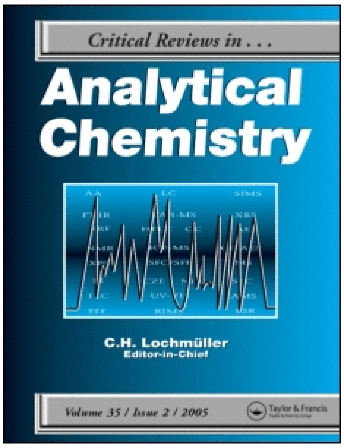

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Textile Wastewater Treatment Technologies: Wet Oxidation *vs.* Ozonation

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Dye wastewaters are extremely variable in composition, due to the large number of dyes and other chemicals used in dyeing processes. They are characterized as containing mainly soluble compounds, little suspended solids, colors that vary between reds and blues, and insufficient concentration of nitrogen and phosphorus to sustain biological activity. In these areas, dyes often receive the most attention from researchers interested in textile wastewater treatment processes. They are required to exhibit a high degree of chemical, photolytic, and microbiological stability in order to fulfill the fastness requirements of consumers. Consequently, dyes do not readily degrade under typical usage conditions, not even under aerobic conditions prevailing in the conventional biological treatment process. Therefore, future efforts should focus on developing new and more efficient dye-containing wastewater treatment processes. Oxidation processes seem to be efficient enough, since high energy intermediates responsible for the destruction of organic compounds in water are generated. In thermal processes (wet oxidation) these intermediates (free radicals) are formed by thermal reactions at high temperatures and pressures. In the advanced oxidation processes (e.g., ozonation), the generation of active oxygen species, such as hydroxyl radicals, takes place at near ambient temperature and pressures. Both types of processes could be even more successfully employed when an appropriate catalyst is added.

The goal of the paper is to give some results of wet oxidation and ozonation of an azo dye aqueous solution and also some general hints for the application of both processes in textile and related industries. Particular emphasis is given to a transformation of especially toxic or refractory substances and to a maximization of mineralization that is to reduce the amount of dissolved organic carbon as completely as possible or as defined by legislative requirements. The potential of coupling oxidation and biological processes to achieve economically the most feasible processes is discussed. Optimization of refractory wastewater treatments and reactor design could not be provided without sufficient data regarding the slowest step of the process. Therefore, particular attention is given to the synergistic effect among the carboxylic acids.

To get sufficient experimental data, wet oxidation and ozonation experiments were performed using Orange II as a model azo dye well represented in the textile, food and pharmaceutical industries. Wet oxidation experiments were performed in a 2-L stainless steel autoclave reactor in a temperature range of 180–240°C and oxygen partial pressure of 10^6Pa. Ozonation experiments were conducted in a 1.5 L mantled glass reactor that operated semibatchwise in a temperature range of 12–37°C and ozone partial pressure of 520 Pa. Orange II concentration was, in both cases, 0.5 g/L (i.e. 274 ppm of organic carbon). Separate wet oxidation experiments were performed at two temperatures (240 and 280°C) and unique oxygen partial pressure of 30 bar for the determination of the synergistic effect between acids, usually identified during wet oxidation and ozonation processes. Equimolar and mixtures with an excessive acid were prepared on the total carbon basis. The catalytic wet oxidation and ozonation of Orange II aqueous solutions were studied using commercially available catalyst comprising of CuO, ZnO and Al_2O_3. Advanced analytical methods were used to follow the above mentioned processes.

The comparison of homogeneous and heterogeneous wet oxidation and ozonation results of an

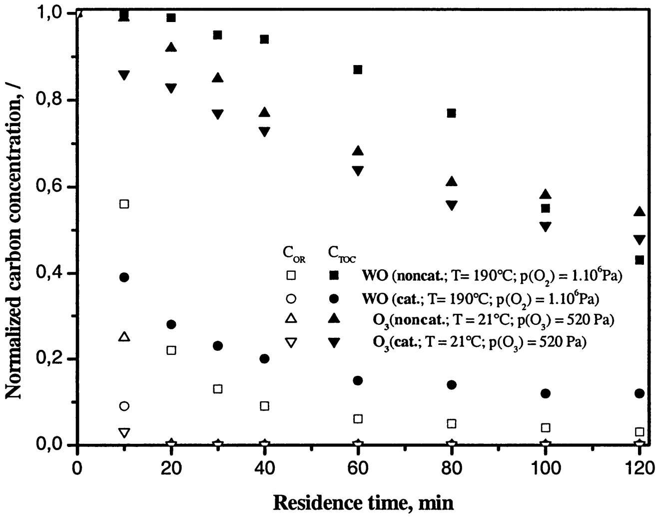

FIGURE 1. Normalized carbon concentration in Orange II and solution as a function of time; noncatalytic and catalytic wet oxidation *vs* ozonation.

aqueous Orange II is depicted in Figure 1, by means of carbon concentration time behavior in Orange II and solution. Inspecting results more closely, one can see, that the data points for Orange II are much lower than those for organic carbon in solution in both processes. The difference between the carbon found in Orange II and the one in the solution obviously accounts for the intermediate products formed during the course of thermal oxidation or ozonation, respectively. In the case of ozonation, Orange II disappears much faster. However, only 20 minutes is needed for the decolorization of solution when the catalyst is added. The addition of catalyst is much more important in the case of the wet oxidation process, since Orange II does not completely break down into invisible intermediates under the thermal oxidation conditions employed. Carbon in solution disappearance results are especially encouraging when catalyst is added in aqueous solution treated under conditions of wet oxidation processes. The conversions of dissolved carbon are almost 60% higher in the presence of catalyst. One should be aware that this comparison is made between results obtained at relatively low temperatures. Therefore, it is expected that the data are even better when higher temperature is involved. In the ozonation process not such an efficient role is played by the presence of the catalyst. It is still obvious, however, that the presence of the catalyst makes the process of carbon in solution disappearance more effective.

