceutical companies constantly produce a wide variety of organic products with complex structures and low biodegradability. In addition, the manufacturing processes of these substances are carried out in batches, which results in wastewater with complex composition and strong fluctuations in the concentration of pollutants[5]. The low biodegradability of these products causes wastewaters containing them to have low BOD values and high COD values, which is a drawback for the biological treatment of such waters, since recalcitrant chemical compounds can restrict the activity of microorganisms[6]. Thus, wastewater generated by pharmaceutical companies tends to be refractory to most conventional physical, chemical and biological treatment techniques. Therefore, it is necessary to search for treatment alternatives aimed at generating strongly oxidizing conditions at ambient conditions to achieve the breakdown and subsequent mineralization of dissolved organic contaminants[2].

In order to achieve the above conditions, advanced oxidation processes (AOP) represent an alternative that allows the mineralization of recalcitrant organic compounds present in wastewater by the action of OH^* radicals, which have high oxidizing power and are not selective[7]. AOPs make use of Fenton's reagent, hydrogen peroxide, ozone and photocatalysis to produce OH^* radicals. These reagents can be employed in the presence of ultraviolet (UV) light, catalysts and ultrasound to accelerate and intensify AOPs, which can be mainly classified into four groups: (i) photocatalytic processes (H_2O_2/UV, O_3/H_2O_2/UV, UV/TiO_2, H_2O_2/TiO_2/UV, O_3/TiO_2/UV); (ii) Fenton reagent-based processes (Fe^{2+}/H_2O_2, Fe^{2+}/H_2O_2/UV, electrofenton); (iii) ozone-based processes (O_3/UV, O_3/H_2O_2, O_3/Fe^{2+}, O_3/metal oxide as catalyst, O_3/activated carbon, O_3/ultrasound); (iv) other processes involving persulfate and ionizing radiation[7].

The popularity of using ozone for wastewater treatment has increased in recent decades because its production costs have decreased and it does not generate dissolved ions after application and decomposition. Commercial ozone generation technologies are based on corona discharge to a dry gas stream (O_2 or air). The mode of pollutant degradation can occur by two routes: direct electrophilic attack by molecular ozone and indirect attack by OH^* radicals generated through ozone decomposition reactions in water. In this regard, although it has been observed that increasing the ozone dose increases the degradation rate of some pollutants, this effect is not noticeable in the degradation of recalcitrant pollutants[7].

Some of the benefits of using ozone for wastewater treatment include the reduction of the amount of sludge generated and the removal of persistent pollutants. Similar to the Fenton reaction, the addition of a catalyst to the ozonation process promotes the decomposition of the oxidant (O_3) to generate active free radicals, such as OH^*. Thus, when compared to other ozonation processes, catalytic ozonation can reduce operating costs by not incurring other energy costs (UV radiation). Likewise, in most cases, catalytic ozonation has shown better performance in pollutant mineralization than sisal ozonation[8,9].

In order to increase the reactivity of O_3 with saturated bonds of organic matter molecules, the decomposition of this should be sought to form OH^* radicals by reaction with OH ions[10–12], i.e., the pH of the water should be alkaline. In addition, to decompose O_3 and increase the generation of OH^* radicals, ferrous sulfate should be used, since this allows Fe^{2+} to act as a catalyst and thus achieve a better performance of ozone as an oxidizing agent for the organic matter in the water.

Similarly, an aspect of special interest in volatile organic products (VOP) using ozone is the mass transfer of the gaseous stream (air/O_3 mixture) that injected into the water. In this case study, a Venturi tube was used to inject ozone into the throat of the tube, where, due to the reduction of the flow area, the pressure drop and the increase in water velocity generate the suction of the gas. Once the air/O_3 mixture is injected, the considerable turbulence and flow pressure recovery allow for increased mass transfer. The suction point in the Venturi was also used for dosing the catalyst.

2. Materials and methods

The project was carried out at the facilities of a pharmaceutical company located in the department of Cundinamarca, Colombia. The tests were carried out at full scale, in a cylindrical tank (1.8 m diameter and 2.4 m useful height) with a capacity of 6.1 m^3. In this company, domestic and industrial wastewater are treated separately. The industrial wastewater is received in a homogenization tank with mechanical agitation. The water is then clarified in a high-rate coagulation, flocculation, and sedimentation system. The clarified water is then introduced into the oxidation tank mentioned above. In the oxidation tank, ozone is added to the water, using a corona-effect ozone generator (Flygoo Eco-Technologies) and a compressor that allows the air/ozone mixture to enter through the bottom of the tank and react with the organic matter. The operation of the ozone oxidation tank and the entire treatment system is carried out in batches.

