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Reactive dyestuff degradation by combined sonolysis and ozonation

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Abstract

The degradation of a reactive dye by combined sonolysis (520 kHz) and ozonation was studied using C.I. Reactive Black 5 as a model dye. It was found that the joint action of ultrasound and ozone induced a synergistic effect on both the decolorization of the dye and the overall degradation process. Due to the inefficiency of ultrasonic irradiation by itself to render any significant degradation under the conditions employed, the synergy was attributed mainly to mechanical effects of ultrasound to enhance the mass transfer of ozone in solution. The radical chain reactions taking place during thermolysis of water and ozone in collapsing cavities may also have contributed chemically to the synergy by providing additional decomposition pathways for ozone, and an excess of electron-deficient chemicals in solution.

Keywords: Sonolysis/sonication; Ultrasonic irradiation (US); Cavitation; Ozonation; Mineralization; Hydroxyl radical; Oxidizing species

1. Introduction

Effluents of textile dyeing/finishing mills are often complex with intense color, chemical oxygen demand (COD), suspended solids, and a variety of refractory matter such as heavy metals and non-ionic surfactants [1]. Moreover, the industry suffers from excessive water consumption, due to manifold washing of dyed fabrics to remove dye residual from their surfaces. Accordingly, the management of dyehouse effluents requires an integrated approach to the problems of “effluent treatment” and “water consumption” by developing suitable treatments that produce harmless effluents and recyclable water.

The expanded use of reactive dyes during the last decade has impacted upon conventional methods for treating dyehouse effluents, due to the generally poor biodegradation of such dyes (especially those containing azo-groups) under aerobic conditions [2]. Furthermore, some precursors of azo-reactive dyes are toxic and carcinogenic, and require separation and advanced treatment of dyebath effluents before discharge into conventional systems or publicly owned wastewater treatment works [2,3].

Recent developments in advanced oxidation processes (AOP), which effectively generate free radical species, have shown that under appropriate conditions, they impart complete color removal,

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detoxification and mineralization in the effluents of textile dyeing mills [4–7]. The advantage of AOP over conventional oxidation processes accrues from the reactivity of the free radical species involved, especially that of the hydroxyl radical (•OH), which is non-selective and much more powerful than molecular oxidants [8].

One of the most common methods of free radical production in AOP practices is ozonation (either in conjunction with or without a source of ultraviolet light) and laboratory scale treatment of textile dyebath effluents with ozone has been found effective for color removal and partial degradation [5,6,9–12]. The attractiveness of ozonation over other chemical oxidation methods is that it provides two possible degradation routes: namely: at basic pH, it rapidly decomposes to yield hydroxyl and other radical species in solution and under acidic conditions, it is stable and can react directly with organic substrates as an electrophile [6,8]. The shortcomings of the method, however, are its energy intenseness (due to the in situ generation of ozone), pH sensitivity, selectivity of O_3 for organic substrates and the increased level of turbidity in effluents [9]. Hence, ozonation requires further research and development for applicability in large-scale operations as part of an environmental management system.

Free radical formation in water by ultrasonic irradiation (US) is a much less popular technique, despite the "extreme" conditions provided by sonic vibrations in liquids for "high energy chemistry" [13]. Research on dyestuff degradation by ultrasonic irradiation is rare, with the exception of a couple of investigations with reactive dyes, which reported that complete decolorization and partial mineralization was achieved after long exposure to ultrasound [14,15].

When a liquid is sonicated, the pressure waves are transmitted through the medium by acoustic cavitations, which comprise microbubbles that entrap dissolved gases of the surrounding medium [13,16]. These bubbles grow and expand within the rarefaction and compression cycles until they reach a critical size, at which point further compression leads to their implosive collapse, with temperature releases of 2000–5000 K [17]. During this collapse stage, water molecules and volatile organic solutes entrapped in the bubble interiors undergo pyrolytic fragmentation, dissociating into hydroxyl, hydrogen and organic radicals, respectively [18,19].

