

Characterization of C.I. Basic violet 10 degradation under ultrasonic treatment

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Abstract

In this work, Basic violet 10 (BV10) sonolysis has been characterized. The experiments have been conducted using an ultrasonic reactor operating at 300 kHz and 60 W. The degradation of the dye during the sonolytic reaction was assessed by absorption abatements at two bands: the visible, which is responsible for the chromophoric compound, and at UV-254, which represents the absorption of aromatic rings in the dye. The obtained results indicate that the rate of the color decay was not first order kinetic as generally reported in the literature. The destruction of the aromatic ring in the dye was slower than that of color, signifying the priority of hydroxyl radical attack on the chromophoric group of the dye. It was also found that the BV10 removal efficiency decreased with increasing initial dye concentration while, initial degradation rate of the dye increased in a non-linear manner with the increase in the initial BV10 concentration.

Keywords: Ultrasonic treatment; dye; Basic violet 10 (BV10); Degradation; Hydroxyl radicals.

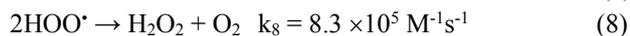
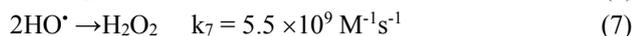
I. Introduction

Dye pollutants in wastewaters are the principal source of environmental aqueous contamination. The release of colored wastewaters in the ecosystem is a dramatic source of aesthetic pollution and perturbations in aquatic life [1]. Their removal from water is thus ecologically necessary to offer a cleaner environment as a requirement for human health and has attracted the most wanted attention of environmentalists, technologists and entrepreneurs. A variety of physical, chemical and biological methods are presently available for the treatment of wastewater discharged from various industries. Conventional methods of the treatment of dye wastewater include adsorption [2], chlorination and ozonation [3,4] electrochemical methods [5,6], biological methods [7-9] and chemical oxidation [10,11]. Recently, photocatalysis has been successfully used to oxidize many organic pollutants and particularly to decolorize and mineralize dyes [12-13].

Over the past two decades, sonochemical degradation of organic pollutants in water has been extensively investigated [14–18]. The chemical effects of sonication arise from acoustic cavitation, namely the formation, growth, and implosive collapse of bubbles in a liquid,

which produces unusual chemical and physical environments [14]. The collapse of the bubbles induces localized extreme conditions (high temperature and high pressure). It has been reported that the gaseous contents of a collapsing cavity reach temperatures as high as 5200 K and pressures higher than 1000 atm inside the collapsing cavity, and about 1900 K in the interfacial region between the solution and the collapsing bubble [19]. The consequences of these extreme conditions are the cleavage of water molecules (into H[•] atoms and HO[•] radicals) and dissolved oxygen molecules (reactions (1) and (2)) [19]. From the reactions of these entities (O, H[•], HO[•]) with each other and with H₂O and O₂ during the rapid cooling phase, HO₂[•] radicals and H₂O₂ are formed [18]. Hydroxyl radical as well as homolytic oxygen are produced in the bubble during the implosion [15,16]. Radicals combine in the bubble (reactions 3–5) or escape from the bubble, which conducts to H₂O₂ release in the medium (reactions 7 and 8) [19].





The two major pathways for the sonochemical degradation of organic compounds in dilute aqueous solution are: (i) thermal decomposition (pyrolysis or combustion reactions if oxygen is present during the implosion) of volatile pollutant molecules entrapped inside the bubble and (ii) the reaction of HO radicals with the solute at the bubble interface and in the bulk solution [18,19]. In this connection, the degradation of pollutants is strictly related to their physicals and chemicals characteristics. The characterization of substrates sonolysis is thus very important for determining the oxidation mechanism under ultrasonic treatment.

The objective of this work was to characterize sonochemical degradation of a cationic organic dye, C.I. Basic violet 10 (BV10), in water. The experiments have been conducted with an ultrasonic reactor operating at 300 kHz and 60 W. The sonochemical degradation of BV10 can also be representative of the reactivity of organic dyes, including textile ones, which can be degraded by ultrasound.

