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Degradation of C.I. Acid Orange 7 by ultrasound enhanced ozonation in a rectangular air-lift reactor

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Abstract

The combination of 20 kHz ultrasound and ozone for the degradation of C.I. Acid Orange 7 was studied. The effect of power density, gas flow rate, initial pH, hydroxyl radical scavenger, and initial dye concentration on the decolorization of C.I. Acid Orange 7 was investigated. The decolorization of C.I. Acid Orange 7 fits the pseudo-half-order kinetic model under most of the operating conditions. The decolorization rate increased with the increase of power density and gas flow rate, but decreased with the increasing initial dye concentration. Either pH or sodium chloride has little effect on the decolorization rate, indicating that the low frequency ultrasound enhanced ozonation process for the decolorization of C.I. Acid Orange 7 is mainly a direct reaction rather than radical reaction. Moreover, the decolorization rate increased with sodium carbonate to dye moalr ratio. The synergistic effect of C.I. Acid Orange 7 mineralization by ultrasound enhanced ozonation was significant when the system temperature was raised due to the heat effect of ultrasonic irradiation.

Keywords: Ultrasound; Ozone; C.I. Acid Orange 7; Decolorization; TOC; Synergistic

1. Introduction

The disposal of wastewater containing azo dyes is an environmental concern since the associated color is quite noticeable to the public, and some dyes may have carcinogenic and/or teratogenic effects on public health [1]. Decolorization of wastewaters is one of the significant problems as the dye will be visible even at low concentration. Most of the dyes are found to be resistant to the conventional sewage treatment process as they are designed to resistant chemical and photochemical degradation [2]. Ozone has been used for the treatment of refractory wastewater such as textile industry wastewater [3]. However, there are a few disadvantages which limit industrial applications of ozonation. The first is the high production cost of ozone and the low ozone utilization due to poor mass transfer rate of ozone [4,5]. Furthermore, though ozone could readily decoloralize dye wastewater, it could not mineralize dye wastewater effectively due to the limit oxidizing power of ozone ($E^0 = 2.07$ V). One method of enhancing ozonation reactions is to simultaneously apply ultrasonic irradiation [2,6–23].

Over the last few years there have been a lot of reports on the application of ultrasound for the destruction of aqueous inorganic and organic pollutants such as azo dyes [24–29]. When the aqueous solutions containing the organic pollutants such as azo dyes are exposed to an acoustic field, dissolved gases and water vapor are entrapped by cavitation bubbles, which expand at rarefaction cycles of the bubbles and release extreme temperatures upon adiabatic collapse. Under these conditions, bubble contents are pyrolytically dissociated into free radicals, some of which could diffuse into the aqueous phase [26]. Pyrolytic reactions inside or near the bubble and radical reactions in the solution are regarded as the two major pathways for sonochemical degradation [29]. Sonochemical destruction is particularly effective for volatile substrates as these solutes can be directly combusted within the gas phase of the hot collapsing cavitation bubbles [6]. The effect of ultrasound waves on the hydrophilic chemical oxidation is due to the production of hydroxyl radicals during the cavitation-induced thermal decomposition of water [30]. The rate constant of radical type reaction is relatively too low as approximately only 10% of the hydroxyl radicals generating in the cavitation bubbles could escape to the bulk liquid [31]. Therefore, much effort has been devoted to accelerate the decomposition rates of hydrophilic compounds by means of the combination with other methods.

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The coupling of ultrasonic irradiation with ozonation (US/O_3) may provide a possible advanced oxidation process (AOP), in which hydroxyl radical, a more effective oxidant ($E^0 = 2.87$ V) than ozone, is generated in sufficient quantity to affect wastewater treatment. In the presence of ultrasonic irradiation, ozone is decomposed thermolytically in the vapor phase of a cavitation bubble [32]:

$$O_3(g) +))) \rightarrow O_2(g) + O(^3P)(g) \tag{1}$$

$$O(^3P)(g) + H_2O(g) \rightarrow 2^{\bullet}OH(g) \tag{2}$$

where the symbol “)))” indicates ultrasonic irradiation. These decomposition reactions occur in the gas phase. The reaction products migrate to the interfacial sheath of the bubble where they subsequently react in the aqueous phase [13]. In addition, ultrasonic irradiation has been demonstrated to increase the mass transfer of ozone to aqueous phase by means of increasing mass transfer coefficient [6,11,15,33,34]. Until now, more attention was paid to the employment of conventional reactors such as stirred tank reactors or bubble columns to perform the combine US/O_3 process. However, the reactor with more efficient mass-transfer was seldom used in the coupled US/O_3 process. The airlift reactors have been regarded as a promising type of gas–liquid reactor due to their good mixing with low shear stress and energy consumption as well as their advantages of high gas–liquid mass and heat transfer [35]. At present airlift reactors have been widely used in biotechnological processes, especially in biological wastewater treatment [35]. An airlift reactor is mainly composed of two zones, the riser and the downcomer. The riser lane corresponds to the zone where the gas phase is injected and the fluid and gas travel upwards together; in the downcomer lane the gas and liquid travel downwards [36]. To our knowledge, only Bando et al. conducted the combined US/O_3 process in a rectangular air-lift reactor [17]. However, the effect of various operation conditions on the coupled US/O_3 process in this kind of reactor was not investigated.

During the US/O_3 process, the system temperature would be raised due to the heat effect of ultrasonic irradiation. The temperature effect on sonochemical reaction and chemical reaction is different. The reactor cooling was usually provided in most of the reports as the largest sonochemical effects are observed at lower temperatures [31]. Martins et al. [18] observed that the combined US/O_3 process for the decolorization of pararosaniline dye was less efficient than ozonation alone due to the temperature increase when no reactor cooling was provided. However, Lall et al. [15] and He et al. [22] reported that the decolorization rate was enhanced by increasing the temperature in the coupled US/O_3 process. Our previous work also demonstrated the synergistic effect of the combined US/O_3 process for the decolorization of methyl orange was more significant when the system temperature was raised from 16 to 28 °C [20]. In this case the cooling water would not be needed and the operation cost for cooling water would be saved. Therefore, the objective of this study was to treat C.I. Acid Orange 7, a model azo dye, by the coupled US/O_3 process in a rectangular airlift reactor. The effects of operating conditions such as power density, gas flow rate, initial pH, hydroxyl radical scavenger, and initial dye concentration on the decolorization efficiency were investigated. The synergistic effect of the combined US/O_3 process for the mineralization of C.I. Acid Orange 7 was also explored.

2. Materials and methods

Stock solution of C.I. Acid Orange 7 was prepared in distilled water before each run. H_2SO_4 or NaOH was used to adjust the initial pH (pH_0) of the dye solution. The stock solution was fed into a rectangular air-lift reactor made of plexy glass (see Fig. 1). This reactor consists of a square column (50 mm × 30 mm) with the height of 120 mm, divided into a riser and a downcomer section by a plexy glass baffle (width: 30 mm; thickness: 4 mm; total height: 55 mm). The riser-to-downcomer cross-sectional area ratio was equal to 1.56. The baffle was located at a distance of 5 mm from the bottom of the reactor. The gas distributor at the bottom of the riser was a perforated tube with six orifices of 1 mm diameter.

Sonication was performed with a KS-250 ultrasonic generator (250 W, 20 kHz, Ninbo Kesheng Instrument Co., China) equipped with a titanium probe transducer. The tip of the probe was 1 cm in diameter and was placed 1.5 cm into the liquid layer. The sonication was administered in pulses with a 50% duty cycle. The acoustic power (P) was determined calorimetrically [37].

Ozone was bubbled into the solution using an ozone generator (XFZ-5QI, China). The gaseous ozone concentration was monitored by the iodometric method with potassium iodide solution [38]. A predetermined amount of aliquot was removed with pipette at different time intervals. The absorbance of the solution was measured using a Shimadzu UV-1600 spectrophotometer after dilution with distilled water. Total organic carbon (TOC) was determined using Multi N/C$^{®}$2100, Analytik Jena AG.

