EFFECT OF ULTRAVIOLET LIGHT AND ULTRASONIC IRRADIATION ON DEGRADATION OF RHODAMINE B DYE

Data de submissão: 17/01/2025 *Data de aceite: 05/03/2025*

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ABSTRACT: The degradation of Rhodamine B dye in water was experimentally studied under two advanced oxidation processes, using ultraviolet light and ultrasound irradiation, in the presence of TiO_2 catalyst. The effect of operational variables affecting the photocatalytic and sonocatalytic processes were studied, including catalyst loading, pH, and addition of H_2O_2 as an oxidizing agent. The optimal operating conditions for higher dye degradation corresponded to ca. 0.5 g L^{-1} catalyst concentration, and pH=2.5, for both photocatalytic and sonocatalytic processes. These experimental conditions were then considered to evaluate a possible synergy by combining both technologies, which showed that combination of both technologies exceed the degradation of each technology separately.

KEYWORDS: Dye degradation; Advanced oxidation processes; Synergetic effect.

INTRODUCTION

According to the United Nations, the textile industry is responsible for 20% of the world's polluted water. This industry not only consumes significant amounts of water (in the order of 80 to 100 L per kg of cotton) but also usually releases chemical substances such as detergents, dyes, starches, among others, into its effluents [1]. Both situations result in the generation of large volumes of contaminated water with high organic loads and an intense color.

There are traditional methods of treating these effluents that are characterized by transferring the pollutant from one phase to another, which is a disadvantage since they require subsequent stages of treatment or disposal of the pollutants. Biological treatment processes, on the other hand, are often not as effective at removing color and other recalcitrant molecules present in textile wastewater [2]. In more recent times, different alternative methods to conventional ones have been studied, which are based on the removal of contaminants through reactions with free radicals such as hydroxyl ($OH^{\bullet}$), sulfate ($SO4^{\bullet}$-), among others. These processes are known as advanced oxidation processes (AOPs), and they can destroy water contaminants and transforming them into less toxic products and eventually even eliminating them. Among these processes, the generation and type of the reactive radicals can differ, as it occurs with ozonation, ultraviolet radiation, and ultrasound-based processes [3, 4, 5, 6]. Photocatalytic oxidation has shown high efficiency in mineralizing pollutants in water, which has been associated to the generation of reactive oxygen species such as hydroxyl ($OH^{\bullet}$) and superoxide ($O^{\bullet 2-}$) radicals [7]. Moreover, due to the physical forces and chemical reactions under sonochemistry, the use of ultrasound can yield effective water treatment processes, where contaminants are mainly degraded by hydroxyl radicals [8]. The hydroxyl radical is the most reactive oxidizing agent in wastewater treatment but once generated it has a relatively short life. It can be produced by irradiation with ultraviolet light, ultrasound application, combined with a catalyst, in addition to its possible combination with chemical agents such as H_2O_2 [9]. More recently, attention has been paid to the combination between AOPs or with more traditional treatments, as is can improve the global effectiveness of the wastewater treatment process, by a global synergetic effect [10].

In the present work, the degradation of a dye is experimentally determined by both ultraviolet (UV) and ultrasonic cavitation (US) light, with and without the presence of alumina as a catalyst and of hydrogen peroxide as an oxidizing chemical agent. Finally, the combined operation of both UV and US on dye degradation is compared with the respective individual processes.

METHODOLOGY

The degradation of Rhodamine B (RhB) under conditions of ultraviolet light and/or ultrasonic soundwaves is studied, using TiO_2 as a catalyst, under different operating conditions. The reacting system consisted of reactors operated sequentially, one operated with a 10-watt UV lamp and the other with a low-frequency sonicator [11].

In the catalytic photodegradation and ultrasonic experiments, the main variables influencing the process (catalyst load, pH, and H_2O_2 concentration) were studied and the best operating conditions for each system were obtained. In each experiment, the analysis of dye degradation over time was determined using UV/VIS spectroscopy.

RESULTS

There are several important variables that affect the degradation of a dye in advanced oxidation processes based on the formation of free radicals using ultraviolet light or ultrasonic irradiation. Among the variables studied for each process modality are the concentration of the catalyst, the pH of the solution and the initial concentration of an oxidizing chemical agent. Figure 1 shows the effect of catalyst concentration on dye degradation both under ultraviolet (UV) light and under ultrasound (US) irradiation, for 10 ppm initial dye concentration and 60 min exposure. The figure shows that even without the presence of catalyst, there is a slight conversion of the dye because of UV light. However, because in the photocatalytic process the reactive species are formed in the active centers on the surface of the catalyst, it is observed that the gradual addition of catalyst shows a continuous increase until a maximum value in the percentage of discoloration is reached. For the present experimental case, the optimal concentration of catalyst was ca. 0.5 g L^{-1}, as a gradual decrease in the percentage of dye degradation was observed at higher catalyst concentrations (not shown in the figure). Such decrease was most likely produced by a “shadowing effect” that takes place at high catalyst loading which inhibits light penetration through the liquid to the catalyst surface [12]. It is evident that determination of the optimal catalyst concentration is of fundamental importance in terms of the economic viability of the process.