II. Materials and methods

Basic violet 10 (Abbreviation: BV10; chemical class: Xanthene; molecular formula: $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$; molecular weight: $479.01 \text{ g mol}^{-1}$) was purchased from Acros Organics. All other chemicals were reagent grade and were used as received: NaOH (Biochem) and H_2SO_4 (Biochem).

Sonolysis experiments were performed in water-jacketed cylindrical glass reactors (Figure 1). Ultrasonic waves (300 KHz, 60 W) were emitted from the bottom of the reactor through a piezo-electric disc ($\Phi = 4 \text{ cm}$) fixed on a Pyrex plate ($\Phi = 5 \text{ cm}$). Ultrasonic energy dissipated in the reactor ($\sim 45 \%$ of the electrical power input) was estimated by the calorimetric method [20].

All the BV10 solutions were prepared with distilled water. Sonolytic degradation of BV10 was carried out under different conditions using constant solution volume of 300 mL. The temperature of the solution was kept at $25 \text{ }^\circ\text{C}$ with circulating water. Aliquot samples were periodically taken from the reactor to determine the BV10 concentration using Jenway 6405 UV-Vis spectrophotometer.

Chemical oxygen demand (COD) was measured according to the method presented by Thomas and Mazas [21], using a dichromate solution (Aldrich) as the oxidizer in a strong acid medium. Test solution (2 mL) was transferred into the dichromate reagent and digested at 150°C for 2 h. The optical density for the color change of

dichromate solution was determined spectrophotometrically.

Hydrogen peroxide concentrations were evaluated using the iodometric method [20] using

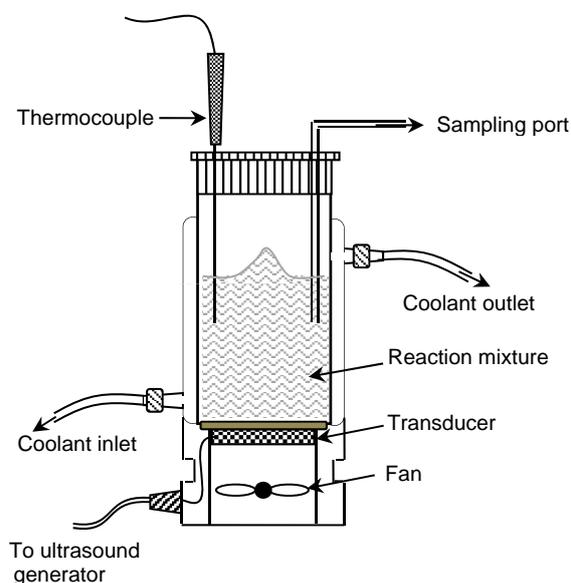


Figure 1. Scheme of the ultrasonic reactor

ammonium heptamolybdate as catalyst for H_2O_2 reaction with iodide ions.

III. Results and discussion

The ultrasonic treatment of 0.5 mg L^{-1} BV10 in aerated solution caused a substantial decrease of the 551 nm absorbance within 40 min of sonication (Figure 2a). The BV10 concentration decreased exponentially with time following apparent first-order kinetics (Figure 2b). Besides the degradation process, the ultrasonic treatment resulted in the formation of hydrogen peroxide (reactions K_7 and 8), which can be used to estimate the amount of HO radicals released by the bubble at determined sonochemical condition ($k_7 \gg k_8$). In absence of substrate, H_2O_2 accumulation increased linearly with time (Figure 2b). BV10 is a charged substrate and is a highly water soluble (Henry's law constant: $2.2 \times 10^{-21} \text{ atm m}^3 \text{ mol}^{-1}$, solubility: 120 g L^{-1} [15]); consequently, it cannot enter the bubble but must be eliminated through reaction with hydroxyl radicals (HO^{\bullet}) at the exterior of the collapsing bubble. From Figure 2b, it can also be seen that if ultrasonic action eliminated BV10 in less than 80, it conducted only to a low decrease in organic matter which can be oxidized. In fact, when BV10 was completely destroyed, only 60% of COD has been removed, and, even at the end of treatment (2h), more than 30 % of initial COD remained in solution. These results underline the fact that degradation products of BV10 are recalcitrant toward

sonochemical treatment. The formation of hydroxylated intermediates with higher hydrophilic character, which were confirmed by Mehrdad and Hashemzadeh [22], explains the low efficiency of the ultrasonic action for COD removal. These intermediates products stay in the bulk solution and do not accumulate at the cavitation bubble interface where the HO^\bullet radical concentration reaches an upper limit [20].