When water is ozonated during ultrasonic irradiation (US), the increase in hydroxyl radical production is synergistic due to an additional pathway that involves thermal decomposition of O_3 [20,21]. A further advantage of such a combination is enhanced O_3 transfer in solution, resulting from larger gas diffusion coefficients in the presence of sonic vibrations than in non-irradiated solutions [22]. A simplified reaction scheme for •OH generation during US/O_3 treatment of water is as follows [18,20,21,23]:

$$O_3\bullet + H_2O \rightarrow 2HOO\bullet \quad (1)$$

$$O_3 + HOO\bullet \rightarrow \bullet OH + 2O_2 \quad (2)$$

$$H_2O +))) \rightarrow \bullet H + \bullet OH \quad (3)$$

$$O_3 +))) \rightarrow O_2(g) + O(^3P)(g) \quad (4)$$

$$O(^3P)(g) + H_2O(g) \rightarrow 2\bullet OH \quad (5)$$

Some of the hydroxyl radicals recombine at the cooler bubble-liquid interface to yield water and hydrogen peroxide while others react with gaseous substrates within the collapsing bubbles and, under proper conditions, some diffuse into the bulk liquid to activate aqueous phase oxidation reactions [18,20,21]. Depending on their solubility and vapour pressures, organic solutes during combined ozonation and US treatment may be destroyed by direct thermal decomposition, •OH-mediated advanced oxidation in the bulk liquid, chemical oxidation and ozonation for hydrogen peroxide, and/or a combination of these processes [22].

The purpose of this study was to investigate the effectiveness of combining ultrasonic irradiation (US) with ozone in treating textile dyebath effluents contaminated with reactive dyes. The degradation process was expected to occur in the bulk solution by hydroxylation and direct reactions of the dye (and the reaction intermediates) with molecular ozone and hydrogen peroxide. Pyrolytic destruction was not an expected pathway because of the hydrophilic nature of reactive dyes, which inhibits their partitioning between aqueous and gaseous phases [18,21].

The method of study involved: (1) preparing synthetic dyebath solutions with C.I. Reactive Black 5 (RBB) which, owing to its high consumption records was selected as a model compound to represent azo-dyes, (2) monitoring the degradation of the dye by means of the decay in its absorbance in the UV–visible region and the reduction in its total organic carbon (TOC), and (3) estimating the rate of dye degradation by regression analysis of the absorbance–time data.

2. Materials and methods

2.1. Materials

C.I. Reactive Black 5 (Remazol Black B) (MW = 991.8 g mol^{-1}) was obtained from Dystar Hoechst (Istanbul) in 80–85% purity. The chemical structure and characteristics of the dye have been reported in previous studies [4,24]. Ozone was generated onsite by electricity using dry pure oxygen.

2.2. Methods

2.2.1. Set-up

The system consisted of a 1.2 l glass reactor to house the test solutions, a water cooling jacket to keep the reactor contents at constant temperature (20±0.5°C), a stainless steel sonication chamber, a piezoelectric transducer emiting ultrasound waves at 520 kHz, and a generator operating between 25–100 W to convert electrical power input into mechanical energy (Undatim Ultrasonics). The irradiation intensity (in 600 ml of air saturated distilled water) was determined by calorimetry [25] as 1.63 W cm^{-2}. Ozone was supplied into the system through a Fischer OZ-500 model generator at a rate of 50 l h^{-1}, yielding (in non-irradiated water) 3.36 g l^{-1} O_3, as determined by iodometry [26]. The reactor was bubbled mildly with a stream of air throughout contact to enhance cavitation events. A schematic diagram of the set-up is presented in Fig. 1.

2.2.2. Preparation of the dye solutions

A 300 μM stock solution was prepared by dissolving 0.363 g of RBB in 1 l ultra pure water, followed by heating to 80°C and adjusting to pH = 11 with dilute NaOH (1 N). The solution was kept in these conditions for 6 h to allow complete hydrolysis of the dye and to simulate dyebath effluents from batch dyeing processes with reactive dyes [27]. Test samples of various concentrations prepared from the stock (stored in the dark at 4°C) by appropriate dilutions were aerated for 2 h to lower their cavitational threshold and to allow rapid bubble formation during initial contact with US. The solutions were readjusted to neutral pH before experimentation.

2.2.3. Analytical

The optical absorption spectra (200–800 nm) and the reduction in UV–visible absorption of the dye solutions were recorded by a Unicam, Helios Alpha/Beta double beam spectrophotometer through a 1 cm path length. The removal of organic carbon via mineralization was monitored by a Fisons 480 TOC analyzer.

