



Influence of bicarbonate and carbonate ions on sonochemical degradation of Rhodamine B in aqueous phase

Slimane Merouani^a, Oualid Hamdaoui^{a,*}, Fethi Saoudi^a, Mahdi Chiha^a, Christian Pétrier^b

^a Laboratory of Environmental Engineering, Department of Process Engineering, Faculty of Engineering, University of Annaba, P.O. Box 12, 23000 Annaba, Algeria

^b LEPMI, Université Joseph Fourier, 38402 Saint Martin d'Hères Cedex, France

ARTICLE INFO

Article history:

Received 12 August 2009

Received in revised form 5 October 2009

Accepted 12 October 2009

Available online 20 October 2009

Keywords:

Ultrasound
Degradation
Bicarbonate ion
Carbonate ion
Carbonate radical

ABSTRACT

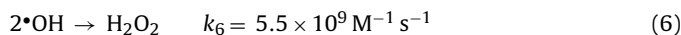
The influence of bicarbonate and carbonate ions on sonolytic degradation of cationic dye, Rhodamine B (RhB), in water was investigated. As a consequence of ultrasonic cavitation that generates $\bullet\text{OH}$ radicals, carbonate radicals were secondary products of water sonochemistry when it contains dissolved bicarbonate or carbonate ions. The results clearly demonstrated the significant intensification of sonolytic destruction of RhB in the presence of bicarbonate and carbonate, especially at lower dye concentrations. Degradation intensification occurs because carbonate radicals sonochemically formed undergo radical–radical recombination at a lesser extent than hydroxyl radicals. The generated carbonate radicals are likely able to migrate far from the cavitation bubbles towards the solution bulk and are suitable for degradation of an organic dye such as RhB. Therefore, at low dye concentrations, carbonate radical presents a more selective reactivity towards RhB molecules than hydroxyl radical. In the presence of bicarbonate, degradation rate reached a maximum at 3 g L^{-1} bicarbonate, but subsequent addition retards the destruction process. In RhB solutions containing carbonate, the oxidation rate gradually increased with increasing carbonate concentration up to 10 g L^{-1} and slightly decreased afterward. Carbonate radicals sonochemically generated are suitable for total removal of COD of sonicated RhB solutions.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Chemical reactions ensuing from ultrasonic irradiation of a solution are produced through the phenomenon of cavitation. Cavitation refers to the rapid growth and implosive collapse of bubbles in a liquid resulting in an unusual reaction environment within and in the vicinity of bubbles [1]. Compression of gas and vapor within the bubbles generates intense heat and can generate local hot spots. The concentration of energy upon collapse results in extreme localized conditions including high temperatures ($\sim 5000\text{ K}$) and pressures ($\sim 300\text{ atm}$) inside the cavity [2]. Under such conditions both inside and in the fluid surrounding cavitation bubbles, a wide range of chemical and physical processes may occur. During the heating of the cavity, homolysis/pyrolysis reactions of the gaseous contents occur, resulting in radical formation. In aqueous systems, water vapor is cleaved into $\text{H}\bullet$ and $\bullet\text{OH}$ radicals, and with other species present, various other radicals may form [3]. The main reactions occurring during collapse of a bubble are shown below

[4].

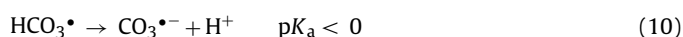


Sonochemical reactions can occur in three different regions, that is, at the interior of the collapsing bubbles, at the interfacial region being the thin shell of fluid surrounding the collapsing cavitation bubble, and finally in the bulk of the solution. The sonolysis of organic compounds in dilute aqueous solution proceeds by two-reaction pathways [2]. First, volatile compounds evaporate during the expansion cycle and degrade via pyrolytic and combustive reactions within the collapsing cavitation bubble. Second, it occurs by the reaction of $\bullet\text{OH}$ radicals with the solute adsorbed at the bubble interface, in the bulk, and to some extent within the bubbles [5]. The extent of oxidation in bulk liquid is limited by the quantity of hydroxyl radicals diffused into the water [6].

* Corresponding author. Tel.: +213 771 578 509.

E-mail addresses: ohamdaoui@yahoo.fr, oualid.hamdaoui@univ-annaba.org (O. Hamdaoui).

Sonolysis is an innovative advanced oxidation process (AOP). The efficacy of AOPs to treat pollutants is eventually dictated by the rate of generation of free radicals and other reactive moieties and the degree of contact between the radicals and the contaminants, both of which should be maximized. Among ubiquitous scavengers, bicarbonate and carbonate ions react with hydroxyl radicals with second-order rate constants of 8.5×10^6 and $3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [7], respectively. These reactions lead to the formation of the carbonate radical ($\text{CO}_3^{\bullet-}$) (reactions (8) and (9)). For many years, by analogy to the carbonate and bicarbonate anions, it was assumed that this radical normally exists as the protonated form (HCO_3^{\bullet}) in the neutral to basic pH range, but it is now firmly established that no protonation of $\text{CO}_3^{\bullet-}$ (reaction (10)) could be observed in the pH range of 0–10 [8], which leaves $\text{CO}_3^{\bullet-}$ as the only relevant carbonate radical species to be considered in this study and in most aquatic chemistry applications. This radical is a strong one-electron oxidant (1.78 [9] and 1.59 V [10] vs. Normal Hydrogen Electrode (NHE) at pH 7.0 and 12.5, respectively). Carbonate radical may be formed when using ultrasound for water treatment (quenching of hydroxyl radical by HCO_3^- and CO_3^{2-}).