Consequently, probabilities of these products to make contact with $\bullet\text{HO}$ radicals are very low.

In addition to DCO measurement, UV band of reaction mixture at 254 nm can also be used to monitor the progress of the sonolytic degradation of the dye [23]. Figure 3 shows the change in UV-254 and visible (color) bands of BV10 solution at different ultrasonic irradiation time. It is observed that the absorbance at 254 nm, which reflect the absorption of aromatic ring [23], decreased during the initial 20 min of sonication (the absorbance decay of UV-254 band was 64 %). This is due to the degradation of the carboxyphenyl substitutes by cleavage of their aromatic ring upon HO^\bullet attack. Note that under the same conditions, total color decay was 68 %. However, when the reaction progressed ($t > 20$ min), absorption in all UV bands increased with increasing irradiation time up to 100 min and decreased afterward, indicating the formation of degradation intermediates, nitrite and nitrate, while the BV10 consequently, the UV-254 absorbance decreases. It is

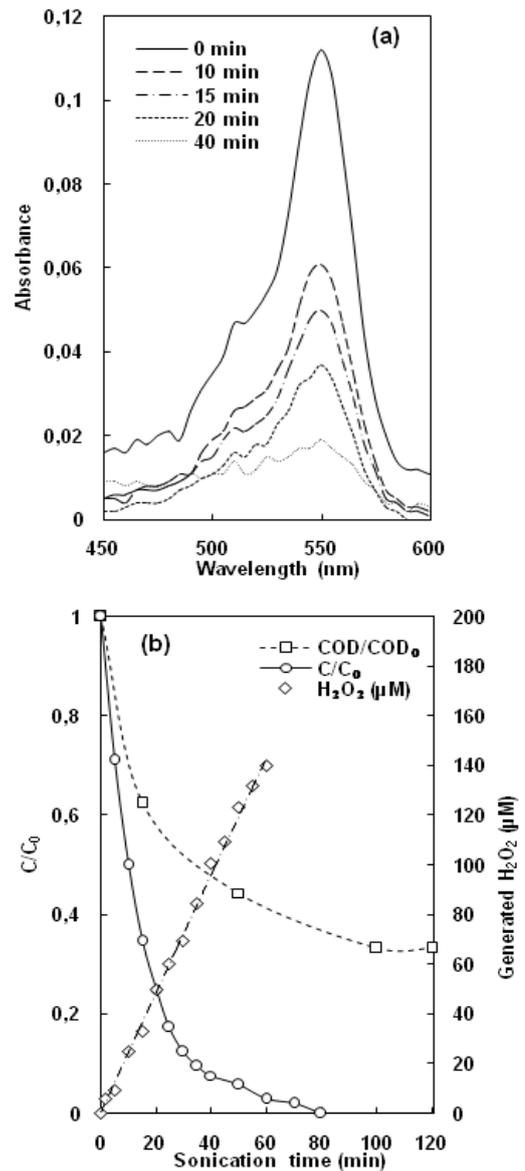


Figure 2: (a) Time evolution of the visible absorption spectrum of BV10 and (b) H_2O_2 formation, BV10 and COD removal upon ultrasonic action (conditions: $V = 300$ mL; $C_0 = 0.5$ mg L^{-1} ; $T = 25$ °C; $\text{pH} = 8.3$; $f = 300$ kHz; $P = 60$ W).

