Linear Alkylbenzene Sulfonate Removal by Oxidative Ozonation Coupled with UV/H2O2 Oxidative Process

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Abstract — In this study, the results of the application of advanced oxidative processes to remove linear alkylbenzene sulfonate (LAS) from wastewater produced in the laundry industry are presented. Photocatalysis with UV radiation and oxygen peroxide (H2O2) was applied followed by ozonation (O3). LAS removal was higher than 90% in the first 60 min. H2O2 application based on COD reached its most effective concentration for the rate of [1:2.5] with O3 acting as a polishing agent. Excessive foam formation caused by the bubbling effect led to the necessity of introducing a lag into the process, retarding the O3 application in 30 min. Therefore, complete oxidation was achieved with a low concentration of LAS, and no foam was observed by the end of the process. The best COD removal results were achieved when low doses of H2O2 were applied. Using UV/H2O2/O3, 51.2% removal was achieved.

Keywords — Advanced Oxidative Processes, Laundry Industry Wastewater, Linear Alkylbenzene Sulfonate, Ozonation.

I. INTRODUCTION

Emerging contaminants are a diversity of synthetic or natural compounds that can be found in environmental matrices. These chemicals, such as medicaments, personal care, and cleaning products, pesticides, surfactants and microplastics, are part of the sanitary effluent composition and, when not removed, can have harmful effects on human health and the environment [1].

Laundry wastewater has large organic molecules in its composition called surfactants. They are responsible for the formation of foam in wastewater treatment plants and in river waters. The main component used in the synthesis of surfactants is linear alkylbenzene sulfonate (LAS), an anionic biodegradable compound. Despite biodegradability, the excessive use of this product has enhanced the concentration of surfactants in wastewaters, principally in those from laundry industries and in surface waterbodies, because of untreated liquid wastes released into the environment [2].

The structural complexity of commercially available LAS makes it difficult to assess the toxicoology of individual components that cause detrimental effects on aquatic fauna and flora. These effects are dissolved oxygen depletion caused by increased surface tension in the air/water interface; absence of light permeability due to suspended particles; increase in xenobiotic compounds such as PCBs and PAHs existing in sediments by micellar solubilization that inhibits its degradation [2].

Industrial wastewaters constituted by toxic or refractory compounds, such as LAS, have to be submitted to a specific treatment because of their difficult characterization, which can make biological conventional processes unfeasible [3]. As an interesting alternative, Advanced oxidation processes (AOPs) are an available technology whose objective is to transform organic contaminants in final products such as CO2, H2O and organic anions by means of degradation reactions that include temporary oxidant species, mainly hydroxyl radicals [4]. In addition, AOPs are considered clean nonselective processes and can react in aqueous or gassy environments as well as be adsorbed on a solid matrix [3].

The objective of this work was to study photolysis with UV, photocatalysis with UV/H2O2 and catalytic ozonation with UV/H2O2/O3 to verify the process efficiency in the removal of anionic surfactants such as LAS from laundry industry wastewater. A kinetic assessment was also made to determine the best conditions of operation in terms of catalyst concentrations and sequence and delay of O3 application to avoid the formation of excessive foam.

II. MATERIALS AND METHODS

A. Experimental System

The system was composed of a 305 mL batch reactor with a UV lamp (low-pressure, mercury, Osram, 15 W) in its central axis, a recycling reservoir, a pump (Sarlo Better, 100 Lph), and an ozone generator (Vigor, 400 mgph). Fig. 1 shows the system used in this study.

Fig. 1. Bench-scale system.

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B. Sampling and Analysis

Raw wastewater was constituted by a 10 L sample taken from a laundry industry. The sample was centrifuged to remove any suspended matter that could interfere with the analysis. After this preliminary treatment, analysis was performed according to methods detailed in APHA [5].

Souza et al. [6] treated hospital laundry wastewater by applying H2O2 as a function of COD in the following ratios [COD]:[H2O2]: high catalyst concentration [1:5.0], medium catalyst concentration [1:2.5] and low catalyst concentration [1:0.5]. The same ratios [COD]:[H2O2] applied by Souza and collaborators [6] for high and medium catalyst concentrations were used in this study. However, a low concentration was fixed at [1:0.3] to optimize catalyst addition.