In contrast to hydroxyl radical, which reacts very rapidly with almost any organic compound, carbonate radical is very selective and the corresponding second-order rate constants cover a range of many orders of magnitude. Carbonate radical may react by electron transfer or hydrogen transfer [11].

Dye removal from industrial effluents has been the subject of great attention in the last few years. Approximately, 10–15% of the overall production of dyes is released into the environment, mainly via wastewater [12]. The presence of low concentration of dyes in the effluent streams is highly visible and undesirable and it reduces the light penetration which leads to inhibiting photosynthesis and stringent restrictions on the organic content of industrial effluents.

In this work, the dye under consideration is Rhodamine B (RhB), which is a highly water soluble, basic dye of the xanthene class. It is widely used as a colorant in textiles and food stuffs, and is also a well-known water tracer fluorescent [13]. It is harmful if swallowed by human beings and animals, and causes irritation to the skin, eyes and respiratory tract [14]. The carcinogenicity, reproductive and developmental toxicity, neurotoxicity and chronic toxicity towards humans and animals have been experimentally proven [15]. Thus, keeping the hazardous nature and harmful effects in view, it was considered worthwhile to make systematic efforts to efficiently remove RhB from wastewaters.

The objective of this study is to clarify the influence of carbonate and bicarbonate ions on the sonochemical degradation of RhB in aqueous solution. The effects of the presence of organic competitor such as glucose, as well as inorganic salts such as sodium sulfate, on the sonolytic destruction of dye in the presence of bicarbonate and carbonate ions were also investigated.

2. Materials and methods

2.1. Materials

Rhodamine B (abbreviation: RhB; C.I. Basic Violet 10; C.I. number: 45170; chemical class: xanthene; molecular formula: $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$) was procured from Sigma–Aldrich. Rhodamine B [molecular weight: $479.01 \text{ g mol}^{-1}$; IUPAC Name N-[9-(ortho-carboxyphenyl)-6-(diethylamino)-3H-xanthen-3-ylidene] diethyl ammonium chloride, which is highly water soluble, was used as a model solute. The molecular structure of RhB is shown in Fig. 1.

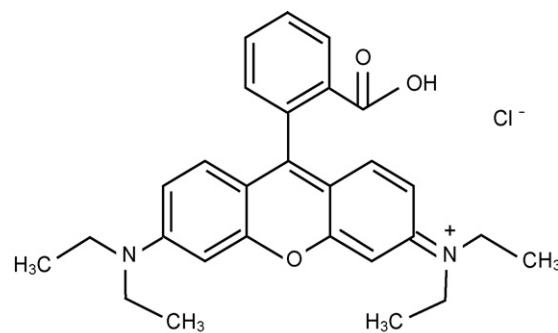


Fig. 1. Chemical structure of Rhodamine B (Basic violet 10).

Sodium bicarbonate, sodium carbonate, sodium sulfate and glucose were commercial products of the purest grade available (analytical grade). All solutions were prepared with distilled water.

2.2. Reactor

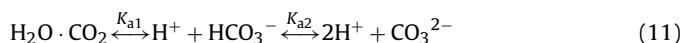
Sonolysis experiments were performed with homemade equipment operating at an ultrasound frequency of 300 kHz. Ultrasonic waves introduced from the bottom of the solution through a plate Pyrex surface (diameter 5 cm) holding the piezoelectric disk (diameter 4 cm). The power output on the generator for all of the experiments was 60 W. The volume of the solutions sonicated was 300 mL. The cylindrical sonochemical reactor was thermostated by a water jacket. The temperature inside the reactor was kept constant. Energy dissipated in the reactor was measured by the calorimetric method [16].

2.3. Procedure

Various aqueous solutions of RhB containing different additives were prepared by adding the required amount of these agents and stirring using a magnetic bar.

Sonochemical degradation of RhB was carried out under different conditions using constant solution volume of 300 mL. Aqueous samples were taken from the solution and the concentrations of dye were determined. The concentrations of RhB in the solution were determined using a UV–visible spectrophotometer (Jenway 6405) at 551 nm. The absorbance data of dye solution determined spectrophotometrically indicated that change of the initial pH of dye solution has no effect on the λ_{max} of RhB in the pH range 4–13.

When bicarbonate ion was added to dye solution, the pH value of RhB solution remained 8.3 due to dynamical equilibrium. The dynamical equilibrium in the bicarbonate solution is in the following form:



$K_{a1} = 4.3 \times 10^{-7}$ and $K_{a2} = 5.61 \times 10^{-11}$ are the dissociation constants of dynamical equilibrium. In the presence of bicarbonate ion, the pH of RhB solution will be imposed by bicarbonate ion that is an amphoteric substance and, in all the used concentration range, the solution pH ($(\text{p}K_{a1} + \text{p}K_{a2})/2$) was around 8.3.

Because addition of carbonate ion to RhB solution increases the solution pH, in the present work, the initial pH of dye solutions containing carbonate ion was adjusted at 11.1. This value was chosen because the most dominant specie at this pH was CO_3^{2-} . For higher carbonate concentration, sulfuric acid was used to adjust the solution pH at 11.1.

