Research Article

Ultrasonic Degradation of Fuchsin Basic in Aqueous Solution: Effects of Operating Parameters and Additives

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Ultrasonic degradation is one of the recent advanced oxidation processes (AOPs) and proven to be effective for removing low-concentration organic pollutants from aqueous solutions. In this study, removal of fuchsin basic from aqueous solutions by ultrasound was investigated. The effects of operating parameters such as ultrasound power (200 W–500 W), initial pH (3–6.5), and temperature (15, 22, 35, and 60°C) on the ultrasonic degradation were studied. The degradation of fuchsin under ultrasound irradiation was found to obey pseudo first-order reaction kinetics. Addition of catalyst Fe(II) had a markedly positive effect on degradation. 84.1% extent of degradation was achieved at initial dye concentration 10 μmol L−1, ultrasound power 400 W, ultrasound frequency 25 kHz, dosage of Fe(II) 4 mg L−1, initial pH 6.5, and temperature 22°C. But addition of heterogeneous catalyst TiO2 affected degradation slightly. Addition of radical scavengers suppressed fuchsin basic degradation significantly.

1. Introduction

Dyes are classified into various groups, such as azo, phthalocyanine, xanthene, and arylmethane, on the basis of their chemical structure. At present, approximately 10,000 different dyes and pigments are utilized in industry, with total estimated annual global consumption of 7 × 105 tonnes [1]. People are aware that cationic dye molecules are more toxic than anionic dye molecules [2]. Furthermore, most of these dyes are biorefractory and do not undergo effective degradation using conventional biological techniques [3].

Advanced oxidation processes (AOPs) are very efficient methods for degradation of recalcitrant organic compounds in industrial and agricultural effluents [4, 5]. They act through the use of free radicals, especially reactive ·OH attack. Sonolytic oxidation is one of the AOPs techniques and has proven to be an effective method for degrading organic effluents into less toxic compounds [6–9]. Sonochrome is a complex process, which depends on physical parameters and also on the process conditions. All efforts have been devoted to the optimization of physical parameters and the process conditions [10, 11]. Some efforts have been devoted to improve the degradation efficiency in sonochemical processes by adding various kinds of catalysts [12–15].

Fuchsin basic, a cationic triphenylmethane dye, was chosen as a typical representative pollutant. Fuchsin basic is traditionally used as colorant in dyeing textiles such as cotton, artificial fiber, leather, and paper [16]. When someone is exposed to fuchsin dye by the physical contact, ingestion, or inhalation, it may cause severe eye and skin irritation, nausea, vomiting, diarrhea, irritation to the respiratory tract, and damage to the organs such as blood, liver, and thyroid [17].

To the best of our knowledge, there is no report on the degradation of fuchsin basic using ultrasonic irradiation. The aim of this work was to investigate the effects of some sonochemical parameters such as ultrasonic power, pH, and temperature on the degradation of fuchsin basic dye. Additionally, effects of additives such as ferrous iron, titanium dioxide, and radical scavenging agents were also studied.

2. Experimental

2.1. Materials and Apparatus. Fuchsin basic (biological pure, SCRC, CAS no. 632-99-5) was not purified before use.
The chemical structure of fuchsin basic is shown in Figure 1. FeSO$_4$$\cdot$7H$_2$O, NaOH, and H$_2$SO$_4$ were of analytical grade. Titanium dioxide (Degussa P25) was used as the heterogeneous catalyst.

An ultrasonic processor (XH-2008DE, Xianghu, China) with a 18 mm diameter probe was used for sonication. The energy output was controlled by setting the amplitude of the sonicator probe.

2.2. Procedure. Sixty milliliters of fuchsin basic solution was put into a three-necked flask. The ultrasound probe was submerged to a depth of 10 mm in the solution. A temperature sensor was also immersed in the solution to measure the temperature. Three-necked flask was placed in the water bath whose temperature was controlled by refrigeration compressor system or heating system (Figure 2). The initial concentration of fuchsin basic was 10 $\mu$mol L$^{-1}$ for all experiments. Ultrasonic power was adjusted at 400 W, excluding runs conducted to investigate the influence of power. Aqueous samples were taken from the fuchsin basic solution, and the concentrations of dye were determined using a UV-vis spectrophotometer (UV-2550, Shimadzu). Chemical oxygen demand (COD) determinations were conducted according to ISO 6060 [18]. Hydrogen peroxide concentrations were determined using the iodometric method [19].

