Heterogeneous Catalytic Ozonation of Rhodamine B Using Spent Alkaline Battery Waste as Catalyst

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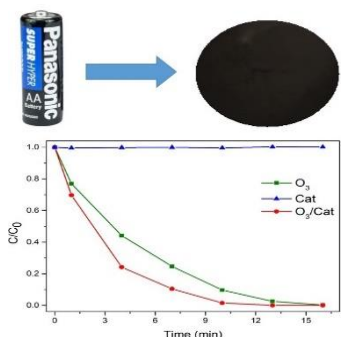
In this study, a non-purified solid waste from post-consumer alkaline batteries was applied as catalyst to water decontamination using ozone in a batch reactor. The catalytic activity of the solid was evaluated using rhodamine B (RhB) as organic pollutant model at pH in the range 4 to 10. No RhB removal was detected by adsorption on the solid, and the non-catalytic ozonation was described as a pseudo-first order kinetic reation. The effect of the catalyst dosage and inital pH on RhB degradation was studied at room temperature. The experimental results indicated that the catalytic ozonation in optimized conditions is 2.4 times faster than the non-catalytic degradation at pH 7. In toxicity tests with arugula seeds, the average growth of roots increased 71% in the samples after RhB catalytic ozonation, and indicated that non-purified solid waste from post-consumer alkaline batteries is a good source for catalyst preparation.

Introduction

Ozone has been widely applied in the degradation of recalcitrant organic pollutants. With the advancement of technology and the optimization of ozone production processes, the costs associated with its generation have decreased, making it more accessible for a variety of industrial and environmental applications. This includes the treatment of drinking water and effluents, water disinfection, remediation of contaminated soils, and even air purification in enclosed environments [1].

Ozone used in isolation has limited degradation power due to having a lower oxidation potential (2.07 eV) than the hydroxyl radical (2.8 eV), which is formed at low rates by the simple decomposition of ozone into water. Nevertheless, ozone can be combined with other oxidizing agents, such as heterogeneous catalysts, resulting in heterogeneous catalytic ozonation and several oxidizing free radicals highly reactive can be formed [2].

This is an advanced oxidative process based on solid materials capable of increasing hydroxyl radical production by interacting with ozone. Transition metal oxides such as Fe, Mn, Zn, and Cu can assist in electron transfer between the solid material and the pollutant, increasing degradation efficiency. Among these, Mn and Zn oxides have great potential in catalytic ozonation due to multiple oxidation states and high surface hydroxyl group density, respectively [1].

Solid catalysts may have high synthesis and production costs, which has led to the search for residual materials with high application potential. In this aspect, post-consumer battery electrolytes containing Mn and Zn can be excellent precursors of oxides for application in catalytic ozonation from a residual matrix, especially if they do not need to be combined with other catalysts or purification to present high efficiency.

Thus, the objective of this work was to study the degradation of Rhodamine B (RhB), a textile dye used as a model pollutant, by catalytic ozonation using an Mn and Zn oxide from a post-consumer battery residue without additional purification.

Material and Methods

The catalyst preparation methodology was based on Viana et al. [3]. The residual electrolyte from batteries Super Hyper UM-3SHSL8P6 (Panasonic) was used. The anodic electrolytic paste (mainly containing manganese oxide and zinc chloride) was mechanically separated from the other constituents (graphite cathode and plastic and metal coatings), macerated, and washed several times with distilled water. After that, the solid material was dried at 105°C for 10 hours, macerated again, and sieved to 100 mesh. Finally, a brown powder was formed after calcination at 500°C for 4 hours. Catalyst characterization analyses can be found in [3].

A 50 mg L^{-1} aqueous solution of RhB (Dinâmica Contemporânea Ltda, Brazil) was prepared for degradation tests. Ozone gas was obtained from a portable ozone generator (GL-3189A, 8W, mass flow rate of 0.6 g h^{-1}). The tests were carried out in batch mode in a cylindrical vessel containing 250 mL of RhB solution at 400 rpm for 16 minutes. For experiments with solid catalyst, an initial dosage of 0.4 g L^{-1} and 15 minutes of adsorption were used before O_3 application. The effect of catalyst concentration (0.4, 0.8 and 1.2 g L^{-1}) and pH (4, 7 and 10) on catalytic ozonation was observed. A pseudo-first-order kinetic model was fitted to the experimental data using Equation 1. The statistical quality of the fit was assessed by the coefficient of determination (R^2) and the reduced chi-squared (X^2).

$$\frac{C}{C_0} = e^{-kt} \tag{1}$$

where k is the rate constant (min^{-1}) and C_0 is the initial concentration. The samples were filtered and the RhB concentration was determined by UV-Vis spectrophotometer (HACH, DR 5000) at λ = 550 nm. Toxicity tests were performed according to the methodology of Aquino et al. [4], using arugula seeds (Eruca sativa).