Chemical oxygen demand (COD) was measured according to the method presented by Thomas and Mazas [17], using a dichromate solution (Aldrich) as the oxidizer in a strong acid medium. Test

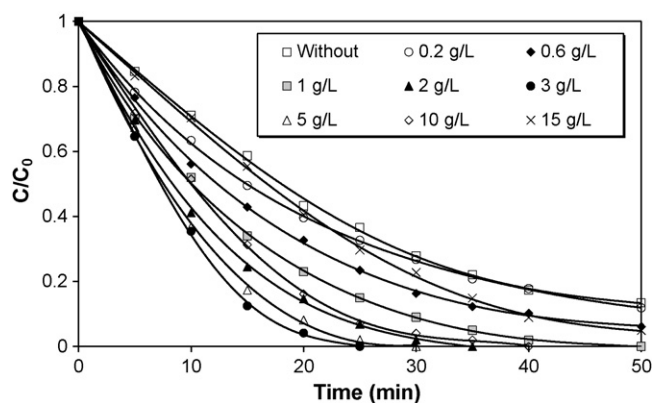


Fig. 2. Influence of bicarbonate on the sonochemical degradation of RhB (conditions: volume: 300 mL; initial dye concentration: 0.5 mg L^{-1} ; temperature: 25°C ; pH: 8.3; frequency: 300 kHz; power: 60 W).

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 with a UV–visible spectrophotometer (Jenway 6405).

3. Results and discussion

3.1. Effect of bicarbonate concentration

All sonication experiments in the absence and presence of bicarbonate ions were conducted at pH 8.3 by applying ultrasound at 300 kHz and 60 W. The effect of different bicarbonate concentrations ranging from 0.1 to 15 g L^{-1} on the sonochemical degradation of 0.5 mg L^{-1} RhB solution is shown in Fig. 2. As can be seen from this figure, the degradation rate of RhB solutions was considerably enhanced by the addition of bicarbonate ions. The sonolytic destruction increased with increasing bicarbonate concentration and reached a maximum at 3 g L^{-1} . The increase of bicarbonate concentration above 3 g L^{-1} retards the process, but the destruction rate was higher than that obtained in the absence of bicarbonate ions. The enhancement of RhB degradation is due to the formation of carbonate radical (reaction (8)), which may react more effectively than $\bullet\text{OH}$ radical with dye molecules [11].

In order to verify the intensification of sonochemical degradation of RhB by the addition of bicarbonate ions, different sonolytic destruction experiments were conducted at pH 8.3 for various dye concentrations of 0.5, 1, 2, 3 and 5 mg L^{-1} . The results presented in the form of initial rate of RhB degradation as a function of bicarbonate concentration for different dye concentrations are shown in Fig. 3. From this figure, it was observed that as the concentration of dye increased, the intensification effect of bicarbonate ions decreased. Additionally, for RhB concentrations of 3 and 5 mg L^{-1} , bicarbonate ions had negative effect on the removal of dye, whatever the amount added to dye solution. Thus, the enhancement of RhB degradation in aqueous solutions containing bicarbonate ions occurs only when the dye concentration is low. For initial dye concentrations of 0.5, 1 and 2 mg L^{-1} , it seems that the best enhancement of the initial degradation rate was obtained for a bicarbonate concentration of 3 g L^{-1} . At this best concentration, the degradation ratio became 2.30 times greater for RhB concentration of 0.5 mg L^{-1} and 1.74 times greater for RhB concentration of 1 mg L^{-1} and 1.20 times greater for RhB concentration of 2 mg L^{-1} .

The presence of salts may increase the hydrophobicity, the surface tension and ionic strength of the aqueous phase and decrease the vapor pressure [18,19]. All these factors help in collapsing of the bubbles more violently, resulting in high degradation of dye for all the tested dye concentrations. This was not true in the present con-

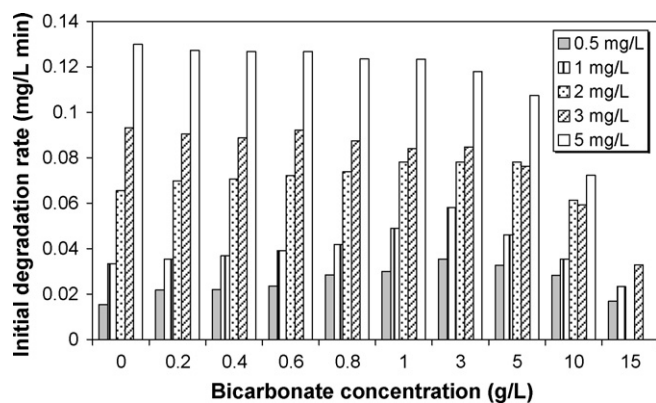


Fig. 3. Initial degradation rate of RhB as a function of bicarbonate concentration (conditions: volume: 300 mL; initial dye concentration: $0.5\text{--}5 \text{ mg L}^{-1}$; temperature: 25°C ; pH: 8.3; frequency: 300 kHz; power: 60 W).

ditions because the addition of bicarbonate had a negative effect on the destruction rate for higher RhB concentrations (3 and 5 mg L^{-1}). Additionally, the addition of sodium sulfate in the concentration interval of $0.5\text{--}10 \text{ g L}^{-1}$ (Fig. 4) had no significant impact on the degradation rate in the presence of bicarbonate that excludes salting effect.