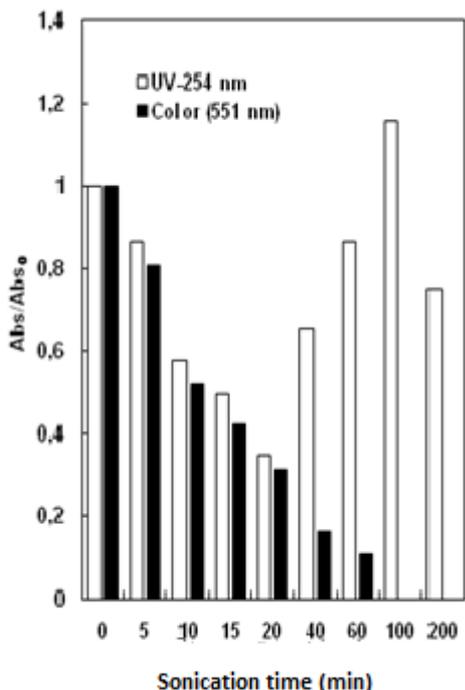


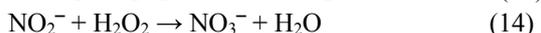
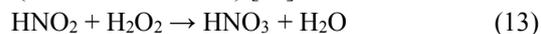
Figure 3: Temporal change in UV₂₅₄ and visible bands of BV10 solution under ultrasonic treatment (conditions: V = 300 mL; C₀ = 0.5 mg L⁻¹; T = 25 °C; pH = 8.3; f = 300 kHz; P = 60 W).

important to note that the degree of UV-254 destruction during the initial phase of sonolysis is lower than that of color, signifying the priority of HO• attack to the chromophoric group of the dye and hence, the rapidly increased mass of aromatic intermediates that likely absorb UV light at 254 nm. Sonolysis of BV10 leads to a decrease of the pH of solution. In our conditions (0.5 mg L⁻¹ BV10, 300 kHz and 60 W), pH of the solution drops rapidly from 8.3 to 3.72 for 80 min of sonication time. The decrease in solution pH during sonochemical degradation can be attributed to:

(i) The formation of nitrous and nitric acids (released generally as nitrite and nitrate ions respectively) under ultrasound action of aerated solution [19,24]. NO, the primary product of the process should be formed at high temperature inside the bubbles according to the reactions 2, 9 and 10 [19, 23]. Reactions 11 and 12 at the interface conduct to NO₂⁻ releases in the medium [19, 24].



Nitrites are in their turn oxidized to nitrates by hydrogen peroxide (reactions 13 and 14) [24].



It is important to note that in the same as our conditions, Torres et al. [24] found that, both nitrite and nitrate ions concentrations increased with sonication time, reaching a maximum (approximately 300 μM for both nitrite and nitrate ions) after 90 and 150 min respectively.

(ii) The formation of aliphatic acids as final degradation products contributes also to the decrease of the pH of the medium.

The variation of both removal efficiency and initial degradation rate of BV10 versus initial dye concentration is shown in Figure 4. As shows this figure, the removal efficiency of BV10 decreased with increasing initial dye concentration in the range 0.5-100 mg L⁻¹. The BV10 elimination was completely achieved after 80 min of sonication for 0.5 mg L⁻¹ BV10, but the removal efficiency decreased to 93.7, 84.5, 76 and 51 % when the initial concentration of BV10 was increased to 5, 20, 40 and 100 mg L⁻¹ respectively. The reduced removal efficiency at high BV10 concentrations was attributed to the competition between various BV10 molecules and/or the intermediate products formed during the sono-oxidation process. Both BV10 and its transformation products can compete for hydroxyl radical generated from the cavitation bubble. The BV10 removal efficiency was, therefore, decreased as a result of increasing competition with the HO• radical when initial dye concentration was higher. From Figure 4, it can also be observed that the higher the substrate concentration was, the higher the initial degradation rate was.

