

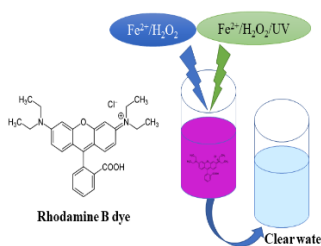
## Synergistic effects between different advanced oxidative treatments for degradation of Rhodamine B

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Rhodamine B is an amphoteric dye, widely used in the textile industry. Its presence in water can be easily detectable and can affect the reproductive and neurological system due to acute toxicity. For evaluate synergistic effects between different advanced oxidative treatments were applied photolysis (UV), hydrogen peroxide ( $H_2O_2$ ), photolysis with hydrogen peroxide (UV/ $H_2O_2$ ), Fenton ( $Fe^{+2}/H_2O_2$ ) and photo-Fenton ( $Fe^{+2}/H_2O_2/UV$ ). Concentrations of  $H_2O_2$  when alone and in Fenton/photo-Fenton and the proportions of  $Fe:H_2O_2$  in Fenton/Photo-Fenton was evaluated. For the results, the combination of the UV and  $H_2O_2$  processes achieved 70% degradation in 2 hours of reaction, using  $14.4 \text{ mmol L}^{-1}$  of  $H_2O_2$ . The complete degradation of the dye in the photo-Fenton process was twice as fast as in the Fenton process, in the  $H_2O_2$  concentration of  $0.5 \text{ mmol L}^{-1}$ , and  $Fe^{+2}:H_2O_2$  ratio of 1:5. Regarding the dye mineralization, an increase of 25% was observed when UV irradiation was applied to the solution.

### Introduction

The presence of dyes in water can be easily detectable. Due to this behavior, a small amount discharged in aquatic effluents can cause a marked change in the color of the rivers and have toxic effects on microbial populations, being harmful and carcinogenic [1]. Rhodamine B is an amphoteric dye, listed in the class of xanthenes, widely used in the textile industry, and it is a carcinogenic product, affecting the reproductive and neurological system due to acute toxicity [2]. Advanced Oxidative Processes (AOPs) have been identified as highly efficient treatments for recalcitrant effluents [3]. Thus, processes such as UV/ $H_2O_2$ , Fenton, photo-Fenton and photocatalytic can be a good option to treat and eliminate dyes. These processes can have the ability to completely discolor and completely or partially mineralize the dyes in a short reaction time. In this context, the present work aims to study the removal of Rhodamine B dye in synthetic aqueous solution via oxidative processes UV,  $H_2O_2$ , UV/ $H_2O_2$ , Fenton and photo-Fenton.

### Material and Methods

The reagents used in the present work were Rhodamine B (Dynamic);  $H_2O_2$  P.A. (Modern Chemistry, 30-32%); ferrous sulfate heptahydrate (Synth, 99%); HCl 1 M (Synth); 1 M NaOH (Synth). For the photolysis, Fenton, and photo-Fenton reactions, was used 12 UV-A lamps ( $\lambda = 365 \text{ nm}$ ) of 8 W of power each and  $0.7 \text{ mW cm}^{-2}$  of average intensity of radiation. Dye degradation was assessed by decreasing light absorption at the maximum absorbance wavelength of the solutions ( $\lambda = 556 \text{ nm}$ ). To evaluate the mineralization, the solutions that presented the highest degradation rate were submitted to Total Organic Carbon (TOC) analysis. For each experiment was used  $20 \text{ mg L}^{-1}$  solution of

Rhodamine B, at times 1, 2, 5, 10, 15, 30, 50, 60, 70, 90, 110 and 120 minutes. To promote the Fenton and Photo-Fenton reactions, the pH of the starting solution was adjusted to 3.

The variables studied was  $H_2O_2$  concentration (1.6, 4.8, 14.4, 43.2 mM), for  $H_2O_2$  and  $H_2O_2/UV$  process, and  $H_2O_2$  concentration (0.53, 1.6, 4.8 mM) and  $Fe^{+2}$  concentration (0.05, 0.11, 0.16, 0.32, 0.48, 0.96 mM) in Fenton and photo-Fenton process.

An *in-silico* approach using QSAR was employed to assess the ecotoxicity of Rhodamine B before treatment. The analysis was conducted using the OECD Toolbox, Version 4.3.1, employing the integral model.