The enhancement of the degradation rates observed for the lower concentrations of RhB should involve the presence of the carbonate radical ($\text{CO}_3^{\bullet-}$) coming from the reaction of bicarbonate ion with $\bullet\text{OH}$ diffused from the cavitation bubble. For a lower concentration of RhB, the combination of $\bullet\text{OH}$ radical (reaction (6), $k_6 = 5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) is dominant, but in the presence of bicarbonate, the formation of $\text{CO}_3^{\bullet-}$ radical is less reactive than $\bullet\text{OH}$ radical, minimizing the combination of $\text{CO}_3^{\bullet-}$ that decays by reacting with itself according to reaction 12 or 13 ($k_{12,13} = 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$). The substitution of $\bullet\text{OH}$ with $\text{CO}_3^{\bullet-}$ could enhance degradation if the latter, although less reactive than $\bullet\text{OH}$, undergoes radical–radical recombination at a lesser extent than the hydroxyl radical. The combination of $\bullet\text{OH}$ is known to be 275 times higher than that the reaction of $\text{CO}_3^{\bullet-}$ with itself [10,20,21].

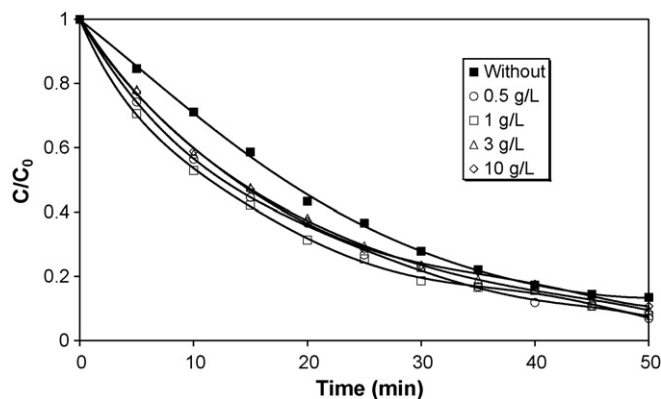
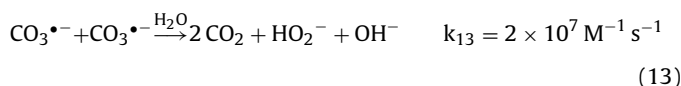
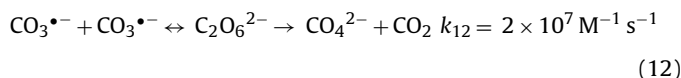


Fig. 4. Effect of sodium sulfate on the sonochemical degradation of RhB (conditions: volume: 300 mL; initial dye concentration: 0.5 mg L^{-1} ; temperature: 25°C ; pH: 8.3; frequency: 300 kHz; power: 60 W).

At higher dye concentrations, the slight negative effect of bicarbonate ions on the rate of dye destruction may be due to the much slower formation of carbonate radical. In this case, the $\cdot\text{OH}$ radicals generated in the bubble, which can diffuse into the bulk solution are intercepted by RhB molecules.

The intensification of degradation at lower RhB concentrations in the presence of bicarbonate ions is similar to that obtained in previous work on the destruction of Acid Blue 40 (4.73 mg L^{-1}) and methylene blue (1.12 mg L^{-1}) using 354.5 kHz ultrasound at 35 W [22]. P etrier et al. [23] have indicated that ultrasonic decomposition of bisphenol A ($27.4 \mu\text{g L}^{-1}$) at 300 kHz and 80 W in the presence of bicarbonate ions was significantly enhanced.

Taking into account the results of the present work, it can be concluded that addition of bicarbonate had a significant concentration-dependant effect on the rate of degradation at lower dye concentrations. The lower the concentration of RhB is, the higher the positive effect of bicarbonate ions on the destruction rate is.

3.2. Effect of carbonate concentration

The influence of carbonate ions added in the concentration range varying from 0.05 to 20 g L^{-1} on the sonolytic degradation of RhB was studied. Both in the absence and presence of carbonate ions, sonication experiments were carried out at pH 11.1. For an initial RhB concentration of 0.5 mg L^{-1} , the obtained results, presented in Fig. 5, show the significant improvement of the rates of dye destruction in the presence of carbonate ions. The degradation rate gradually increased with increasing carbonate concentration up to 10 g L^{-1} and slightly decreased afterward.

The results of the effect of addition of carbonate ions presented in terms of initial degradation rate for different RhB initial concentrations ranging from 0.5 to 5 mg L^{-1} are shown in Fig. 6. From this figure, it was observed that the rates of dye destruction increased in the presence of carbonate ions, especially at lower dye concentrations. It can also be noticed that the carbonate enhancement effect decreased with increasing initial dye concentration. In all cases, it seems that the higher degradation rate was obtained for a carbonate concentration of 10 g L^{-1} . By the addition of a carbonate concentration of 10 g L^{-1} , the rate of degradation increased 6.18, 2.95, 1.45 and 1.67 times for initial RhB concentration of 0.5 , 1 , 3 and 5 mg L^{-1} , respectively. In contrast to the degradation of RhB in the presence of bicarbonate ions that decreases for higher dye concentrations, the destruction rate in the presence of carbonate ions increases for all the tested dye concentrations.

In general, depending on the nature of the contaminants, addition of salt to the solution can decrease their solubility and

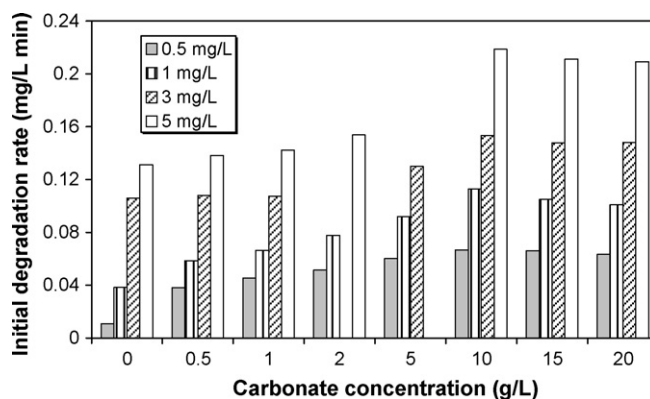


Fig. 6. Initial RhB degradation rate as a function of carbonate concentration (conditions: volume: 300 mL; initial dye concentration: 0.5 – 5 mg L^{-1} ; temperature: $25 \text{ }^\circ\text{C}$; pH: 11.1; frequency: 300 kHz; power: 60 W).