Table 1. Conditions under which each of the tests was carried out

Day	Initial pH of water	Fe^{2+} dosage (mg/L)	O_3 dosage (g/h)	Volume of water treated (m^3)	Reaction time (hours)
1	8.5	5	10	6.1	3.5
2	9.0	5	10	6.1	4.5
3	9.0	10	10	6.1	2
4	9.5	10	10	6.1	5
5	10.0	10	10	3.05	4

Based on the results obtained at the time of this project, the oxidation system was only able to remove 10% of the COD. Therefore, the following modifications were made. First, a 745.7 W pump was installed, which sucks water from the bottom of the oxidation tank. At the outlet of the pump, a Venturi tube was installed with a 1-inch diameter inlet and a 0.5-inch reduction at the throat. Subsequently, the water is returned to the bottom of the tank and distributed through perforated pipes. The pressure drop in the Venturi was used to inject ozone into the process. Thus, the turbulence in the Venturi throat causes the increase in velocity and the pressure in the pipe favors the dilution of the ozone in the water. In addition, the return of water through the bottom of the tank improves the O_3/water mass transfer[13]. The characteristics of the full-scale tests are presented in **Table 1**.

The source of Fe^{2+} to catalyze the process was ferrous sulfate with 95% purity. The analyses of pH, conductivity, COD and TOC were performed according to the protocols established in the standard methods for the analysis of drinking water and wastewater. The project was developed with the purpose of evaluating catalytic ozonation and improving the mineralization of organic matter present in the wastewater in terms of COD and TOC. Throughout each test, samples were taken every 1 h of reaction in order to analyze the kinetic trend of the process that achieved the highest COD and TOC concentration reduction effectiveness.

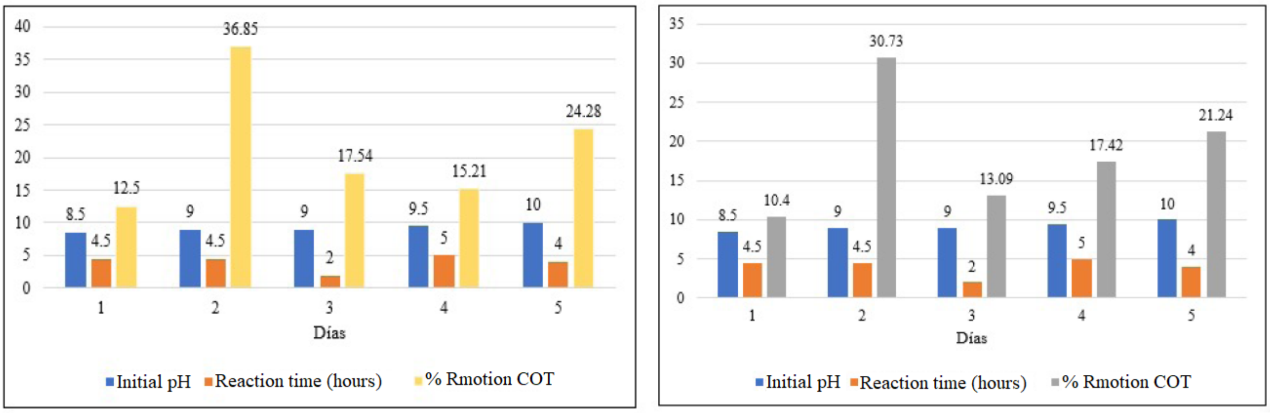
3. Results and discussion

The tests were performed at full scale for a period of 5 days. **Table 2** shows the results obtained in each test performed.

Table 2. Experimental results

Day	Initial pH	Reaction time (hours)	Initial COD (mg/L)	Initial TOC (mg/L)	Final pH	Final COD (mg/L)	Final TOC (mg/L)
1	8.5	4.5	404.00	115.42	8.1	362.00	101.00
2	9.0	4.5	423.00	130.85	8.6	293.00	82.64
3	9.0	2	359.00	102.10	8.6	312.00	84.19
4	9.5	5	333.00	102.00	8.7	275.00	86.49
5	10.0	4	457.70	148.70	9.7	360.50	112.60

The reaction times are different in some tests due to plant operating conditions. Nevertheless, this situation is useful to analyze the influence of the reaction time and therefore the ozone dose applied on the process. **Table 2** shows that the initial concentration was variable; therefore, the analysis of results was performed in terms of percentage of COD and TOC removal. However, it is also observed that the pH of the water decreases, which may be caused by the formation of oxidized organic species (organic acids) and by the formation and dilution of CO_2 in the water as a result of the complete mineralization of organic matter. The reduction of TOC in all tests confirms the mineralization of a portion of the organic matter present in the wastewater. **Figure 1** shows the COD and TOC removal percentages achieved in each experiment.



(a) (b)

Figure 1. Removal percentages achieved in the COD (**a**) and TOC (**b**) tests.