### Results and Discussion

As *in-silico* analysis shows the biochemistry effect concentration (LOEC) is  $2.39 \text{ mg L}^{-1}$ , for the rotifer in 4h of exposure. Also, the concentration of  $5 \text{ mg L}^{-1}$  resulted in 50% mortality in *Daphnia magna* (LC50). The results demonstrate the importance of reaching final concentrations lower than  $2.39 \text{ mg L}^{-1}$ , for maintaining good water quality.

Table 1. Information on aquatic ecotoxicity for Rhodamine.

Endpoint	Value	Specie, duration, database
LOEC	$2.39 \text{ mg L}^{-1}$	<i>Brachionus koreanus</i> ; 4 h; ECOTOX
LC50	$5 \text{ mg L}^{-1}$	<i>Daphnia magna</i> ; 24 h; ECHA REACH

Regarding the results of AOPs, as expected it was observed that UV radiation showed little efficiency in pollutant degradation [4,5], even after 120 minutes of reaction, with less than 10% of degradation. Likewise, the use of  $H_2O_2$  reaches values lower than 11% of discoloration. Thus, UV and  $H_2O_2$  alone has little

influence on the degradation. When  $H_2O_2$  is the only oxidizing agent, the absence of an activating agent will not produce  $\bullet OH$  required for pollutant degradation [6].

A higher level of dye degradation was observed when the oxidative processes UV/ $H_2O_2$  were combined. At 120 minutes of reaction, with  $H_2O_2$  concentrations above 14.4 mM, about 70% degradation was obtained, confirming the synergetic factor of oxidizing agents in the degradation of pollutants. When evaluating the influence of  $H_2O_2$  concentrations with the incidence of UV light, it is noticed that there is an increase in discoloration as the amount of peroxide increases up to 14.4 mM. This occurs because when large amounts of peroxide are present, there is an increase in the fraction of absorbed radiation and, consequently, its photolysis speed also increases. However, this only happens up to a certain limit.

As observed in Fig. 1, the rate of dye degradation increases as the  $H_2O_2$  concentration increases, to the same  $Fe^{+2}:H_2O_2$  ratio. For  $[H_2O_2]=0.53$  mM, slower discoloration was observed, even so it was considered the best operating condition for Fenton as it uses the smallest amount of reagents and achieves total discoloration within 60 minutes.

As Fig. 2 shows, UV radiation provided an increase in the rate of dye degradation for all conditions studied. The presence of UV radiation increased the degradation [7] rate by about 15% in 10 minutes of reaction, in the proportion  $Fe^{+2}:H_2O_2$  of 1:10 and  $[H_2O_2]=0.53$  mM, obtaining 100% of degradation. That way, both Fenton and photo-Fenton treatment delivered final concentration below  $2.39$  mg  $L^{-1}$ , carrying out safe disposal according to the aquatic ecotoxicity information reported by QSAR-OECD.

## Conclusions

When used alone, the UV and  $H_2O_2$  processes did not show significant results for the dye treatment. However, the synergistic factor between these processes proved to be important, especially on Fenton reaction.

## Acknowledgments

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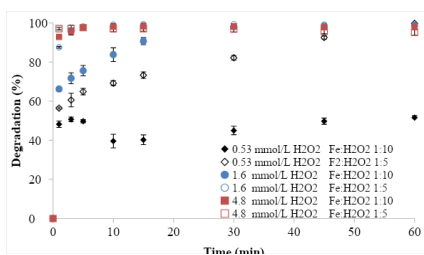


Figure 1. Effect of  $Fe^{+2}:H_2O_2$  concentrations in Fenton on the degradation of Rhodamine B over time.

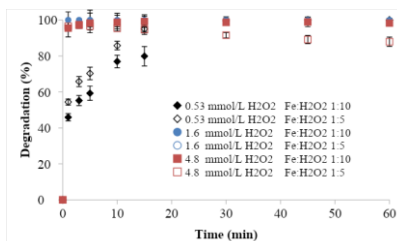


Figure 2. Effect of  $Fe^{+2}:H_2O_2$  concentrations in Photo-Fenton on the degradation of the Rhodamine B over time.

TOC analysis was carried out with the Fenton process conditions:  $Fe^{+2}:H_2O_2$  of 1:5 and  $[H_2O_2]=0.53$  mM, and the Photo-Fenton  $Fe^{+2}:H_2O_2$  of 1:10 and  $[H_2O_2]=0.53$  mM after 60 minutes of reaction. A partial mineralization was observed, which in Fenton condition was 23.9% and in photo-Fenton condition was 28.7%, corresponding to an improvement of 25%. Finally, with regard to AOPs, it is important to evaluate byproducts, however there was no prediction for rhodamine metabolism in the *in silico* toolbox.