Messias et al. [7] observed foam formation in the first 10 minutes of application of O2 due to the rapid degradation of effluent into carbon dioxide (CO2). As was also observed in experiments, two scenarios were studied: in the first scenario, O2 was applied from the beginning along with the catalyst, and in the second scenario, the O2 application began 30 minutes after the catalyst application. For both scenarios, the ratio was [1:2.5]. Table I shows the details of the oxidants applied with the type of treatment and the respective concentrations of H2O2.

Once prepared according to the denominations described above, the reactor and recycling reservoir was filled with this fluid, and the lamp and pump were turned on. Each 120-minute batch was divided into 30-minute intervals in which samples were taken for analysis. After each 120-minute batch, the unit was cleaned and rinsed with deionized water.

Data regarding the characterization of the effluent and the analysis of the parameters of dissolved organic carbon (COD), electrical conductivity and pH are also presented in this work. All analyses were performed according to APHA [5].

| TABLE I: OXIDANTS APPLICATION DATA AND STAGES OF EXPERIMENTAL STUDY |
|-------------------------------------------------------------|
| Process | Stage denomination |
| UV | A |
| UV + H2O2 [1:0.3] | B |
| UV + H2O2 [1:2.5] | C |
| UV + H2O2 [1:5.0] | D |
| UV + H2O2 [1:2.5] + O3 | E |
| UV+H2O2 [1:2.5] + O3 (after 30 min) | F |

III. RESULTS AND DISCUSSION

The raw influent had the following characteristics: COD of 1126 mg L-1, LAS of 172.62 mg L-1, pH of 8.91, and electrical conductivity of 3840 µS cm-1. Studies developed by Braga and Varesche [8] observed a variation of 12.24 mg L-1 to 1023.70 mg L-1 of LAS in commercial laundry wastewater, monitored for a period of 30 days. According to Table II, there was a significant reduction in LAS concentration during the experiments.

During the first 30 min of operation, treatment E showed the highest removal, reaching 95.30%. However, the operation was prejudiced because of the formation of a high quantity of foam in the recycling reservoir. Due to O3 addition by the gas diffuser.

Souza et al. [6] observed the best results operating with a 1:2.5 [COD:H2O2] ratio and pH of 9.0, with the removal of 98.2% surfactant after 60 min. In stage F, foam formation was diminished since photocatalysis had already reduced LAS loading by 79.35% in 30 min. Therefore, O3 can be considered a polishing agent since it removes the surfactant beginning from 20.50%. Comparing types E and F, we can see that at t=60 min, the efficiency of surfactant removal was approximately the same, reaching 99.00%.

For stages C and D, where the H2O2 concentration was doubled, the efficiency reached more than 94% in the first 60 min of treatment. In this way, using a higher concentration of catalyst does not mean an increase in efficiency, as also noted by Dezotti [9].

In stage A, photolysis showed a low removal efficiency of LAS (48.62%) even after 120 min of treatment. According to Teixeira and Jardim [3], this condition occurs because some compounds are not mineralized by direct photolysis and need other oxidants in the process. In stage B, the low concentration of H2O2 had low interference in the efficiency of the removal of surfactant, resulting in 63.46% by the end of the process. Souza et al. [6] also identified this behavior at a concentration of 1:0.5 [COD:H2O2], since this amount of oxygen peroxide was not sufficient to oxidize the compounds as a result of the low hydroxyl radical production.

As shown in Fig. 2, it is noted that the effluent submitted to the advanced oxidative process showed a tendency to reduce the concentration of LAS. Fig. 3 presents the LAS degradation profiles based on the differential method to determine the reaction order and the reaction rate constant.

![Degradation profiles of LAS concentration during photocatalysis under conditions defined in Table III.](http://dx.doi.org/10.24018/eje.2022.7.5.2876)
Equation 1 does not accuse of significant effects on the results being reduced to the value of 0.4706. According to Kuo [10], this is a consequence of the low residual concentration of H$_2$O$_2$ incorporated in COD by the end of the treatment, probably less than 0.8 mg L$^{-1}$, making it almost negligible.