consequently increase their hydrophobicity. This is due to the salting-out effect where fewer water molecules are available for dissolving the analyte molecules, preferably forming hydration spheres around the salt ions [24]. In order to demonstrate that the enhancement of dye degradation by carbonate ions was not due to the salting effect, the influence of the addition of sodium sulfate in the concentration range of 0.5 – 10 g L^{-1} on the rate of RhB destruction at pH 11.1 was investigated. The obtained results, shown in Fig. 7, indicate that the rate of dye degradation was not significantly different from the control, whatever the concentration of sodium sulfate. This demonstrates that the improvement of RhB degradation in the presence of carbonate is not due to the salting effect.

It was known that carbonate ions react with $\cdot\text{OH}$ approximately 46 times faster than bicarbonate, and more marked intensification of degradation effect was obtained by the addition of carbonate compared to bicarbonate. It is possible to account for the improvement of dye sonolytic destruction by carbonate under the hypothesis that $\text{CO}_3^{\cdot-}$ undergoes more limited radical–radical recombination (reactions (12) and (13)) compared to $\cdot\text{OH}$ (reaction (6)) in the liquid–bubble interface. In this way, $\text{CO}_3^{\cdot-}$ could be more available than $\cdot\text{OH}$ to react with RhB and induce its destruction.

The positive effect of carbonate ions on the sonolytic degradation of RhB increased with decreasing initial dye concentration. Additionally, in all cases, the higher intensification effect of carbonate on the rate of RhB sonochemical destruction was obtained for a carbonate ions concentration of 10 g L^{-1} . For carbonate concentrations higher than 10 g L^{-1} , a slight decrease of the sonochemical

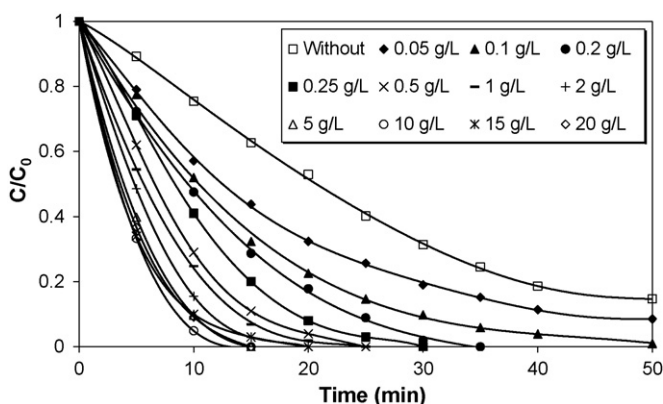


Fig. 5. Influence of carbonate on the sonochemical degradation of RhB (conditions: volume: 300 mL; initial dye concentration: 0.5 mg L^{-1} ; temperature: $25 \text{ }^\circ\text{C}$; pH: 11.1; frequency: 300 kHz; power: 60 W).

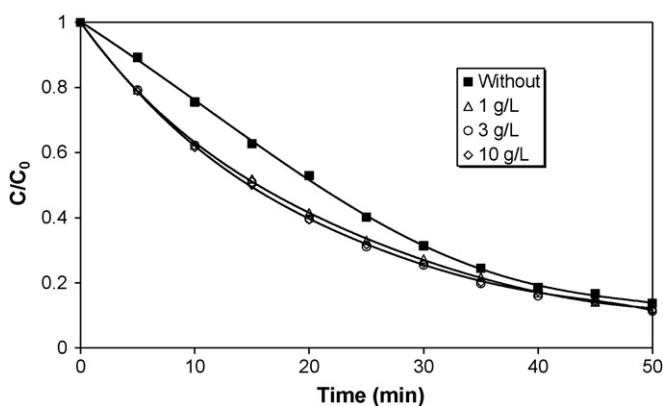


Fig. 7. Influence of sodium sulfate on the sonochemical degradation of RhB (conditions: volume: 300 mL; initial dye concentration: 0.5 mg L^{-1} ; temperature: $25 \text{ }^\circ\text{C}$; pH: 11.1; frequency: 300 kHz; power: 60 W).

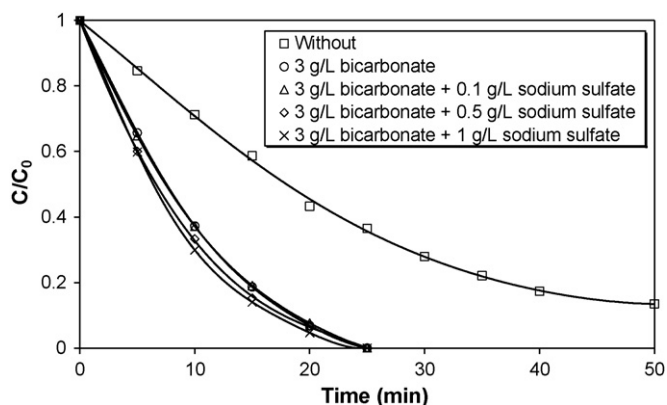


Fig. 8. Effect of sodium sulfate on the sonochemical degradation of RhB in the presence of 3 g L^{-1} bicarbonate (conditions: volume: 300 mL; initial dye concentration: 0.5 mg L^{-1} ; temperature: 25°C ; pH: 8.3; frequency: 300 kHz; power: 60 W).

destruction of RhB was observed for all the tested initial dye concentrations. Similarly, Minero et al. [22] have indicated that the degradation rate of Acid Blue 40 (4.73 mg L^{-1}) gradually increased with increasing the concentration of carbonate ions up to a plateau above 6 g L^{-1} .