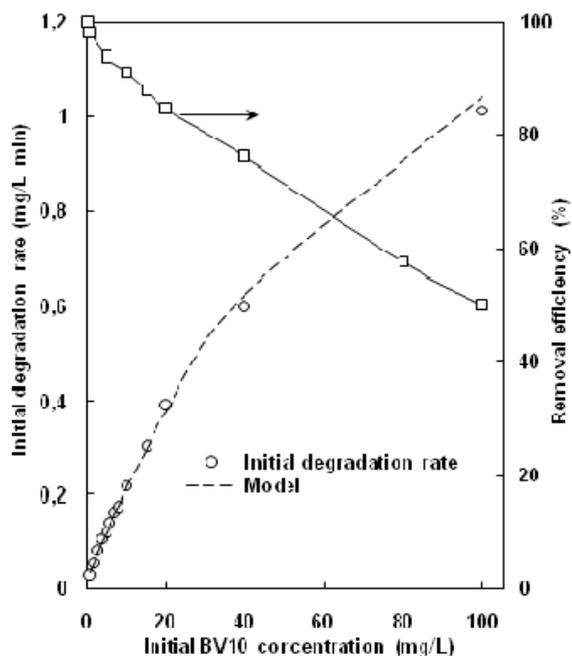


Figure 4: Initial degradation rate and efficiency removal of BV10 for various initial dye concentrations (conditions: V = 300 mL; C₀ = 0.5-100 mg L⁻¹; T = 25 °C; pH: 5.3; f = 300 kHz; P = 60 W)

However, a linear relationship was not observed, as expected, for a first-order kinetic law. The absence of linear relationship between the initial degradation rate and the initial BV10 concentration clearly indicate that, as evidenced in the case of several organic compounds [16,25-27], sonochemical BV10 elimination is not only related to the dye concentration but also to the local concentration of HO• radicals. Therefore, sonolytic removal of BV10 cannot be associated with first-order kinetics, as generally reported in the literature [28,29]. However, even if the overall rate for the degradation of BV10 cannot be associated with first-order kinetics, the degradation rate displays a biphasic behavior. At low (< 20 mg L⁻¹), degradation primarily occurs with HO• radicals in the bulk [30], and the rate of BV10 decay can be related to a first order kinetics ($r_1 = 0.018[\text{BV10}]_0$, $R^2 = 0.995$). At high concentration (> 20 mg L⁻¹), much of the sonochemical activity occurs at bubble/liquid interface and degradation can be assimilated by: $r_1 = 0.004 [\text{BV10}]_0 + 0.356$ with $R^2 = 0.93$. The overall BV10 degradation rate is given as a combination of the two regimes, and is shown in Equation 15.

$$r_1 = a + \frac{b[\text{BV10}]_0}{1+c[\text{BV10}]_0} \quad (15)$$

where $a = 5.42 \times 10^{-3} \text{ mg L}^{-1} \text{ min}^{-1}$, $b = 22.33 \times 10^{-3} \text{ min}^{-1}$ and $c = 11.76 \times 10^{-3} \text{ L mg}^{-1}$.

Equation 15 indicates that the rate of disappearance of the pollutant follows a concentration independent path and a concentration-dependent course. The first term in Equation 15 represents a pathway which is independent of BV10 concentration for low initial dye concentrations. At high concentrations the sonoreactivity shows characteristics given by the second term in Equation 15, which are similar to Langmuir adsorption processes involving a gas/liquid interface [30]. A perfect description of the sonolytic destruction of BV10 was obtained by the used model as shown in Figure 4.

V. Conclusion

This paper described the sonochemical degradation of Basic violet 10 (BV10) using a high frequency of ultrasound wave (300 kHz). The obtained results clearly indicate that the ultrasonic action can be efficiently used to eliminate Basic violet 10 dye from aqueous solution. The rate of the color decay was not first order kinetic as generally reported in the literature. The destruction of the aromatic ring in the dye was slower than that of color. It was also found that the BV10 removal efficiency decreased with increasing initial dye concentration while, initial degradation rate of the dye increased with the increase in the initial BV10 concentration. A perfect description of the

sonolytic destruction of BV10 was obtained by the use of heterogeneous kinetics model based on a Langmuir type mechanism.

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