When comparing the results of the tests with the same retention time (day 1 and 2), it is observed that when the initial pH of the water is 9, greater removal is achieved for COD (30.71%) and TOC (36.8%), which is explained by the greater presence of OH^- ions to promote the formation of OH^* radicals as an effect of the decomposition reactions of O_3. On the other hand, if the results of day 2 and day 5 are compared, which were carried out with similar retention times, it can be seen that the removal at initial pH 9 is higher than that at initial pH 10. The conditions for this last test vary, since the volume of water treated was 3.05 m^3, with a reaction time of 0.5 hours more. Thus, the ozone dose was higher in this test, although the removal of COD and TOC was lower. This situation can be explained by the fact that the catalyst (Fe^{2+}) is oxidized to Fe_3+, and for such a high pH value (10), the concentration of OH ions is high enough to rapidly form $Fe(OH)_3$, thus reducing the amount of catalyst available for the reaction and decreasing the rate of formation of the OH^* radicals necessary for the complete oxidation of the organic matter. The same occurs when comparing the results of the tests on days 2 and 4, since the initial pH value in the test on day 5 is slightly higher than for day 2, although the reaction time is 0.5 hours longer. Thus, it is possible to explain the reduction in the effectiveness of the process due to the effect of $Fe(OH)_3$ formation and the reduction in the amount of catalyst. Based on the above, the highest COD and TOC removal is achieved for an initial pH of 9, 10 mg/L catalyst dose and 10 g/h O_3 dose (day 2 trial). The COD and TOC concentration results obtained for this test as a function of time are presented in **Table 3**.

Table 3. Variation of COD and TOC concentration over time for the test carried out on day 2

Time (hours)	COD (mg/L)	TOC (mg/L)
0	423.00	130.85
1	398.00	106.85
2	364.00	97.30
3	342.00	88.40
4.5	293.00	82.64

Regarding COD removal, the experimental data generally fit the first order kinetics[14,15], since the ozone dose is constant and it is assumed that the concentration of ozone in the water is also constant; that is, the rate of COD reduction depends on the concentration of this parameter in the water and the reaction time. In this regard, the statistical adjustment of the data indicates that the kinetic coefficient takes a value with a correlation coefficient R^2 equal to 0.9905. In the case of TOC, the second-order kinetic model achieved the highest correlation (R_2 = 0.9525) and a kinetic coefficient. From the above, it can be inferred that the mineralization of organic matter by Fe^{2+} catalyzed ozonation depends on at least two variables: pH and TOC concentration in the water when the ozone and catalyst doses are constant. Accordingly, the equations for determining the COD and TOC concentration as a function of time for the catalytic ozonation process analyzed are:

$$COD = COD_O * e^{-(0.08119\,h^{-1} * t)} \tag{1}$$

$$\frac{1}{TOC} = \frac{1}{TOC_O} - 0.0009714\frac{L}{mg * h} * t \tag{2}$$

In the above equations, COD and TOC are the concentrations (mg/L) of each of these parameters at any instant of the reaction, COD_o and TOC_o the concentration (mg/L) at the start of the reaction and *t* the reaction time (expressed in hours). These two equations are valid for the pH, ozone dose and catalyst conditions employed, assuming that the ozone concentration in the water is constant because the application rate is equally constant.

Finally, when contrasting the removal values achieved throughout the experimental phase with the preliminary operating data of the treatment system, it is observed that the system went from having COD removals of less than 10% to achieving a removal of 30.73% and similar TOC removal values, which indicates the complete mineralization of the organic matter present in the water. In other words, the results obtained show that ozonation catalyzed by Fe^{2+} allows achieving greater mineralization of organic matter compared to direct ozonation.

On the other hand, and in relation to the ozone application mode, the injection system through the Venturi throat represents an effective alternative in terms of energy consumption and O_3/water mass transfer, since instead of making use of the ozone generator and a compressor for ozone dosing to water, the proposed system uses the ozone generator and a pump that allows to simultaneously perform the mixing and dilution of the oxidizing agent in the water, as well as to carry out the agitation of the contents of the oxidation tank.

4. Conclusions

For the operating conditions analyzed, it was determined that it is possible to achieve up to 30.76% COD removal and 36.85% TOC removal in a period of 4.5 hours of oxidation for an initial wastewater pH equal to 9, a catalyst dose of 10 mg/L Fe^{2+} and 10 g/h of O_3. However, it is desirable to explore the effect of increasing the O_3 dosage to reduce the reaction time and thus avoid the accumulation of wastewater in the homogenization tank or the installation of additional tanks to complete the reduction of COD and TOC concentration.

Throughout the tests carried out, no sludge formation was observed, although a slight change in the color of the water caused by the catalyst dose was observed. This suggests that in addition to increasing the ozone dose, it is advisable to reduce the catalyst dose to eliminate this problem or, alternatively, to pass the water through a decantation system and then filter the water to eliminate the $Fe(OH)_3$. At a pH above 9.5, the catalyst loses effectiveness. It is possibly due to the rapid formation of $Fe(OH)_3$, which reduces the rate of production of OH^* radicals by the decomposition of O_3.

Conflict of interest

The authors declare no conflict of interest.

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