3.3. Effect of sodium sulfate in the presence of bicarbonate or carbonate ions

Apart from altering the physicochemical properties of an aqueous reaction mixture, addition of salt in sonicated reaction mixture results in reduced vapor pressure and increased surface tension, thus promoting a more violent collapse of the cavitating bubble. It should be mentioned here that depending on the target contaminants the effect of salt on cavitation may be negligible when compared to the partitioning effect.

To evaluate the influence of salt, RhB at an initial concentration of 0.5 mg L^{-1} in the presence of 3 g L^{-1} bicarbonate (pH 8.3) or 10 g L^{-1} carbonate (pH 11.1) was subject to ultrasonic irradiation at 300 kHz in the presence of sodium sulfate concentrations of 0.1, 0.5 and 1 g L^{-1} . Figs. 8 and 9 present the effect of sodium sulfate salt added on sonochemical degradation of RhB in aqueous solution in the presence of carbonate and bicarbonate, respectively. As it can be seen from these figures, addition of sodium sulfate up to 1 g L^{-1} had practically no impact on the removal of dye, which demonstrates the selectivity of carbonate radical, formed during sonication of aqueous solutions containing bicarbonate or carbonate ions, towards dye molecules.

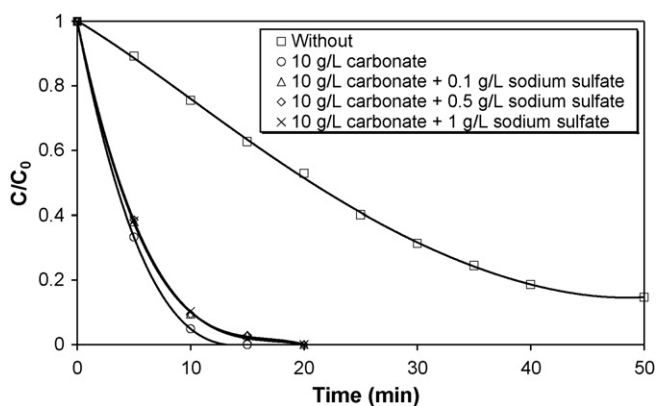


Fig. 9. Effect of sodium sulfate on the sonochemical degradation of RhB in the presence of 10 g L^{-1} carbonate (conditions: volume: 300 mL; initial dye concentration: 0.5 mg L^{-1} ; temperature: 25°C ; pH: 11.1; frequency: 300 kHz; power: 60 W).

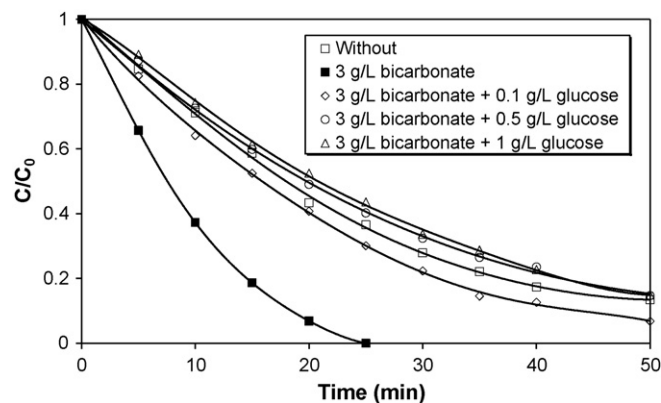


Fig. 10. Effect of glucose on the sonochemical degradation of RhB in the presence of 3 g L^{-1} bicarbonate (conditions: volume: 300 mL; initial dye concentration: 0.5 mg L^{-1} ; temperature: 25°C ; pH: 8.3; frequency: 300 kHz; power: 60 W).

3.4. Effect of glucose in the presence of bicarbonate or carbonate ions

The sonochemical degradation of RhB solutions containing bicarbonate or carbonate ions was investigated in the presence of organic competitor such as glucose (water solubility: $0.661 \times 10^3 \text{ g L}^{-1}$, K_{ow} : 1.5×10^{-3} , Henry's law constant: $4.28 \times 10^{-20} \text{ atm m}^3 \text{ mol}^{-1}$). Figs. 10 and 11 show the influence of the addition of glucose (0.1 – 1 g L^{-1}) on the sonochemical destruction of RhB (0.5 mg L^{-1}) in the presence of 3 g L^{-1} bicarbonate and 10 g L^{-1} carbonate, respectively. It was observed that the intensification effect of bicarbonate ions on the ultrasonic treatment of aqueous dye solution was drastically reduced for the lower concentration of glucose and completely inhibited for the higher glucose concentrations. The positive effect of carbonate was significantly diminished but not completely inhibited even for the higher glucose concentrations. In contrast, addition of glucose in the absence of bicarbonate and carbonate ions had no effect on the sonochemical degradation of RhB (figure not shown). These results indicated the significance of interfacial reactions in the destruction pathway of RhB by hydroxyl radicals. In contrast, the degradation by carbonate radical occurring in the solution bulk was slowed down in the presence of glucose by scavenging carbonate radicals in the liquid bulk. Finally, the degree of scavenging of glucose was much larger in the presence of carbonate radical than hydroxyl radical, showing the significance of interfacial reactions in the destruction pathway of RhB by hydroxyl radical, while the degradation by carbonate radical occurs in the liquid bulk.