2.2.4. Procedure

Concentrations of 10, 20, 40, 50 and 60 μM of RBB were selected in accordance with typical dye residuals found in dyebath effluents of batch processes after rinsing [27]. Six-hundred millilitres of air-saturated test solutions were ozonated simultaneously with ultrasonic irradiation for 20 min, and samples were collected within short intervals for spectrophotometric analyses at the UV–visible region. Exposure was periodically extended to 1 h or more to allow time for mineralization, which was monitored by periodic TOC analysis in effluent samples.

Control experiments with ozone and ultrasound alone were performed on air-saturated dye solutions to compare rates of decolorization, oxidation and total mineralization with those accomplished in the simultaneous scheme, and to assess synergistic effects.

3. Results and discussion

3.1. Decay of the UV–visible absorption bands

CI Reactive Black 5 is a strongly absorbing dye in the UV–visible region with a distinct band in

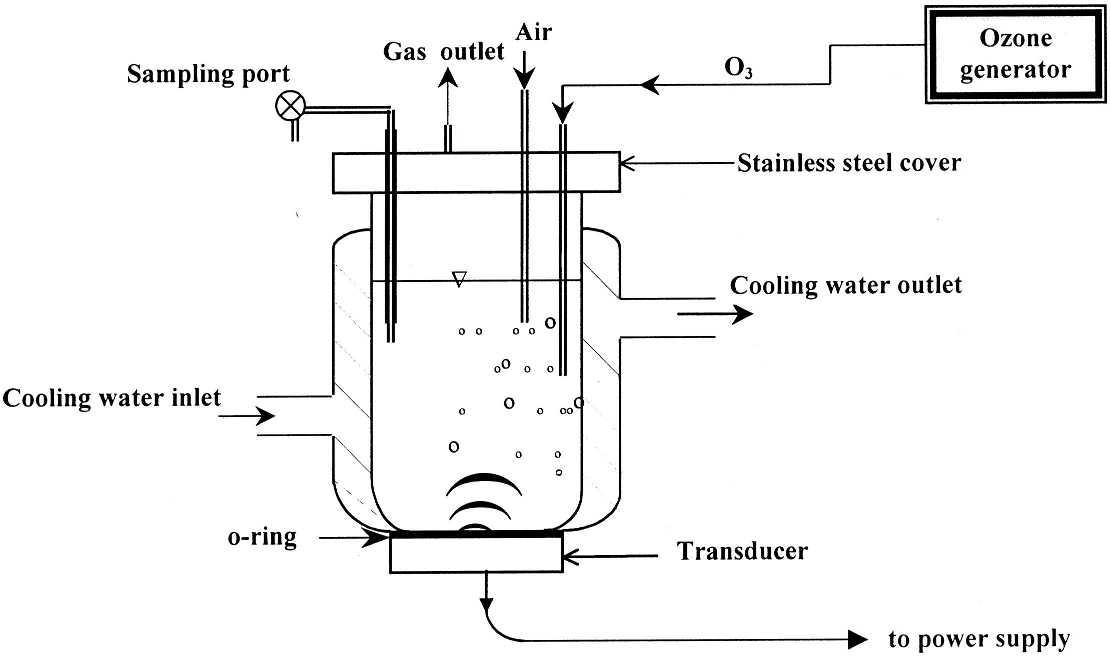

Fig. 1. Schematic diagram of the experimental set-up.

the near-UV region ($\lambda = 312$ nm) and another one in the visible ($\lambda = 596$ nm). The latter is responsible for the dark blue color arising from aromatic rings connected by azo groups, and the former is associated with "benzene-like" structures in the molecule [4]. The absorption spectrum of 20 μM air-saturated RBB before and during exposure to US/O_3 is presented in Fig. 2. The disappearance of the visible band within the first few minutes is due to the fragmentation of the azo links by immediate •OH attack (hydroxylation), which is proposed as the first step in the degradation of azo dyes [15]. In addition to this rapid bleaching effect, the decay of the absorbance at 312 nm is considered as evidence of aromatic fragment degradation in the dye molecule and its intermediates. The rate of abatement of the two absorption bands and a comparison of their first order rate constants are presented in Fig. 3. The significantly faster rate of decay of the visible band is attributable to the priority of hydroxylation of the azo-links in the oxidation process, resulting in the rapid disappearance of chromophores in the dye structure [14,15].