Experiments were performed at pH 6.5, which resulted from dissolution of fuchsin basic in distilled water without further adjustment. When the effect of pH was investigated, the solution pH was adjusted using dilute H$_2$SO$_4$ aqueous solutions.

In the research of adding TiO$_2$, mixture of fuchsin basic solution and TiO$_2$ was stirred for one hour in the dark to obtain adsorption equilibrium before ultrasonic irradiation. The concentration of fuchsin basic after adsorption equilibrium was taken as $C_0$ for calculating degradation ratio. Each experiment was performed in triplicate. The standard deviations of the values were calculated and used as error bars in the figures.

2.3. Analyses. Absorbance values of the solutions were measured at a wavelength of 542 nm, which corresponds to the maximum absorbance of fuchsin basic. The percentage of dye degradation was calculated as follows:

\[
\text{Extent of degradation } (\%) = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \tag{1}
\]

where $C_0$ is the initial dye concentration and $C_t$ is the dye concentration at measurement time.

3. Results and Discussion

3.1. Effect of Operating Parameters

3.1.1. Effect of Power. The effect of power on the degradation of fuchsin basic was studied by varying the ultrasonic power at 200 W, 300 W, 400 W, and 500 W, which corresponds to the actual acoustic power density injected into the sample solution at 0.042 W/mL, 0.084 W/mL, 0.14 W/mL, and 0.224 W/mL, respectively, by calorimetry [20]. According to Andaluri et al. [10] and Capocelli et al.’s [11] research, power density is an essential factor for ultrasonic degradation of organic pollutants. This agrees with our research result, as depicted in Figure 3; the extent of degradation of fuchsin basic increased markedly with an increase in the ultrasonic power. For example, extent of degradation 75.4% was obtained at 500 W whereas only about 38.3% was observed at 200 W after 60 min irradiation. The increase in fuchsin basic degradation with an increase in ultrasonic power may be explained by the increase in the number of active cavitation bubbles. In other words, at higher power intensity the concentration of hydroxyl radicals and the mass transfer are higher which lead to the more degradation of fuchsin basic [21, 22]. However, the efficiency of energy transfer to solution can also decrease with higher power intensities which are mostly due to the coalescence of the cavities at higher intensities [23]. Because 500 W is the upper limit of this ultrasonic equipment, it is not recommendable to use this power during all the ultrasonic processes. And in the following experiments, ultrasonic power was fixed at 400 W.

The degradation of fuchsin basic in aqueous solution under stirring condition (without sonication) was examined as a control experiment. As shown in Figure 3, in the absence of ultrasound irradiation the degradation did not take place...
at all. It is apparent that the ultrasound can accelerate the degradation of fuchsin basic from aqueous solution. The effects of ultrasound during reactions are due to cavitation which can induce instantaneous high local temperatures and pressures. Under such extreme conditions, the solvent water and/or dye molecular suffers hemolytic bond breakage to generate reactive species, for example, radicals, which then undergo a series of reactions resulting in the degradation of fuchsin basic rapidly [24].

3.1.2. Formation of Hydrogen Peroxide during Ultrasonic Irradiation. Under the sonic degradation of dye, water molecules suffer hemolytic bond breakage to generate H⁺ and •OH radicals, which then undergo a series of reactions resulting in the production of H₂O₂ [24]. The rate of H₂O₂ formed reflects the active •OH generation in the sonic process and also affects the extent of the sonic degradation of fuchsin basic. The iodometric method [19] was employed for detecting H₂O₂ in the absence and presence of fuchsin basic.

As shown in Figure 4, the formation of hydrogen peroxide was found to increase linearly with time of ultrasonic irradiation. It is noteworthy that in the presence of dye, the hydrogen peroxide production was lower than that in the substrate free water. The reaction of hydroxyl radicals with fuchsin basic competes with •OH radical combination; consequently, the presence of dye will decrease the hydrogen peroxide formation.

