



## Degradation of acid red 88 by the combination of sonolysis and photocatalysis

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### ABSTRACT

Acid red 88 (AR88) is a mono-azo textile dye and a widely used colorant in the textile and food industries. The sonolytic, photocatalytic and sonophotocatalytic degradation of AR88 in the presence of homogeneous ( $\text{Fe}^{3+}$ ) and heterogeneous ( $\text{TiO}_2$ ) photocatalysts were studied. The effects of initial dye concentration and ultrasound power on the sonochemical degradation were also investigated. The degradation by sonolysis and photocatalysis followed first-order like kinetics with respect to the concentration of AR88. The sonophotocatalytic degradation rates using  $\text{TiO}_2$  or  $\text{Fe}^{3+}$  were found to be higher than that observed with sonolysis or photocatalysis. The synergy index calculated for  $\text{TiO}_2$  sonophotocatalysis was 1.3, suggesting that the combination of sonolysis and  $\text{TiO}_2$  photocatalysis resulted in a small synergetic effect. Also, the sonophotocatalysis in the presence of  $\text{Fe}^{3+}$  was synergistic with a synergy index of 2.3. Total organic carbon (TOC) analysis was performed to study the extent of mineralization. TOC data showed that the mineralization using  $\text{TiO}_2$  sonophotocatalysis was additive whereas a synergistic mineralization was observed for the sonophotocatalysis in the presence of  $\text{Fe}^{3+}$ . The simultaneous operation of sono-Fenton and photo-Fenton reactions is likely to be the underlying reason for the observed synergy in the presence of  $\text{Fe}^{3+}$  assisted sonophotocatalysis. Electrospray mass spectrometry (ESMS) was employed for the identification of the degradation intermediates. The sonication of AR88 led to the formation of its mono and di-hydroxylated products as the primary intermediates. A possible degradation pathway has been proposed.

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### 1. Introduction

Azo dyes are among the notorious environmental pollutants associated with textile, food, cosmetic, printing and pharmaceutical industries. It has been estimated that more than 1–20% of the dye is released from the production sites into the aqueous environment and presents a major threat to the ecosystem. Several advanced oxidation processes (AOPs) have been proposed and widely applied for the degradation of many non-biodegradable, toxic, mutagenic and carcinogenic pollutants [1]. Many researchers have used AOPs such as photocatalysis, sonolysis, Fenton and modified Fenton reactions, ozonation and  $\text{UV}/\text{H}_2\text{O}_2$  for the degradation of azo dyes [2–6].

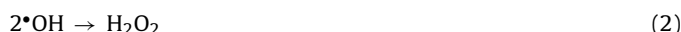
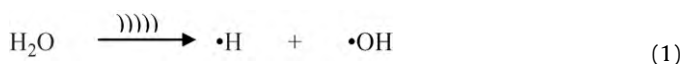
In recent years, much attention has been given to the sonochemical degradation of organic contaminants in aqueous environments [7–10]. Sonochemistry generally involves the chemical effects of ultrasound that arise when a sound wave is passed through an aqueous medium. Often, the generation of highly reactive radical species such as,  $\cdot\text{H}$  and  $\cdot\text{OH}$  are observed as a consequence

of the homolytic cleavage of water within the cavitation bubbles. Once these active radicals are formed, they non-selectively attack any organic pollutant present in the water phase and convert them into a variety of products. Sometimes the degradation products are more toxic than the parent compound itself. So the complete mineralization (conversion of organic pollutant into harmless products such as  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and mineral acids) is essential for any advanced oxidation process to be industrially applicable. The sonochemical degradation of azo dyes has been studied by many researchers world wide [9,11–14]. However, this technique often fails to achieve complete mineralization over short irradiation times due to several reasons, such as the formation of hydrophilic intermediate products, volatility of the pollutants, and reaction volume [15,16]. Hence, the combination of sonolysis with other advanced oxidation processes has been generally recognized as a suitable tactic in order to overcome the limitations of the sonochemical degradation process alone [17–19]. Peller et al. [15] reported that the formation of hydrophilic intermediates derived from the sonolytic degradation of hydrophobic substrates tends to slow down the mineralization rate. Therefore, the combination of sonolysis with photocatalysis (sonophotocatalysis) is often considered to be a suitable adaptation because sonolysis is

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able to degrade the hydrophobic products and photocatalysis can degrade the hydrophilic products.

The most commonly used heterogeneous photocatalyst is titanium dioxide (Degussa P25). The general mechanism of action of TiO<sub>2</sub> mediated degradation of organic pollutants has been widely reported in the literature [4]. Similarly, homogeneous photocatalysis using Fenton (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) and modified Fenton reagents (Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub>, ferrioxalate, Fe<sup>3+</sup>/oxone, etc.) has also been reported as a useful method for the degradation of aqueous organic pollutants [20]. The Fenton oxidation process operates by producing hydroxyl radicals through the splitting of hydrogen peroxide by iron salts. The ultrasound assisted water splitting to produce hydrogen peroxide (Reactions (1) and (2)) is considered to be the main advantage of combining sonolysis with Fenton (sono-Fenton) since the external addition of hydrogen peroxide is not required.



The combination of two individual processes may show a negative or an additive or a synergistic effect. The synergistic degradation and mineralization of organic solutes by sonophotocatalysis has been reported in the literature [15,16,21–25]. For example, Theron et al. [23] observed a synergy between photocatalysis and sonolysis at 30 kHz for the degradation of phenyltrifluoromethylketone. Kaur and Singh [24] studied the sonophotocatalytic degradation of reactive red 198 using dye sensitized TiO<sub>2</sub> and reported that the combined process yielded synergistic degradation with a synergy index of 2.5 when compared to the individual sonolysis and visible light assisted photocatalysis. An et al. [25] reported that the sonophotocatalytic degradation rate of reactive brilliant orange K-R using a 47 kHz sonicator was about 3.7 times higher than that of the individual processes. Madhavan et al. [8] recently showed that the synergy index of the sonophotocatalytic degradation of orange G in the presence of Fe<sup>3+</sup> ions was about 1.4.