The rate of decolorization of RBB upon exposure to the combined scheme was compared with the rates observed in the control sets using O_3 and US individually. The degradation in all schemes as monitored by the decay of absorbance at 596 nm was found to follow pseudo-first order kinetics. Under the same conditions and for identical contact times, color removal with US/O_3 was twice as fast than that with ozone alone, while no significant removal was observed in the control experiments with ultrasound alone (the data are presented in Fig. 4). The lack of decolorization by US alone can be attributed to the relative shortness of the contact period, which is consistent with literature, where minimum contact for appreciable degradation of color in 33 μM RBB under similar conditions was reported as 2 h [4]. Despite the insignificance of decolorization by ultrasound, the coefficient of degradation in combinative treatment with ozone was much larger than the sum of the coefficients of the two individual treatments, indicating a synergistic effect. This synergy, however, must principally emerge from enhanced ozone dissolution, resulting in excess decompo-

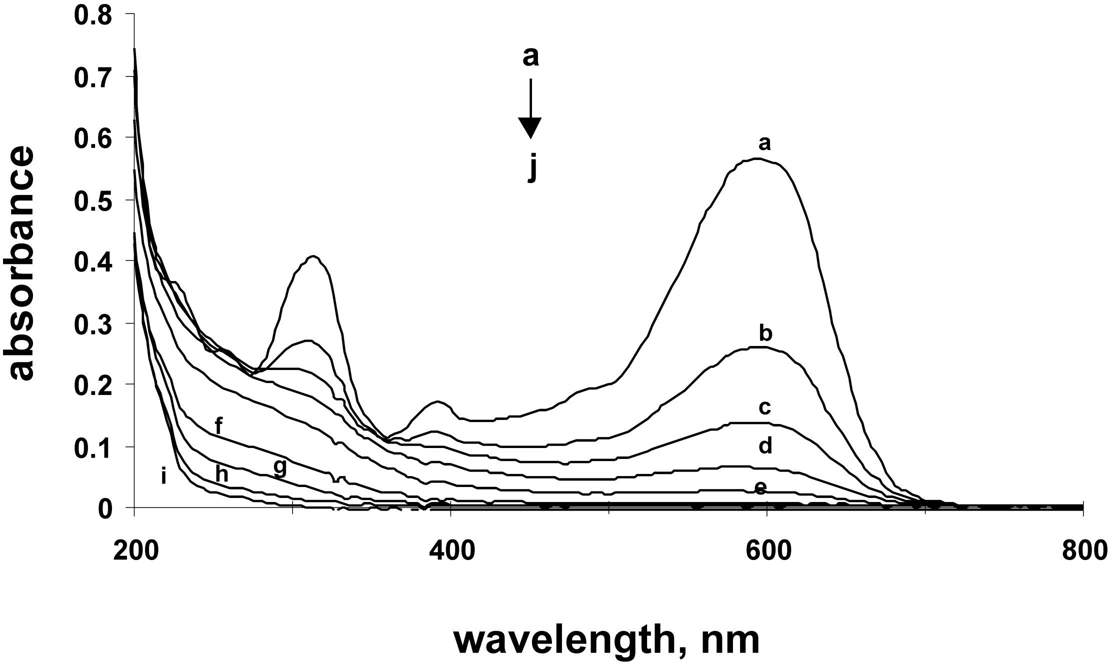

Fig. 2. Changes in the absorption spectra of 20 μmol l^{-1} pre-aerated RBB during 20 min irradiation with US in the presence of O_3. The legends a, b, c, d, e, f, g, h, i refer to contact times as 0, 1, 1.5, 2, 3, 5, 8, 12 and 15 min, respectively. Reactor conditions as irradiation intensity, O_3 input and volume were 1.63 W cm^{-2}; 50 l h^{-1}; and 600 ml, respectively.

sition of O_3 (in aqueous and gas phases) which enhanced the rates of radical and peroxide production.

3.2. Effect of dye concentration

The impact of initial dye concentration on color degradation was studied by comparing the absorbance decay rates for a variety of concentrations of RBB. It was found that the coefficient of decay decreased with increasing dye concentrations. The experiments were repeated with ozone alone. Comparative evaluation of the combined system and the ozone control set for color degradation coefficient as a function of RBB concentration is presented in Fig. 5. It was found that, in both cases, degradation slowed down with increasing dye concentrations, while the kinetics remained unchanged. However, the combined system was less responsive to an increase in dye concentration in the higher range, suggesting that perhaps thermal degradation reactions occurred at high dye concentrations. This is in agreement with the results of other researchers, who showed that at appreciable concentrations, hydrophilic solutes might slightly move away from solution and adsorb on the bubble–liquid interface to undergo thermal decomposition [18].