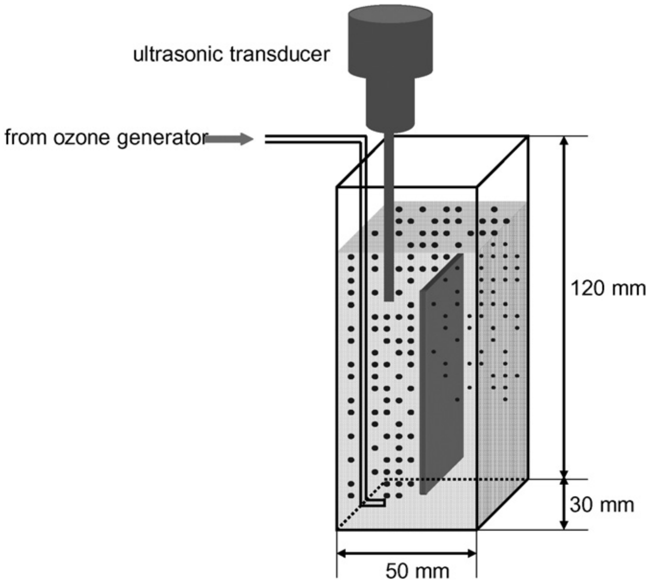

Fig. 1. The experimental set up.

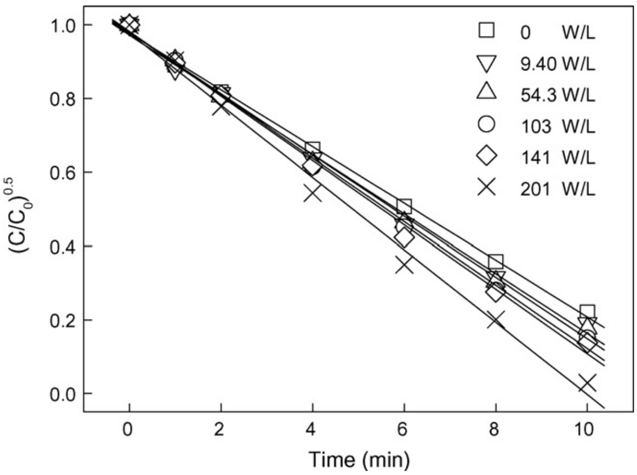

Fig. 2. The effect of power density on the decolorization ($C_0 = 0.91$ mmol/L, $[O_3]_g = 0.79$ mmol/L, $Q = 833$ mL/min, pH$_0$ 4.5).

3. Results and discussion

3.1. The effect of power density on the decolorization of C.I. Acid Orange 7

Fig. 2 displays decolorization of C.I. Acid Orange 7 in the coupled US/O$_3$ system at different power densities when the dye concentration C_0 was 0.91 mmol/L, ozone concentration $[O_3]_g$ was 0.79 mmol/L, the ozone gas flow rate Q was 833 mL/min and the initial pH was 4.5. It can be seen that the decolorization follows apparent pseudo-half-order kinetics according to the following rate equation:

$$-\frac{dC}{dt} = k_{0.5}C^{0.5} \tag{3}$$

where C is the dye concentration at time t and $k_{0.5}$ is the pseudo half order decolorization rate constant. This is in agreement with Dahi's report when Rhodamine B were degraded by US enhanced ozonation [33] though apparent pseudo-first-order kinetics was also observed by other researchers [14–16,20,22].

Decolorization of C.I. Acid Orange 7 by US enhanced ozonation can be regarded as a mass transfer process coupled with chemical reactions. Gaseous ozone was absorbed into the aqueous phase and then reacted with C.I. Acid Orange 7 dissolved in the liquid with an irreversible 1,1-order reaction, i.e., first order with respect to both ozone and solute concentrations [39]. The decolorization rate was considered to be equal to the ozone absorption rate $N_A a$,

$$-\frac{dC}{dt} = zN_A a \tag{4}$$

where z is the stoichiometric ratio, N_A is mass transfer flux, and a is specific interfacial area. This equation holds for the first 10 min of reaction in which ozone only reacts with C.I. Acid Orange 7, and no other competitive reactions with intermediates formed can be expected.

On the other hand, the ozone absorption rate can be expressed by the following equation according to the film theory [31],

$$N_A a = Ek_L a[O_3]^* \tag{5}$$

where $[O_3]^*$ is ozone equilibrium concentration, and E is the enhancement factor, defined as the ratio of the rate absorption in the presence of a chemical reaction to the maximum rate of physical absorption.