The photocatalytic degradation and mineralization of acid red 88 (AR88) in the presence of doped/undoped TiO<sub>2</sub> using either UV or visible radiation has already been reported [26–28]. To the best of our knowledge, the sonochemical and sonophotocatalytic degradation of AR88 using Degussa P25 TiO<sub>2</sub> has not been studied. The present investigation examines the sonolytic, photocatalytic and sonophotocatalytic degradation of acid red 88 using TiO<sub>2</sub> and Fe<sup>3+</sup> in order to expand the knowledge base in the area of sonophotocatalysis.

## 2. Experimental details

### 2.1. Experimental conditions

All experiments involving ultrasound, except power variation, were performed at an ultrasound (US) frequency of 213 kHz in a continuous wave mode with a power output of 55 mW mL<sup>-1</sup>. The actual power experienced by the aqueous dye solution was calculated by the calorimetric method [29]. A commercially available ELAC LVG-60 RF generator coupled with an ELAC Allied Signal transducer with a plate diameter of 54.5 mm used as the source of ultrasound. Unless otherwise mentioned, all chemicals used were of analytical grade and were used without further purification. The desired concentration of acid red 88 (C.I. 15620, Sigma–Aldrich) was prepared from the stock solution using Milli-Q water. Titanium dioxide (TiO<sub>2</sub> Degussa P25; surface area 55 m<sup>2</sup>/g) was used as the heterogeneous photocatalyst. Hydrated iron (III) nitrate (Fe(NO<sub>3</sub>·9H<sub>2</sub>O) purchased from Sigma–Aldrich was used for carrying out the Fenton-like degradation reactions. The temperature (25 ± 2 °C) around the reaction cell was maintained by a constant

temperature water bath. A Xenon arc lamp (450W, Oriel, USA) was used for photocatalytic reactions and a 320 nm cut-off filter was fitted at the exit of the light set-up to ensure that only the radiations with wavelength above 320 nm reach the reactor.

All sonolytic, photocatalytic and sonophotocatalytic experiments were performed in the same experimental setup and the volume of the solutions taken was 250 mL. A desired concentration of AR88 was prepared by dissolving the appropriate amount in 250 mL water and then 1 g L<sup>-1</sup> of TiO<sub>2</sub> was added to the dye solution. The pH was adjusted to 2.7 using HCl (1 M). In our previous study [30], a maximum photocatalytic degradation rate was observed at 1 g L<sup>-1</sup> and therefore experiments at lower or higher catalyst loadings were not carried out. The aqueous suspensions were mixed continuously using a mechanical stirrer in the dark for 45 min to allow the equilibrium adsorption of AR88 onto the photocatalyst surface. The concentration of the dye in solution obtained after equilibrium adsorption was used for further kinetic analysis [31]. During irradiation, 3 mL aliquots were withdrawn at appropriate time intervals and the photocatalyst was filtered immediately through a 0.45 μm syringe filter (Pall Corporation).

### 2.2. Analytical determinations

The degradation products were analyzed using electrospray mass spectrometry (ESMS). The mass spectrometer used was a Micromass QUATTRO 11 coupled to a Hewlett Packard series 1100 degasser. The instrument was calibrated using the automatic tuning procedure with respect to the parent compound as the standard. The mass range scanned was *m/z* 50–1000 and several spectra were obtained across each chromatographic peak. The analysis was carried out in negative electrospray ionisation mode at cone voltages of 30 V, 50 V and 80 V. The mobile phase consisted of 50/50 (acetonitrile/water). The flow rate of the solvent was 0.03 mL/min and the capillary voltage was set at 3.5 kV. The concentration of AR88 was determined by a high-performance liquid chromatograph, Shimadzu LC-10 AT VP system with a Shimadzu SPD-M10 A VP photo diode array detector with a Phenomenex reversed phase column (Kromasil, C18, 250 mm × 4.6 mm inner diameter, 5 μm beads). The separation was carried out using a binary gradient elution (Solvent A = 0.1 M ammonium acetate and Solvent B = 100% acetonitrile). The gradient used was 25% B reaching 50% in 20 min and the flow rate was maintained at 1.0 mL/min. The peak for AR88 appeared at the retention time of 18.5 min in the chromatogram.

TOC was determined using a TOC-V<sub>CSH</sub> (Shimadzu) instrument which operates through oxidative combustion followed by infrared detection. The instrument was calibrated before each use with standard solutions in the range 1–100 mg L<sup>-1</sup>. A Cary Varian 50 Bio UV–visible spectrophotometer was used to record the absorption spectrum of the AR88 solution. The samples were placed in a quartz cell and the spectra were recorded in the wavelength range 200–600 nm.

## 3. Results and discussion

### 3.1. Effect of [AR88]

The effect of concentration of AR88 on the sonolytic degradation was studied by varying its concentration in the range 0.025–0.09 mM. It was observed that the sonolytic degradation followed first-order-like kinetics with respect to the concentration of AR88. Plots of ln[AR] vs. time were linear (data not shown). The slope of the plot yielded first-order rate constants. It was observed that the first-order rate constants decreased with increasing initial concentration of AR88. Hence, the sonolytic degradation of AR88 cannot be strictly considered as a first-order reaction. The observed

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