3.3. Carbon mineralization

Oxidative degradation processes produce organic intermediates which may be more harmful than the parent molecule if released into the environment without further treatment. Bleaching of a dye solution produces intermediates, which compete with the parent dye for •OH, O_3 and H_2O_2. Consequently, destruction of the dye should be evaluated as an overall degradation process, involving the ultimate mineralization of both the parent dye and its intermediates. The most practical means of estimating this overall process is to monitor the reduction of total organic carbon (TOC).

The rate of TOC removal in 20 μM RBB over 1-h contact with the combined scheme and the two controls (with O_3 and US alone) is presented in

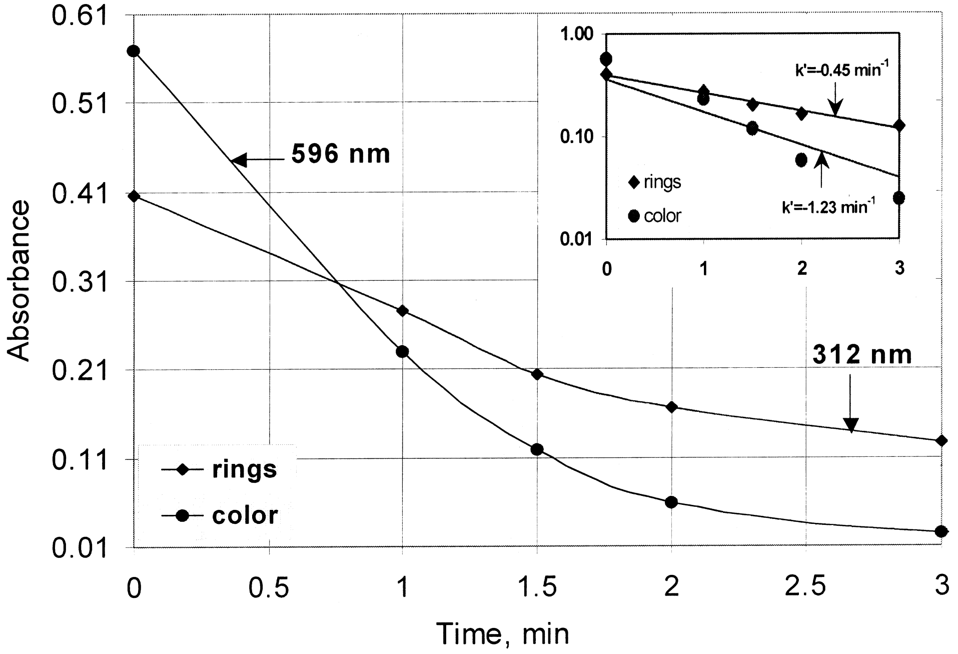

Fig. 3. Degradation of 20 μmol l^{-1} RBB (monitored by the absorption at the near-UV and visible bands) during 3-min contact with US/O_3. The plot on the top right corner shows the graphical estimation of first order absorption decay rate by log-linear regression analysis of absorbance–time data.