3.1.3. Effect of Initial pH. The effect of the initial pH on the degradation of fuchsin basic was investigated. The solution pH value could have important implications on the chemical structure of the substrate and therefore also affected the performance of the sonochemical process [25, 26]. The typical range considered to study the effect of initial pH in this research was from pH 3 to pH 6.5. Because of keeping increasing pH to about 9, the structure of fuchsin basic changes and results in fading and red sediment.

As shown in Figure 5, the extent of degradation follows the order: pH 6.5 > pH 5 > pH 4 > pH 3. Fuchsin basic is a nonvolatile compound, and the region of degradation would be at the exterior of the cavitation bubbles. Thus, the reaction between the radicals generated and fuchsin basic would be enhanced if its hydrophobicity is enhanced. Fuchsin basic has a superior hydrophobic character when its structure is in the molecular state which occurs at higher pH value. Under this condition, fuchsin basic is accumulated in the interface of the cavitation bubbles, and highest degradation rate is reached. However, at low pH values the amino group of fuchsin basic reaches the ionized state and its hydrophilicity and solubility are enhanced, and thus, the degradation is carried out in the bulk of the solutions, where there is a lower concentration of •OH because only about 10% of the •OH generated in the bubble can diffuse into the bulk solutions [27] and thereby results in lower decomposition of fuchsin basic in aqueous solutions.

3.1.4. Effect of Temperature. The effect of temperature on the sonochemical degradation of fuchsin basic was observed, and the results are shown in Figure 6. The raise in temperature from 15°C to 22°C resulted in a slight increase of extent of degradation from 62.7% to 66.5%. However, as the temperature continued to increase to 35°C, extent of degradation declined to 57.8%. With further increase to 60°C, the degradation was reduced obviously. Similar results were found in Emery et al.'s research [28]: the liquid bulk temperature of 5 and 20°C almost led to the same extent of degradation of triphenylphosphine oxide. However, further increase up to 70°C led to severely reduced degradation.

The effect of temperature on sonochemical degradation rate is complicated [27]. Increasing the reaction temperature will raise the equilibrium vapour pressure and lead to easier
cavitation, which will afford an increase in sonochemical effects. But at higher temperature a large number of cavitation bubbles are generated and will act as a barrier to sound transmission and dampen the effective ultrasonic energy from the source to the solution [24], which will lead to a decrease in sonochemical effects. Thus, there is no completely consistent report on the impact of temperature on the decomposition of organic compounds in the literature. Bhatnagar and Cheung [29] and Wu et al. [30] reported that the degradation of trichloroethylene and carbon tetrachloride remained constant between −7–20°C and 20–60°C, respectively. Whereas Destaillats et al. [31] indicated that the sonochemical degradation efficiency of trichloroethylene increased with increasing temperature.

3.1.5. Kinetics of Degradation and COD Removal by Ultrasound. In order to study the kinetics of the ultrasonic degradation of fuchsin basic in aqueous solution, the degradation rate constants were determined assuming pseudo first-order reaction kinetics as follows:

\[-\frac{dC}{dt} = kc \iff \ln \frac{C_0}{C_t} = kt, \tag{2}\]

where \(k\) is the pseudo first-order rate constant and \(C_0\) and \(C_t\) are the dye concentrations at time zero and \(t\), respectively. If the results of Figure 6 are plotted in the form of (2), \(k\) values can be computed from the slopes of the straight lines. These values are shown in Table 1. The highest value of \(k\) at temperature 22°C was obtained. Similar results have been reported in previous studies [11,32,33], where the ultrasonic degradation was found to obey pseudo first-order reaction kinetics.

Table 2 shows the degradation and the COD removal percentages under ultrasonic irradiation. It can be observed from the table that the fuchsin basic aqueous solution was decolorized within 120 min, but the mineralization was a relatively slow process with COD decrease. And the mineralization was found to be 35.2% and 40.3% after 60 min and 120 min radiation, respectively. These results underline that degradation products of fuchsin basic are recalcitrant toward ultrasonic treatment [34]. This may be due to the fact that the intermediate products have very low probabilities of making contact with \(\cdot\)OH radicals, which react mainly at the interface of the bubble [35].