At the later stage of the process, organic low-molecular-mass acids are formed. Since they are very refractory, their oxidation may be the slowest step. Thus, their distribution needs to be inspected very carefully.

In the experiments performed without the catalyst, acetic, formic, oxalic, and glycolic acids were found in both type of effluents, but their distribution differed significantly at the same residence time. In the case of noncatalytic wet oxidation, acetic and formic were found as prevailing acids. While formic acid exhibited a maximum appearance after 20 minutes, a concentration of acetic acid tended to increase and remained in the solution as the main intermediate acid. It may be speculated that formic, as well as oxalic and glycolic acids, decomposed into acetic acid. In this case, the total amount of acids accounted for 71% of organic carbon in the solution.

In the noncatalytic ozonation process oxalic and formic were found as prevailing acids. The concentration of formic acid increased to a maximum after 60 minutes, while the concentration of oxalic acid continued to increase under the experimental conditions employed. There are also acetic and glycolic acids present, but their concentrations are very low. The total amount of acids accounted for 34.3% of organic carbon in the solution. The typical distribution of acids formed by noncatalytic processes is depicted in Figure 2.

In a catalytic wet oxidation, acetic acid was found to be dominant. It seems that acetic acid is the last intermediate, which could not be destroyed into CO_2 under the conditions employed. In a catalytic ozonation, formic acid was found to be the main intermediate acid.

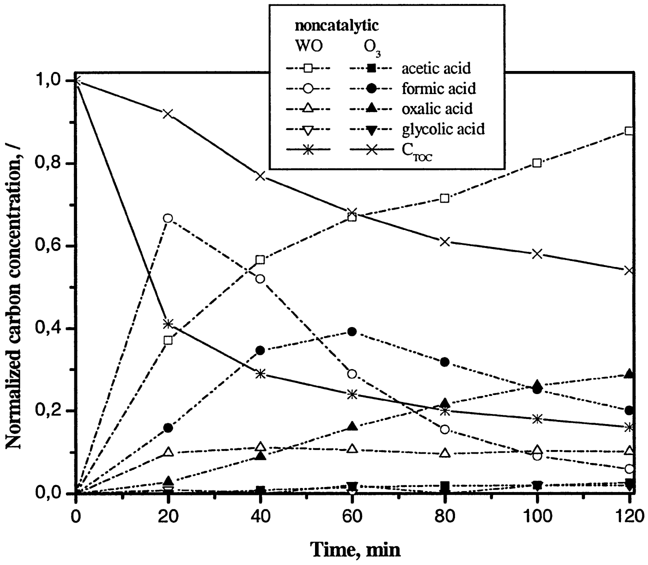

FIGURE 2. Normalized carbon concentration in intermediate acids and solution as a function of time; noncatalytic wet oxidation (T = 230°C) *vs* ozonation (T = 20°C).

Oxidation results of aqueous solutions prepared in different ratios from formic, acetic, oxalic, and glyoxalic acids showed that refractory acetic acid attains much higher oxidation rates when it is oxidized in a mixture with formic, oxalic, and glyoxalic acids. The oxidation rate of acetic acid is more pronounced when oxalic and/or glyoxalic acids are in excess. Oxalic and glyoxalic acids decompose extremely fast, resulting in the production of formic and acetic acids. Due to the synergistic effects in acid mixtures, the actual TOC reduction was found to be much higher than expected on the basis of the TOC kinetics for individual acids. This finding needs to be taken into consideration, especially when the oxidation/ozonation process is coupled with biological processes. Biodegradation of refractory species is known to be strongly dependent on acids present in effluent. In processes studied, we found a tendency to increase biodegradability expressed by BOD_5/COD ratio. Relevant data for more efficient catalytic processes are presented in Figure 3.

Enhancement of biodegradability during oxidation processes enables coupling with biological processes. If both oxidation and biological methods are compared, the capital and operating costs of the biological processes are much lower than those of oxidation (thermal and advanced) processes. Therefore, it is worthwhile to design integrated processes with prior detailed determination of optimal reaction

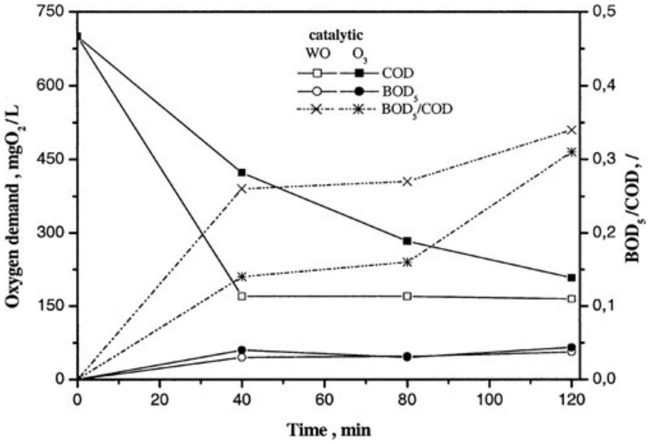

FIGURE 3. COD, BOD_5 and BOD_5/COD values of the effluent samples treated by catalytic oxidation and ozonation as a function of time.

conditions (reactor volumes, flow rates, treatment time, catalyst efficiency and catalyst dose), as well as economic costs.

Generally speaking, catalytic wet oxidation processes could be efficient enough to stand as lone processes for refractory species from textile and related industries, while ozonation calls for coupling with biological processes, due to the persistence of intermediates that tend to remain in the solution.