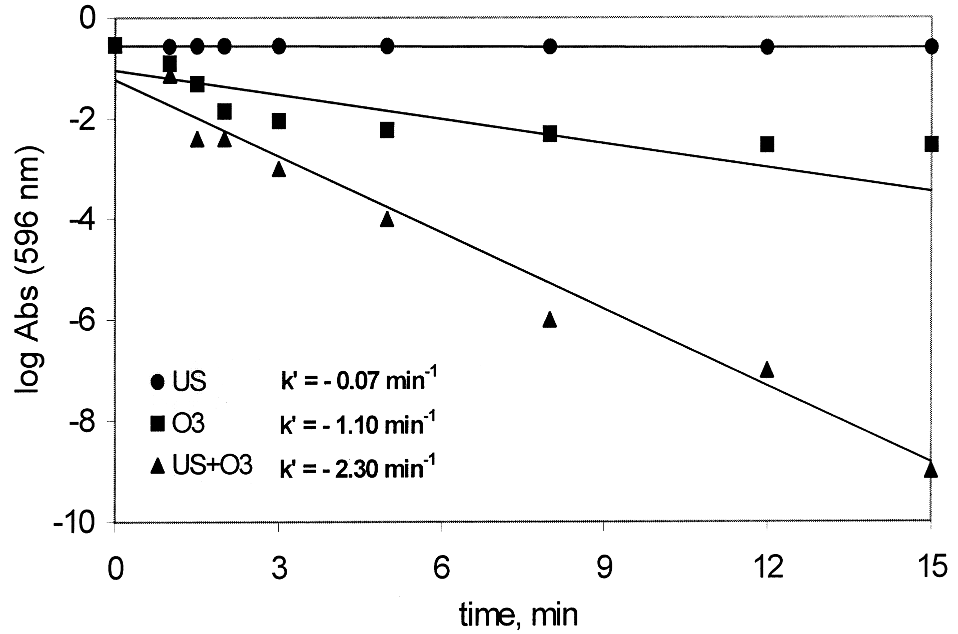

Fig. 4. First order color degradation kinetics of 10 μmol l^{-1} preaerated RBB during 15-min contact with US, O_3 and US/O_3 combined schemes. The solid lines and k' denote the regression fits and the pseudo-first order rate coefficients, respectively. Reactor conditions as irradiation intensity, ozone flow and volume were same as listed in the caption of Fig. 2.

Fig. 6. It was found that total mineralization in US, O_3 and US/O_3 schemes was 2, 50 and 76%, respectively. The inefficiency of US by itself is consistent with its poor performance for color degradation. The data suggest that much longer contact is necessary for appreciable conversion of TOC to CO_2 by ultrasonic treatment alone. In a similar study by Vinodgopal et al., it was reported that 60% mineralization was accomplished in 33 μM RB after 6 h irradiation under similar conditions [14]. In the same work, the authors detected oxalic acid as one of the reaction intermediates, suggesting that degradation should not be assessed in terms of total mineralization alone, because some of the organic carbon may be converted to stable and environmentally acceptable forms other than carbon dioxide.

Ozonation alone was relatively more effective than US for total mineralization, but the combination of the two resulted in a synergistic increase in the overall process rate. The synergy suggests that cavitation events accelerate degradation of the ozone-induced intermediates of RBB. This is particularly obvious from the lack of TOC reduction between 15 and 30 min in both US/ozone and ozone alone treatments as opposed to the linear reduction in TOC in the combined treatment. (Note that total mineralization with ozonation, and ozonation combined with US after 30 min were 14.4 and 59.7%, respectively.) Hence, despite its inefficiency when used alone, ultrasound when combined with ozonation was extremely effective in accelerating mineralization of the dye. It is most likely that during simultaneous operation, the early oxidation reactions resulting in bleaching of the dye are governed by ozone and its decomposition products, whereas the destruction of the oxidation intermediates is achieved by the joint action of US and ozone. It is likely that the observed synergism involves factors such as (1) enhanced efficiency of ozone dissolution induced by the mechanical action of ultrasound, (2) larger decomposition of ozone in water by additional pathways such as chain reactions (involving the production of peroxy and superoxide radicals), (3) reduced competition for •OH, O_3 and H_2O_2 by thermal decomposition of some intermediates, and (4) increased quantity of oxidizing species in