Figure 1 also shows the effect of catalyst presence under US conditions. The application of an acoustic field of ultrasonic waves in water can generate small bubbles of water vapor by cavitation, which when imploded locally produce extreme pressures and temperatures that generate highly reactive free radicals capable of degrading the dye [13]. As can be seen in Figure 1, this phenomenon can occur with and without the presence of the catalyst. The effect of the addition of catalyst produced a slight increase in the degradation of the color of the solution, less significant compared to what is observed with ultraviolet light. Something that was observed for US is that the optimal concentration of catalyst concentration is like that found for UV.

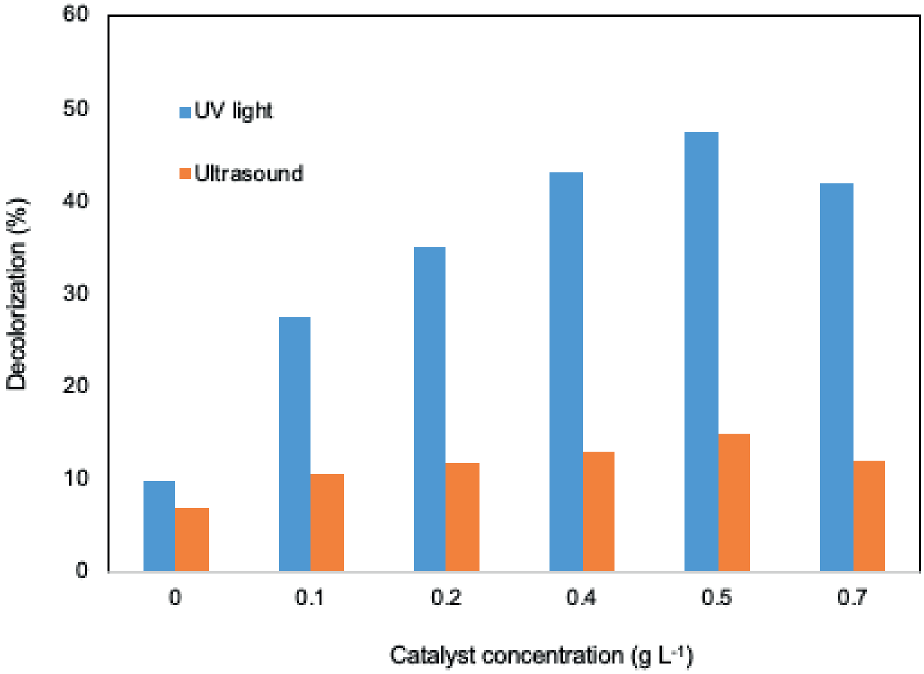

Figure 1. Color degradation as a function of catalyst concentration under ultraviolet light and ultrasound.

The pH value is an important operational variable in water treatment that influences the rate of degradation. This is because pH is related to the ionization state of the TiO_2 surface as well as the dye which influences their physical interaction. The ionization states of the catalyst surface are affected by pH according to following reactions, where the surface is positively charged in acidic medium and negatively charged in alkaline condition [14].

$$TiOH + H^+ \rightarrow TiOH_2^+ \tag{1}$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O \tag{2}$$

Figure 2 presents the effect of pH of the solution on dye decolorization, after 1 h exposure to either UV or US. It is observed that the degradation of the dye is favored at relatively low pH values, for both treatment processes, and it is also observed in this case that, for similar conditions, comparatively higher levels of degradation with UV light are observed (67% and 36%, respectively at pH 2.5). This effect has to do with the fact that pH affects the surface charges of the catalyst, with net positive charges of TiO_2 in acid medium and negative charges in basic media. On the other hand, it has been reported that under acidic conditions, the RhB dye in water is ionized and under such conditions the carboxylic group is dissociated and negatively charged, which favors its attraction to the positive surface of the catalyst [15]. At alkaline pH values the catalyst surface is negatively charged and the RhB molecule is in the switterionic form ($RhB^{\pm}$), and certain part of the molecule can be attracted to the catalyst surface by an electrostatic force and increase dye degradation [16].