Results and Discussion

Tests were conducted to compare the degradation efficiency of different processes (Figure 1). The RhB removal in absence of ozone is negligible indicating that no adsorption occours. Comparing the rate constants in Table 1, the combined process achieved higher degradation rates more quickly (up to 1.6 times) compared to O_3 alone. Ozone is a powerful oxidant (2.07 eV), however the presence of the catalyst leads to an increase in free radicals with greater oxidizing power, effectively improving degradation [5].
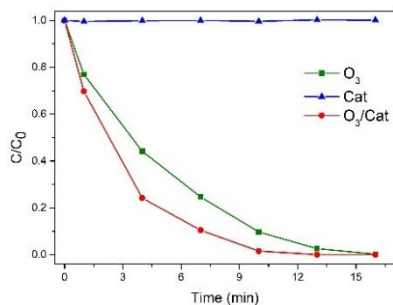
Figure 1. Comparison of RhB degradation under different processes.

The effect of catalyst concentration (Figure 2a) and initial pH (Figure 2b) on the O_3/Cat process was investigated. The optimal catalyst concentration was determined to be 0.8 g L^{-1}. Increasing the catalyst concentration enhances the oxidation process due to the availability of more active sites for interaction with ozone. However, further increasing the concentration to 1.2 g L^{-1} resulted in a slower degradation rate. Regarding the decline in performance due to excessive catalysts, two factors come into play. Firstly, there's a reduction in the number of available active sites due to the stacking and agglomeration of materials. Secondly, there's heightened competition between catalysts and organic compounds in reacting with the formed reactive oxygen species (ROS) [6]. In the initial pH study, pH 7 yielded the best results. This is favorable as it is close to the natural pH of the solution (6.80).
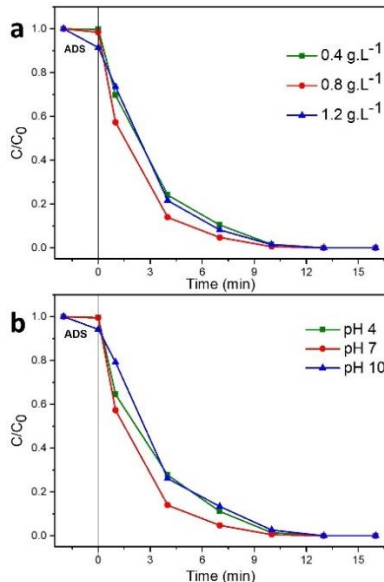
Figure 2. Effect of catalyst concentration (a) and initial pH (b) on RhB degradation.

A toxicity study was conducted using arugula seeds under the optimal conditions. The germination percentage was above 90% in all cases. The average growth for the samples before and after treatment were 0.7 ± 0.2 cm and 2.1 ± 0.1 cm, respectively. Compared to the positive control (mineral water), the relative growth for the sample before treatment was 36%, indicating inhibition as reported in [4]. For the sample after treatment, a relative growth of 105% was observed, significantly reducing toxicity.

Table 1. Parameters obtained from the kinetic fitting in the pseudo-first-order model.

Experiment	k_1 (min^{-1})	R^2	X^2 (x 10^{-4})
O_3	0.218	0.995	7.91
O_3/Cat (0.4 g L^{-1}, pH 7)	0.353	0.999	0.82
O_3/Cat (0.8 g L^{-1}, pH 7)	0.523	0.999	1.25
O_3/Cat (1.2 g L^{-1}, pH 7)	0.358	0.991	10.50
O_3/Cat (0.8 g L^{-1}, pH 4)	0.352	0.995	6.10
O_3/Cat (0.8 g L^{-1}, pH 10)	0.306	0.992	9.54

Conclusions

The catalytic ozonation process employed in this study demonstrated enhanced degradation of rhodamine B compared to the use of ozone alone. The optimal conditions were determined to be 0.8 g L^{-1} catalyst and pH 7. Toxicity assays revealed that the treatment significantly reduced the inhibition of radicle growth in seeds. The utilization of a waste product as a catalyst in the process proved beneficial for both RhB degradation and toxicity reduction.

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