3.2. Effect of Various Additives

3.2.1. Effect of Fe(II). Figure 7 depicts the influence of bivalent iron on the sonolytic degradation of fuchsin basic. In these systems, the ultrasonic degradation of fuchsin basic was
enhanced by Fe(II) addition. In the presence of Fe(II), the extent of degradation increased to 73.5%, 84.1%, and 83.1% for Fe(II) concentrations of 2, 4, and 6 mg/L, respectively. As discussed in this and other researches [36, 37], hydrogen peroxide can be formed from the combination of $\text{H}_2\text{O}_2$ and hydroxyl radical generation in the Fenton (Fe(II)/$\text{H}_2\text{O}_2$) and Fenton-like (Fe(III)/$\text{H}_2\text{O}_2$) processes (reactions (3)–(7)):

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^- \quad (3) \\
\text{Fe}^{2+} + \cdot \text{OH} & \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (4) \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe} - \text{OOH}^{2+} + \text{H}^+ \quad (5) \\
\text{Fe} - \text{OOH}^{2+} & \rightarrow \text{Fe}^{2+} + \text{HOO}^- \quad (6) \\
\text{Fe}^{3+} + \text{HOO}^- & \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \quad (7)
\end{align*}
\]

The slight decrease of degradation for 6 mg/L Fe(II) may be attributed to the addition of $\text{H}_2\text{SO}_4$ in preparing FeSO$_4$ solution, which prevented the hydrolysis of Fe(II). The addition of $\text{H}_2\text{SO}_4$ caused the decline of solution pH and the lower degradation ratio, which was described in the research of pH effect.

3.2.2. Effect of TiO$_2$. The effect of TiO$_2$ on the sonolytic degradation of fuchsin basic was also investigated, and the results are shown in Figure 8. When the dosage of TiO$_2$ was 1.2 g/L and 1.5 g/L, the extent of degradation reached 73.1% and 71.6%, respectively. Compared to that without TiO$_2$ (66.5%), the extent of degradation increased by 6.6% and 5.1%. While for the dosage of 0.6 g/L, the extent of degradation even decreased slightly. These results show no obvious enhancement of degradation by adding TiO$_2$. The results are shown in Figure 8. When the dosage of TiO$_2$ was 1.2 g/L and 1.5 g/L, the extent of degradation reached 73.1% and 71.6%, respectively. Compared to that without TiO$_2$ (66.5%), the extent of degradation increased by 6.6% and 5.1%. While for the dosage of 0.6 g/L, the extent of degradation even decreased slightly. These results show no obvious enhancement of degradation by adding TiO$_2$. The results demonstrate that TiO$_2$ can accelerate the sonolytic degradation of dye pollutants markedly. TiO$_2$ in sonocatalytic degradation may play the role like photocatalyst on the surface of which $^\cdot$OH radicals can form. However, it can also lead to screening effect, that is, shielding fuchsin basic molecules from receiving sonic waves to result in a drop of degradation. Furthermore, TiO$_2$ can also play as an adsorbent for dye molecules, so roles of adsorbent and catalyst should be distinguished. Differences of the type (i.e., anatase or rutile) and diameter of TiO$_2$ catalyst may also lead to these discrepant findings between this research and others.

3.2.3. Effect of Radical Scavenging Agents. To study the role of $^\cdot$OH in ultrasound degradation of fuchsin basic, the effect of $^\cdot$OH scavenging agents (DMSO, methanol, and mannitol) on the degradation of fuchsin basic under ultrasound irradiation for 60 min was examined [39]. As shown in Figure 9, the addition of the radical scavenging agents methanol (1%), DMSO (1%), and mannitol (5 $\mu$mol L$^{-1}$) significantly suppressed the degradation of fuchsin basic, possibly by quenching the $^\cdot$OH. Among the scavengers, DMSO was the most effective. The results demonstrate that $^\cdot$OH plays an important role in the ultrasound degradation of fuchsin basic, and the degradation process follows free radical mechanism.

4. Conclusions

The conclusions drawn from this study are summarized as follows. (1) Fuchsin basic can be readily eliminated by the ultrasound process, but the complete mineralization of dye did not occur. Ultrasonic degradation of fuchsin basic was found to obey pseudo first-order reaction kinetics. (2) The use of suitable catalysts (e.g., Fe(II)) that behave as radical promoters can improve process efficiency. (3) The radical
scavengers reduced the extent of degradation, which indicates that *OH plays an important role in the degradation of fuchsin basic, and the degradation process follows free radical mechanism.

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