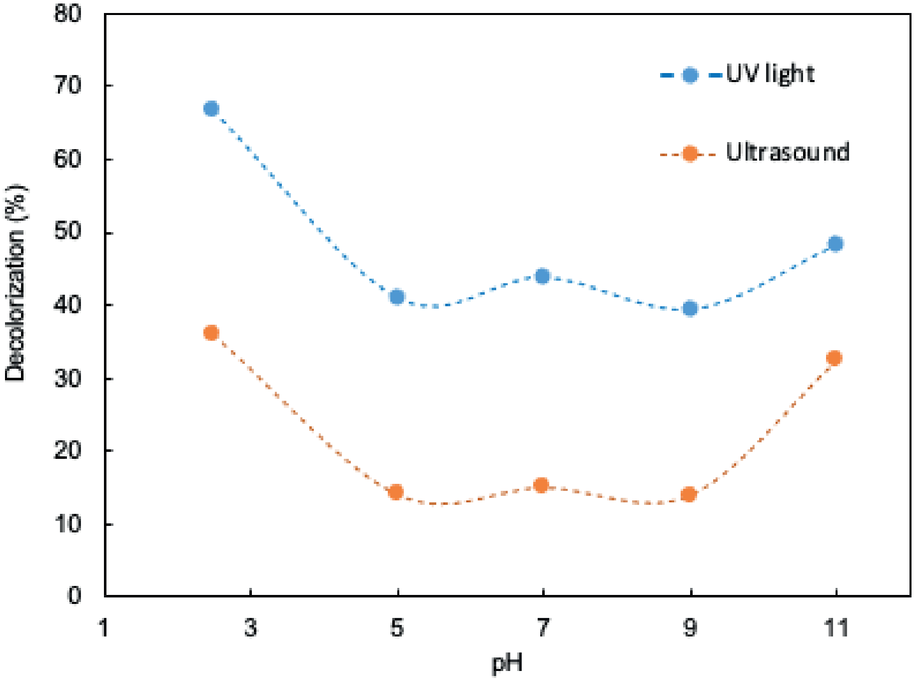

Figure 2. Color degradation as a function of pH under ultraviolet light and ultrasound.

In advanced oxidation processes, the degradation of contaminants can be favored by the addition of oxidizing substances. In the present work, hydrogen peroxide was used as an oxidizing agent and the effect of its concentration on the discoloration of the RhB dye was analyzed using Titania as a catalyst, ultraviolet light, and ultrasound waves. Figure 3 shows that for photocatalysis, the addition of H_2O_2 at 150 ppm allows an increase in dye degradation of up to approximately 10%. As shown in equations 3 and 4, the reagent H_2O_2 can generate hydroxyl radicals and thereby increase the degradation of the dye. This effect has a limited benefit since it is found that when the concentration of H_2O_2 continues to increase, the degradation of the dye decreases (see Figure 3), which is the result of a reduction of available hydroxyl radicals [17], due to its consumption when reacting with an excess of hydrogen peroxide as described in reaction 5.