It is generally well-accepted that the gas–liquid reaction can occur in different regimes depending upon the relative rates of gas–liquid mass transfer and chemical reaction involved [40]. The reaction between dissolved ozone and C.I. Acid Orange 7 is fast and occurs within the liquid film [41], which falls in the fast kinetic regime according to the film theory [40]. Furthermore, inside the fast regime there is a particular situation when the reaction can be considered of pseudo-first-order with respect to the dissolved ozone and $E = Ha$, where Ha is the Hatta number which indicates the relative importance of the chemical reaction compared to the mass transfer, and is defined as [40],

$$Ha = \frac{\sqrt{k_2 D_{\text{ozone}} C}}{k_L} \tag{6}$$

where k_2 is the intrinsic rate constant of irreversible 1,1-order reaction, D_{ozone} is molecular diffusion coefficients of ozone in the liquid, and k_L is liquid side mass transfer coefficient.

With the condition $E = Ha$ and combining Eqs. (5) and (6), it is obtained,

$$N_A a = a[O_3]^* \sqrt{k_2 D_{\text{ozone}} C} \tag{7}$$

Substituting the above equation into Eq. (4),

$$-\frac{dC}{dt} = \left(za[O_3]^* \sqrt{k_2 D_{\text{ozone}}}\right) C^{0.5} \tag{8}$$

At the fixed operating conditions, z, a, $[O_3]^*$, D_{ozone}, and k_L would keep constant. k_2 could also be approximately supposed as a constant in this study. The temperature increased around 0, 0, 2.5, 6, 9, and 11 °C after 10 min reaction when power densities were 0, 9.40, 54.3, 103, 141 and 201 W/L, respectively. In addition, the activation energy of ozonation of azo dye is relatively low [42]. Therefore the effect of temperature on k_2 is insignificant based on the Arrhenius equation and k_2 could be regarded as a constant. Then assuming,

$$k_{0.5} = za[O_3]^* \sqrt{\bar{k}_2 D_{\text{ozone}}} \tag{9}$$

where $\bar{k}_2$ is the average rate constant over the range of temperature, and $k_{0.5}$ could be approximately assumed as a constant and accordingly the decolorization followed apparent pseudo-half-order kinetics. This can be verified by the very high correlation coefficients R^2 which ranged from 0.9932 to 0.9981.

As can be seen in Fig. 2, the decolorization rate increased with the increasing power density. The apparent rate constants were 0.147, 0.154, 0.158, 0.164, 0.166 and 0.187 mmol$^{0.5}$ L$^{-0.5}$ min^{-1} when power densities were 0, 9.40, 54.3, 103, 141 and 201 W/L, respectively. The ozonation of azo dyes in water was observed to be in mass transfer limited region [43], and the controlling resistance of mass transfer is in liquid film [44]. When gas bubbles containing ozone enter the ultrasonic reactor, the greater mixing due to ultrasonic irradiation leads to the turbulence [6], which reduces the liquid film thickness [15]. According to the two-film theory, mass transfer coefficient k_L is inverse proportional to the liquid film thickness. The decrease of the liquid film thickness would result in the increase of k_L. In addition, one of the mechanical effects of ultrasound is the break up of gas bubbles containing ozone [6], which lead to the larger specific surface area a. Therefore volumetric mass transfer coefficient k_La would increase in the presence of ultrasonic irradiation. An increase in power density would increase turbulence and enhance the mechanical effect to break up ozone bubbles which would increase the mass transfer rate of ozone in aqueous phase. Hence the decolorization rate would increase with power density.

3.2. UV–vis spectra changes in the combined US/O_3 system

To clarify the changes of molecular and structural characteristics of C.I. Acid Orange 7 as a result of US enhanced ozonation, representative UV–vis spectra changes of the dye solution as a function of reaction time were depicted in Fig. 3. As could be observed from these spectra, before the oxidation, the absorption spectrum of C.I. Acid Orange 7 in water was characterized by one main band in the visible region, with its maximum absorption at 484 nm, and by two other bands in the ultraviolet region located at 229 and 310 nm, respectively. The peaks at 229 and 310 nm were associated with "benzene-like" structures in the molecule, and that at 484 nm was based on the azo group. The disappearance of the visible band with the time was due to the fragmentation of the azo links by direct ozone attack. In addition to this rapid bleaching effect, the decay of the absorbances at 229 and 310 nm was considered as evidence of aromatic fragment degradation in the dye molecule and its intermediates [14].