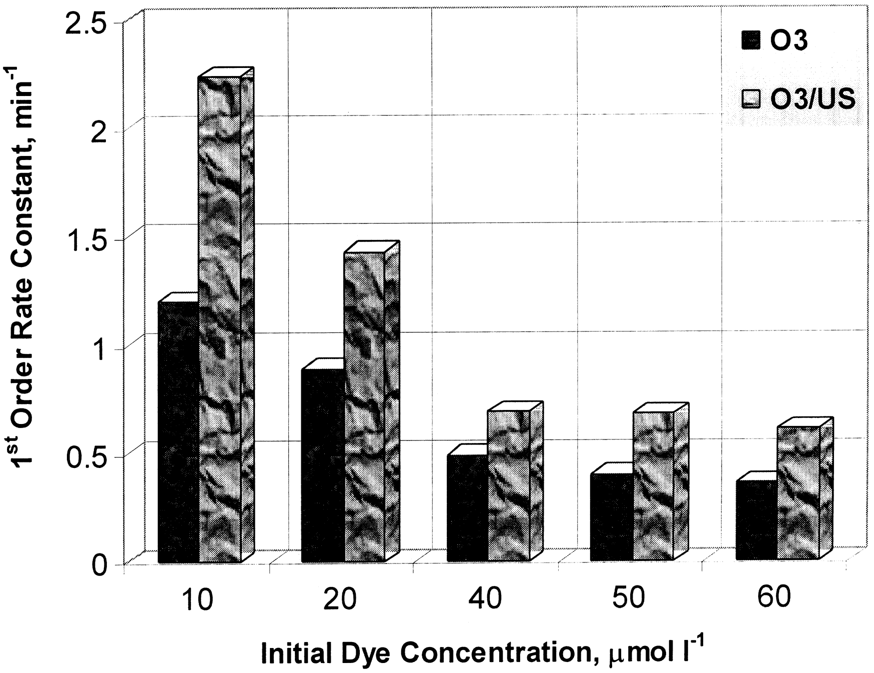

Fig. 5. The response of pseudo-first order colour degradation rate coefficient to the initial dye input.

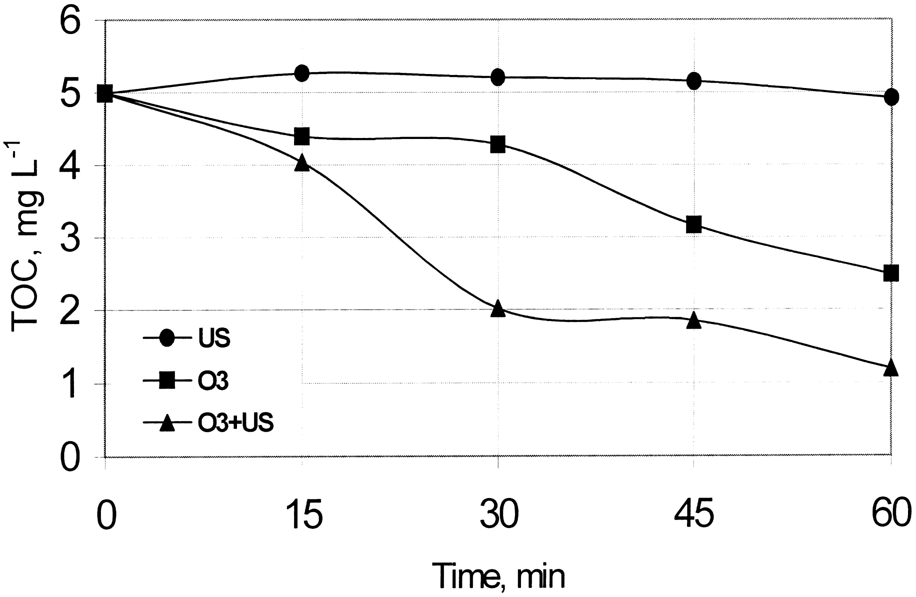

Fig. 6. Comparison of US/O_3 combined scheme with the two control sets for rates of total organic carbon removal (mineralization) in 20 μmol l^{-1} pre-aerated RBB.

solution upon migration of some relatively stable thermolysis products from collapsing cavities into the solution bulk.

4. Conclusions

Ozonation is a widely practiced method of color degradation in dyehouse effluents, but it is inefficient for the more challenging problem of effluent mineralization to meet current discharge standards and/or to recycle the spent water in the process. This study showed that the efficiency of ozone treatment is significantly enhanced by simultaneous irradiation of the treated solution with ultrasound.

It was found during lab-scale treatment of a reactive dyebath effluent with ozone, that the rate of color degradation achieved in conjunction with sonolysis was twice as fast as that accomplished by ozonation alone. The synergism observed for the overall degradation (mineralization) of the dye reflects the potential of the US/ozone combination treatment to minimize the survival time of the reaction intermediates. Its effects can be attributed to the mechanical effects of cavitation, which increased the mass transfer and decomposition of ozone, thus enhancing both the rate of direct reactions and that of •OH-mediated oxidation of intermediate products.

The proposed combination may be applicable in the management of dyehouse effluents, particularly in the search of new alternatives to achieve recycling of spent waters in the dyeing process. Our future work, therefore, will focus on reaction mechanisms and kinetics, and the economic feasibility of the system.

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