$$H_2O_2 + e^-_{(BC)} \rightarrow OH^- + OH^* \quad (3)$$

$$H_2O_2 + h\upsilon \rightarrow 2OH^* \quad (4)$$

$$H_2O_2 + OH^* \rightarrow H_2O + O_2^- + H^+ \quad (5)$$

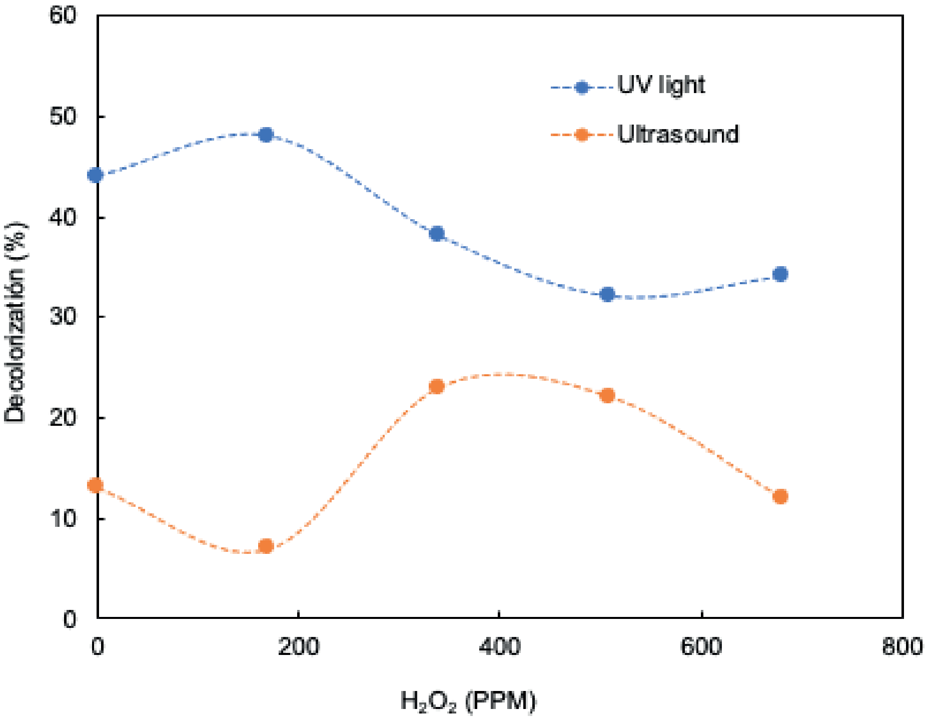

Figure 3. Effect of the addition of hydrogen peroxide on dye degradation in photocatalytic and ultrasound irradiated systems.

Also, in Figure 3 the effect of the addition of hydrogen peroxide under the presence of catalyst and under an ultrasonic wave field is presented. Ultrasound generates cavitation points under which conditions free radicals are generated from the breakdown of water molecules as shown in equation 6 [18]. Similarly, hydrogen peroxide can also be broken down into hydroxyl radicals by ultrasound (reaction 7). As in the case of photocatalysis, the addition of H_2O_2 helps break down the dye molecule through the formation of highly reactive free radicals. After a maximum value in degradation (about 400 ppm), at higher concentrations of peroxide, a decrease in the degradation rate is also observed, probably because of the possible consumption of hydroxyl radicals by the reaction with the peroxide itself (eq. 5).

$$H_2O \overset{)))}{\rightarrow} H^* + OH^* \qquad (6)$$

$$H_2O_2 \overset{)))}{\rightarrow} 2OH^* \qquad (7)$$

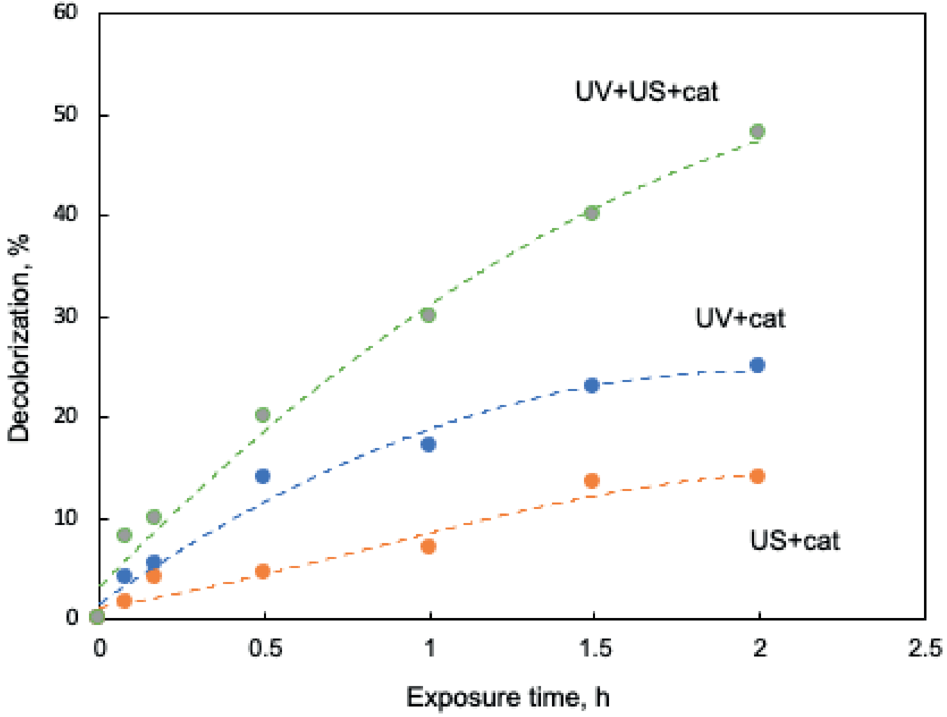

Figure 4 Dyestuff degradation kinetics for three different reaction processes using catalyst, UV, and US.

In the present work, the dye degradation kinetics in aqueous solution are also presented for three cases: i) sonocatalysis, ii) photocatalysis, and iii) photosonocatalysis, which results from a combination of the previous two. Figure 4 presents these results in terms of percentage of color loss of the solution over a period of 2 h. It is evident that the process that showed the highest degradation was that produced by photoocatalysis (close to 50%) followed by photocatalysis (slightly below 25%) and finally sonocatalysis (approximately 13% degradation).