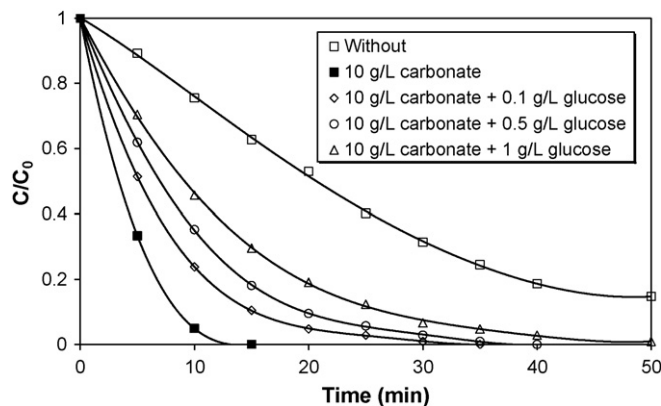


Fig. 11. Effect of glucose on the sonochemical degradation of RhB in the presence of 10 g L^{-1} carbonate (conditions: volume: 300 mL; initial dye concentration: 0.5 mg L^{-1} ; temperature: 25°C ; pH: 11.1; frequency: 300 kHz; power: 60 W).

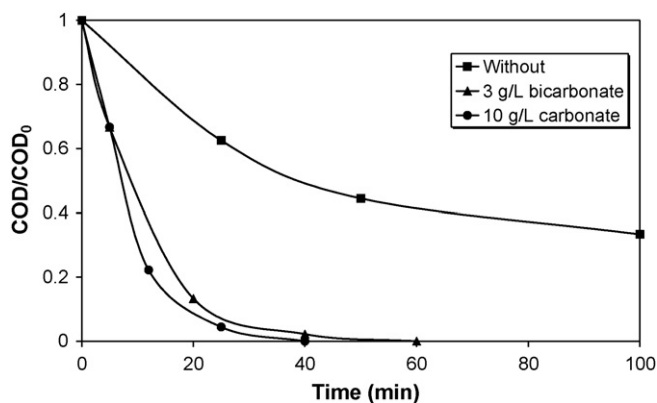


Fig. 12. COD profile during sonication of RhB solutions in the absence and presence of bicarbonate and carbonate (conditions: volume: 300 mL; temperature: 25 °C; frequency: 300 kHz; power: 60 W).

3.5. COD removal of sonicated RhB solutions

It is known that complete degradation of RhB does not mean that the dye is completely oxidized, and so the degradation of dye in terms of COD removal was investigated. Fig. 12 depicts the evolution of COD/COD₀ during sonication of 0.5 mg L⁻¹ RhB solution at 300 kHz and 60 W in the absence (pH 8.3 and 11.1) and presence of 3 g L⁻¹ bicarbonate (pH 8.3) and 10 g L⁻¹ carbonate (pH 11.1). It can be observed from this figure that in the absence of bicarbonate and carbonate ions, the oxidation is a relatively slow process with COD decrease being as low as about 54 and 66% after 50 and 100 min of sonication, respectively. For the control experiment, COD was not completely removed under the ultrasonic action. These results underline the fact that degradation products of RhB are recalcitrant towards sonochemical treatment. This is due to the fact that the intermediate products have very low probabilities of making contact with •OH radicals, which react mainly at the interface of the bubble. Thus, the sonochemical action that gives rise to products bearing more hydroxyl (or carboxylic) groups is of low efficiency towards COD abatement.

The addition of bicarbonate or carbonate ions exhibit considerable enhancement in oxidation of RhB. COD can be completely removed from the medium within 60 and 40 min of sonolysis in the presence of 3 g L⁻¹ bicarbonate and 10 g L⁻¹ carbonate, respectively. The enhancement of the oxidation rates observed in aqueous RhB solutions containing bicarbonate and carbonate ions is due to the formation of carbonate radicals coming from the reaction of bicarbonate and carbonate ions with •OH radicals ejected from the cavitation bubbles. The generated carbonate radicals are likely able to migrate far from the cavitation bubbles towards the bulk of the solution and are suitable for oxidation of an organic dye such as RhB. Thus, carbonate radical presents a more selective reactivity towards RhB molecules than hydroxyl radical.

4. Conclusion

The removal of the recalcitrant dye pollutant RhB by ultrasonic irradiation was reached in the absence and presence of bicarbonate and carbonate ions. As a consequence of ultrasonic cavitation that generates •OH radicals, carbonate radicals were secondary products of water sonochemistry when it contains dissolved bicarbonate or carbonate ions. The effectiveness of the sonolytic destruction of RhB is clearly intensified in the presence of bicarbonate and carbonate ions, especially at lower dye concentrations. Degradation intensification occurs because carbonate radicals sonochemically formed on the surface of the collapsing cavitation bubbles undergo radical–radical recombination at

a lesser extent than hydroxyl radicals. The generated carbonate radicals are likely able to migrate far from the cavitation bubbles towards the bulk of the solution and are suitable for decomposition of an organic dye such as RhB. In the presence of bicarbonate, degradation rate reached a maximum at 3 g L⁻¹ bicarbonate, but subsequent addition retards the destruction process. The sonodegradation rate gradually increased with increasing carbonate concentration up to 10 g L⁻¹ and slightly decreased afterward. The initial degradation rate at low dye concentration (0.5 mg L⁻¹) in the presence of bicarbonate and carbonate increased by a factor 2.30 and 6.18 in the presence of bicarbonate and carbonate, respectively. The impact of large concentrations of organic competitor such as glucose in the presence of bicarbonate and carbonate ions was to decrease the rate of degradation, particularly when the scavenger concentration was considerably larger than that of RhB. During sonication of water containing bicarbonate and carbonate ions, carbonate radicals generated are suitable for total COD abatement of an organic dye such as RhB.

