



Ultrasound-assisted homogeneous photocatalytic degradation of Reactive Blue 4 in aqueous solution



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ABSTRACT

The catalytic degradation of Reactive Blue 4 (RB4) by an emerging ultrasound-assisted photo-Fenton process with artificial ultraviolet light was investigated. The photocatalytic degradation efficiency was determined by the decrease in Total Organic Carbon (TOC) content. The influences of pH and initial concentrations of Fe(II) and H₂O₂ on the RB4 solution mineralization were studied. Under the optimal conditions, TOC removal increased up to 94% in 60 min, and this system permitted the use of a low ferrous concentration of only 5 mg L⁻¹. The RB4-mineralization process in the sono-photo-Fenton system can be described by a mechanism involving mineralization by direct photolysis, ultrasonically generated oxidative species, direct oxidation reaction with H₂O₂, radical reaction (mainly HO•) and thermal pyrolysis inside the bubble. The radical reaction in the bulk solution or in the vicinity of the bubble was found to be the main mineralization pathway. The contribution of different mechanisms to overall mineralization was the following: radical reaction (93.60%), direct reaction with H₂O₂ (2.56%), photolysis (1.92%) and reaction by ultrasonically generated oxidative species (1.92%). The influence of the Fe catalyst on the radical reaction was evaluated by conducting the reaction in the presence and absence of the scavenging agent potassium iodide (KI). The toxicity profile of sono-photo-Fenton process was also evaluated.

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1. Introduction

Reactive dyes are extensively used in the textile industry. Under typical reactive dyeing conditions, up to 50% of the initial dye remains in the spent dyebath in its hydrolyzed form resulting in effluent containing high levels of organic and color contaminants [1]. The color and toxicity of dyes influence the quality of life by causing health problems, in addition to influencing the efficiency of some water treatment techniques. One of the major difficulties in treating this type of colored wastewater is that biological processes tend to be ineffective despite the fact that they are generally more economic in comparison with other treatments options [2,3]. Conventional treatment processes for textile wastewater usually involve coagulation–flocculation, adsorption, and activated sludge, all of which are quite ineffective for the decoloration of wastewater due to the high molecular weight and high water solubility. Additionally, these processes do not destroy or degrade dyes; they only remove them physically from the effluent, leaving sludge for eventual disposal in landfills [4–6].

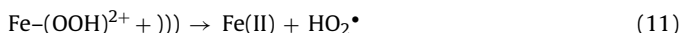
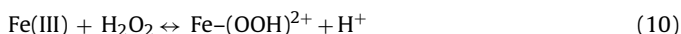
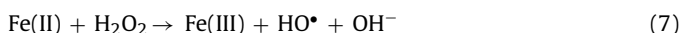
In order to overcome these weaknesses, efficient treatments of these effluents by the so-called advanced oxidation processes (AOPs) such as ozonation, photocatalysis, Fenton or a combination of photo-Fenton, UV/O₃, UV/H₂O₂, UV/TiO₂ have been developed in the last decades [7–9]. In addition, ultrasonic dye degradation in the homogeneous and heterogeneous solutions as basic or auxiliary process for dye remediation has also been widely studied [10]. These studies have shown that ultrasonic irradiation alone is ineffective for dye degradation, but quite effective when combined with other AOPs [11–15]. The sonochemical reaction pathways for the degradation of pollutants species involve the reaction with hydroxyl radicals and a thermal reaction. The hydroxyl radicals are produced by the sonolysis of water as the solvent inside the collapsing cavitation bubbles under extremely high temperature and pressure [16]. The ultrasound-induced splitting of water molecules causes the reactions shown in Eqs. (1)–(6) [17–19].



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The hydroxyl radicals generated by sonolysis can react with the dye molecule and a large majority of them are recombined to H_2O_2 inside the cavitation bubble and at the gas–liquid interface before being ejected into the bulk solution. Depending on the frequency of irradiation and applied power, only a small fraction of HO^\bullet escape from the interfacial region and diffuse into the bulk solution [20]. Alternatively, compounds inside or in the vicinity of a collapsing bubble may undergo pyrolytic decomposition due to the high local temperature and pressure [21]. It is generally believed that hydrophilic and non-volatile compounds mainly degrade through hydroxyl radical mediated reactions in the bulk solution, while hydrophobic and volatile species degrade thermally inside or in the vicinity of the bubble [22]. Previous studies have demonstrated that the addition of chemicals, such iron ions or combination with UV radiation, can amplify ultrasonic action [23,24]. Among these combination methods, photo-Fenton system in conjunction with ultrasonic irradiation (sono-photo-Fenton) produces extra hydroxyl radicals, regenerates Fe(II) and promotes the rate of degradation of pollutants [25–27] according to the following reactions:



Anthraquinone dyes constitute the second largest class of textile dyes after azo dyes, and they are used extensively in the textile industry. Reactive Blue 4 (RB4) was selected as model reactive anthraquinone dye for this investigation. Recently, many AOPs using Fenton reaction with or without UV light, heterogeneous catalysts such as TiO_2 combined with artificial UV or solar light sources or solar photocatalytic-Fenton system have been evaluated for the decoloration and degradation of RB4 dye. Neppolian et. al. reported that direct solar light induced and TiO_2 process achieved complete degradation of 4×10^{-4} M RB4 solution within 8 h in the presence of 300 mg L^{-1} of H_2O_2 [28]. Photo-Fenton degradation of RB4 was investigated and 75% TOC removal of 20 mg L^{-1} RB4 solution after nearly 120 min at pH 2 in the presence of 300 mg L^{-1} of H_2O_2 and 4 mg L^{-1} of Fe^{2+} was attained [29]. Photo-Fenton process under artificial and solar irradiation of RB4 was studied and the best results were obtained using 1.0 mM ferrioxalate and 10 mM of H_2O_2 . In this case, 80% TOC and 100% of color removal were obtained for 0.1 mM RB4 dye in 35 min of solar irradiation [30]. The heterogeneous photocatalytic mineralization of RB4 solution under a UV/Fenton/ TiO_2 system with concentrated solar light irradiation using a Fresnel lens was also studied. After 120 min, total decoloration was reached, whereas only 50% of TOC was removed [31]. The effect of operational conditions on decoloration of RB4 solutions using zero-valent iron reductive transformation has been reported [32]. 90% color removal of RB4 solution was achieved by combined Fe(III)/ TiO_2 catalyst and ultrasonic irradiation but no data of mineralization were presented [15]. To our knowledge, no study of mineralization of RB4 solution under homogeneous sono-photo-Fenton process has also been reported to date.

The aim of our work was to study the decoloration and mineralization of RB4 solutions by low frequency (24 kHz) ultrasonic irradiation in conjunction with photo-Fenton's reagent (sono-photo-Fenton system). An initial comparative study on RB4 mineralization by using different degradation systems has been carried out. The effects of pH and initial concentrations of Fe(II) and H_2O_2 on mineralization reaction by the sono-photo-Fenton process were determined. Finally, a kinetic and degradation mechanism study of the sono-photo-Fenton process was performed. The toxicity profile of such treatment was evaluated.

2. Experiment

2.1. Materials

RB4 ($\text{C}_{23}\text{H}_{14}\text{Cl}_2\text{N}_6\text{O}_8\text{S}_2$) solutions were prepared from pure compound purchased from Aldrich. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Panreac, analytical grade) and hydrogen peroxide (30% w/v, Merck) were used as received. pH was previously adjusted (between 2 and 8) by using 0.1 M H_2SO_4 and 6 M NaOH solutions. The initial concentration of TOC in the RB4 solution was always 30 mg L^{-1} .

2.2. Experimental runs

All experiments were carried out in a 400-mL stirred photoreactor with an external jacket connected to a thermostatic bath to maintain a constant temperature ($30 \pm 0.5^\circ\text{C}$). A Heraeus UV Hg immersed lamp TNN 15/32 with a nominal output of 15 W and emitting a monochromatic radiation at 254 nm was used to irradiate the solution. The UV-radiation intensity of the UV-lamp as measured with potassium ferrioxalate was $7.81 \times 10^{-6} \text{ Einstein s}^{-1}$. A 24 kHz, 200 W direct immersion horn sonicator (UP200S with an S14 sonotrode, Hielscher) was used to generate ultrasonic sound waves in the sonoreactor. The amplitude of the oscillatory system (power output) can be steplessly adjusted between 20% and 100%. The pulse mode factor (cycles) can be continuously varied between 10% and 100%. The set value equals the acoustic irradiation time in seconds, the difference to 1 s is the pause time. Thus, a setting of 1 implies that it is continuously switched on, whereas a setting of 0.6 means a power discharge of 0.6 s and a pause of 0.4 s. Amplitude and pulse length (cycles) were maintained constant at 60% and 1%, respectively.

The scavenging of hydroxyl radicals was accomplished with potassium iodide to quantify the oxidation levels from radical reactions. Before data analysis was done, all samples were withdrawn from the reactor for H_2O_2 analysis and immediately treated with excess Na_2SO_3 solution to prevent further oxidation (this procedure was performed to prevent an overestimation of the degradation).

2.3. Analysis

The mineralization grade of RB4 solution was determined by TOC variation, which was measured with a TOC-5050 Shimadzu analyzer (standard deviation $< 0.2 \text{ mg L}^{-1}$). The H_2O_2 content in the solution was determined by titration through an aqueous solution of potassium permanganate (0.02 M) using an automatic Titrino SET/MET 702 (Metrohm). The ferrous concentration was obtained via photometric measurement with 1,10-phenanthroline (according to ISO 6332) using a UV-Vis spectrophotometer (Zuzi 4418PC). Toxicity was evaluated by determining the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (Luminescent bacteria test; 30 min incubation time) using a

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