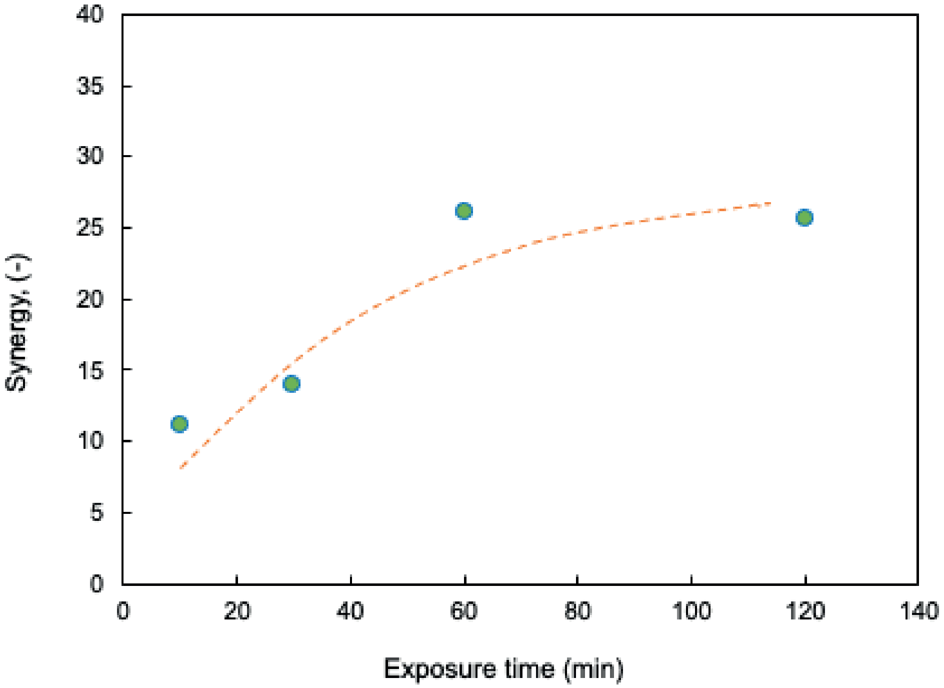

Figure 5 Effect of the synergy of applying simultaneously UV and US in the dye degradation process.

In addition to the evident differences between the three cases in Figure 4, it has been verified whether a positive combined effect of UV and US is achieved when they are operated simultaneously, that is, by a synergistic effect between the two. For this purpose, equation 8 has been used to compare the discoloration of the system operated with UV and US simultaneously in the reactor, and the result of adding the discoloration results of the processes operated separately from UV and US.

$$Synergistic\ effect = \frac{Photosonocatalysis-(Photocatalysis\ plus\ sonocatalysis)}{(Photocatalysis\ plus\ sonocatalysis)} x100\% \qquad (8)$$

Figure 5 shows the synergistic effect of degradation defined according to equation 8, at different reaction times in a two-hour period. It can be seen in this figure that when operating the rector under the combined application of UV and US, a synergistic effect can be generated that exceeds the sum of the individual results. This effect is less important at shorter times and turned out to be in the order of 13%, while at longer reaction times values close to 25% were reached. A possible explanation for the increased synergistic effect observed with increasing reaction time is that US helps limit some problems that occur in the operation of the photocatalytic system [19]. One of them is that with the operating time of the photoreactor, the aggregation of fine catalyst particles occurs, thus reducing the catalytic area exposed to light and causing the consequent reduction in the efficiency of the process

[20]. In this respect, the application of ultrasound helps to disperse the particle aggregates again. The presence of US can also be attributed to a better liquid-solid mass transfer on the particle surface in addition to a cleaning effect on the catalytic surface, which helps to remove adsorbed material that accumulates over operating time [21].

CONCLUSIONS

The degradation of dye Rhodamine B in aqueous solution was compared using ultraviolet light and ultrasound. For each of these two advanced oxidation methods, the optimal concentration of the catalyst, the effect of the addition of hydrogen peroxide as a chemical oxidizing agent, as well as the initial pH of the solution were experimentally determined. The degradation with UV light was not only higher than that observed with US individually, but also turned out to be more efficient from the point of view of energy use. However, from the joint operation of both, a synergy was observed that exceeded the sum of these separately. This synergistic effect appears to have become more noticeable with the passage of reaction time, and this can be attributed to the fact that ultrasonic waves can help reduce problems in the photocatalytic system, as it is known that they can be useful in reducing the formation of catalyst aggregates by surface forces as well as improving the transport and cleanliness of the catalytic surface

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