Acknowledgement

The financial support by the Ministry of Higher Education and Scientific Research of Algeria to the project J 0101120090018 is greatly acknowledged.

References

- [1] A. Henglein, Sonochemistry: historical developments and modern aspects, *Ultrasonics* 25 (1987) 7–16.
- [2] C. Pétrier, Y. Jiang, M.-F. Lamy, Ultrasound and environment: sonochemical destruction of chloroaromatic derivatives, *Environ. Sci. Technol.* 32 (1998) 1316–1318.
- [3] L.A. Crum, Comments on the evolving field of sonochemistry by a cavitation physicist, *Ultrason. Sonochem.* 2 (1995) S147–S152.
- [4] T.J. Mason, C. Pétrier, Advanced oxidation processes for water and wastewater treatment, in: S. Parson (Ed.), *Ultrasound Processes*, IWA Publishing, London, 2004, pp. 185–208.
- [5] M.R. Hoffmann, I. Hua, R. Höchemer, Application of ultrasonic irradiation for the degradation of chemical contaminants in water, *Ultrason. Sonochem.* 3 (3) (1996) S163–S172.
- [6] A. Henglein, Contributions to various aspects of cavitation chemistry, *Adv. Sonochem.* 3 (1993) 17–83.
- [7] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH/O⁻) in aqueous solution, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886.
- [8] G. Czapski, S.V. Lyman, H.A. Schwarz, Acidity of the carbonate radical, *J. Phys. Chem. A* 103 (1999) 3447–3450.
- [9] V.W. Cope, S.-N. Chen, M.Z. Hoffman, Intermediates in the photochemistry of carbonato-amine complexes of cobalt(III). CO₃^{•-} radicals and the aquocarbonato complex, *J. Am. Chem. Soc.* 95 (1973) 3116–3121.
- [10] F. Boccini, A.S. Domazou, S. Herold, Pulse radiolysis studies of the reactions of carbonate radical anion with myoglobin and hemoglobin, *J. Phys. Chem. A* 108 (2004) 5800–5805.
- [11] P. Mazellier, C. Busset, A. Delmont, J. De Laat, A comparison of fenuron degradation by hydroxyl and carbonate radicals in aqueous solution, *Water Res.* 41 (2007) 4585–4594.
- [12] H. Zollinger, *Color Chemistry: Synthesis, Properties and Application of Organic Dyes and Pigments*, VCH Publishers, New York, 2004.
- [13] S.D. Richardson, C.S. Wilson, K.A. Rusch, Use of rhodamine water tracer in the marshland upwelling system, *Ground Water* 42 (2004) 678–688.
- [14] J. Rochat, P. Demenge, J.C. Rerat, Toxicologic study of a fluorescent tracer: rhodamine B, *Toxicol. Eur. Res.* 1 (1978) 23–26.
- [15] R. Jain, M. Mathur, S. Sikarwar, A. Mittal, Removal of the hazardous dye rhodamine B through photocatalytic and adsorption treatments, *J. Environ. Manage.* 85 (2007) 956–964.
- [16] S. Koda, T. Kimura, H. Kondo, H.A. Mitone, A standard method to calibrate sonochemical efficiency of an individual reaction system, *Ultrason. Sonochem.* 10 (2003) 149–156.
- [17] O. Thomas, N. Mazas, La mesure de la demande chimique en oxygène dans les milieux faiblement pollués, *Analisis* 14 (1986) 300–302.
- [18] J.D. Seymour, R.B. Gupta, Oxidation of aqueous pollutants using ultrasound: salt induced enhancement, *Ind. Eng. Chem. Res.* 36 (1997) 3453–3457.
- [19] S. Findik, G. Gunduz, Sonolytic degradation of acetic acid in aqueous solutions, *Ultrason. Sonochem.* 14 (2007) 157–162.
- [20] G. Czapski, J. Holcman, H.J. Bielski, Reactivity of nitric oxide with simple short-lived radicals in aqueous solutions, *J. Am. Chem. Soc.* 116 (1994) 11465–11469.

- [21] J.L. Weeks, J. Rabani, The pulse radiolysis of deaerated aqueous carbonate solutions. I. Transient optical spectrum and mechanism. II. pK for $\cdot\text{OH}$ radicals, *J. Phys. Chem.* 70 (1966) 2100–2106.
- [22] C. Minero, P. Pellizzari, V. Maurino, E. Pelizzetti, D. Vione, Enhancement of dye sonochemical degradation by some inorganic anions present in natural waters, *Appl. Catal. B: Environ.* 77 (2007) 308–316.
- [23] C. Pétrier, R. Torres-Palma, E. Combet, G. Sarantakos, S. Baup, C. Pulgarin, Enhanced sonochemical degradation of Bisphenol-A by bicarbonate ions, *Ultrason. Sonochem.* (2009), doi:10.1016/j.ultsonch.2009.05.010.
- [24] E. Psillakis, N. Kalogerakis, Developments in liquid phase microextraction, *Trends Anal. Chem.* 22 (2003) 565–574.