As H$_2$O$_2$ concentrations under 200 mg L$^{-1}$ were applied in the treatment stages, Equation 1 does not accuse of significant effects on the results being reduced to the value of 0.4706. According to Kuo [10], this is a consequence of the low residual concentration of H$_2$O$_2$ incorporated in COD by the end of the treatment, probably less than 0.8 mg L$^{-1}$, making it almost negligible.

Another possible interference to COD values is chloride ions present in laundry wastewaters [11], which can cause variations in the results [12].

In stage E, the time of exposure of the solution to O$_3$ was higher than that in stage F. For Teixeira and Jardim [3], the reactions between strong oxidants such as O$_3$ and H$_2$O$_2$ with UV generate hydroxyl radicals that have high oxidation potential. That can potentialize the removal of COD by the value of 51.2% because the presence of organic compounds in the solution was low from the first 30 min of treatment. Because the degradation of surfactant reached 95.5% removal efficiency.

According to Table V, there was an adequate behavior between pH and electrical conductivity. In stage A, only UV radiation did not promote a significant decrease in these parameters. However, from stages B to F, whose processes used oxygen peroxide, an increase in conductivity and a reduction in pH was verified, principally in stage D since it had a higher concentration of H$_2$O$_2$ and in stage F after the addition of O$_3$. Nagel-Hassemer et al. [11] observed this behavior in the posttreatment of textile effluents through the UV/H$_2$O$_2$ process due to the evolution and/or increase of species in the solution.

Deng and Zhao [34] observed that the presence of hydroxyl radical scavengers, such as carbonate and bicarbonate ions, makes the oxidative process more efficient in acidic media. In this study, the pH was not adjusted and was kept the same as in the industrial effluent sample.

Table III shows the removal of LAS kinetics from each stage. Depending on the removal efficiency, it is confirmed that treatment type E has a higher reaction rate (0.08542 min$^{-1}$) and first-order reaction, followed by stages F, D, and C. With low LAS removal efficiencies, stages A and B resulted in lower reaction rates and zero-order reactions. Fig. 4 illustrates the LAS removal kinetics, as shown in Table III.

Table IV shows the removal of soluble COD for each treatment stage. There was linearity in the soluble COD removal for stages A and B due to the absence of catalyst or low catalyst concentration. According to Kuo [10], there is an increase in COD with the increase in H$_2$O$_2$ dose, caused by the concentration of H$_2$O$_2$ remaining in the effluent, as in the case of stages C, D, and F.

The adjustment proposed by Kuo [10] was calculated using Equation (1).

\[
\text{COD (mg L}^{-1}) = \text{CODm} - f[H_2O_2] \\
\text{where } f = 0.4706 - 4.06 \times 10^{-5} [H_2O_2] \tag{1}
\]

IV. CONCLUSION

Photolysis with UV radiation did not present satisfactory results in surfactant removal, indicating that it is necessary to amend this method with other oxidants. An increase in exposure time could enhance the efficiency of LAS removal. When H$_2$O$_2$ was not present in the solution, COD removal was higher since there were no interferences, such as residual H$_2$O$_2$ and chloride ions, and there was no significant pH and conductivity variation.

With H$_2$O$_2$ application at high and low concentrations, photocatalysis enhanced the efficiency to values higher than 79.00% in the first 30 min. With the lower concentration, however, only 63.50% removal was achieved at t = 120 min.

There was a decrease in the efficiency of COD removal, and conductivity and pH showed great variations due to the
increase in ionic species in the solution. Catalyst concentration was not the principal factor for the removal of organic compounds since excess H₂O₂ can act as a free radical prejudicing efficiency. However, when we combined H₂O₂, O₃, and UV radiation, the efficiency of removal was enhanced due to the high-oxidizing capacity hydroxyl radical formation. The removal efficiency reached 95.30% after 30 min of exposure.

The negative point of this process was foam formation due to O₃ bubbling in the recycling reservoir. This can prejudice the submersed pump operation and cause a loss of liquid from the reactor. COD presented the same behavior since large amounts of exposure time to H₂O₂/O₃/UV caused higher oxidation and consequently lower COD values by the end of the process. The pH and electrical conductivity varied due to the evolution of ionic species in the solution.

**CONFLICT OF INTEREST**

The authors declare that they do not have any conflict of interest.

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