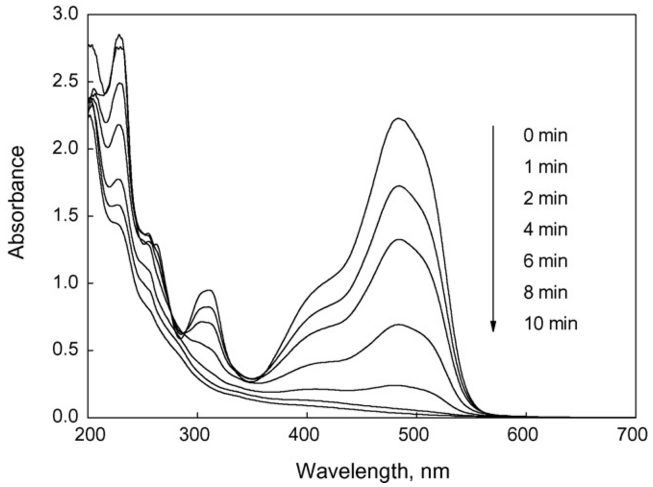

Fig. 3. The evolution of absorbance with reaction time.

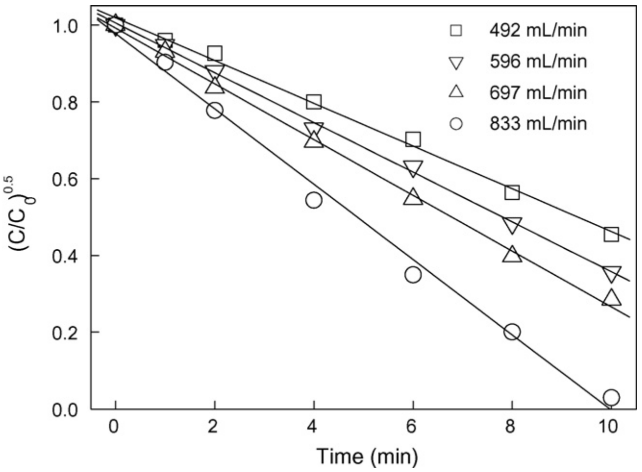

Fig. 4. The effect of gas flow rate on the decolorization ($C_0 = 0.91$ mmol/L, $[O_3]_g = 0.81$ mmol/L, pH_0 4.7, $P = 201$ W/L).

3.3. The effect of gas flow rate on the decolorization of C.I. Acid Orange 7

Fig. 4 showed the decolorization of C.I. Acid Orange 7 in the combined US/O_3 system at different ozone gas flow rate when the dye concentration was 0.91 mmol/L, ozone concentration was 0.81 mmol/L, ultrasonic power density was 201 W/L and the initial pH was 4.7. It illustrated that the decolorization rate increased with the increase of gas flow rate. The apparent rate constants were 0.106, 0.124, 0.138, and 0.187 $\text{mmol}^{0.5}\,\text{L}^{-0.5}\,\text{min}^{-1}$ when gas flow rates were 492, 596, 697 and 833 mL/min, respectively. Increasing the flow rate corresponds to a larger net surface area for mass transfer of ozone to the aqueous phase [11], and hence increases the volumetric mass transfer coefficient of ozone. This results in the increase of mass transfer rate of ozone from gas phase to liquid phase and hence the decolorization rate due to the mass transfer controlled characteristics in the coupled US/O_3 system.

3.4. The effect of initial pH and hydroxyl radical scavengers on the decolorization of C.I. Acid Orange 7

The initial pH values investigated for the combined US/O_3 system were 4.1, 6.4, 7.2, 8.6 and 9.4, respectively when the dye concentration was 0.91 mmol/L, ozone concentration was 0.81 mmol/L, the gas flow rate was 833 mL/min, and ultrasonic power density was 201 W/L (see Fig. 5). The apparent half-order rate constants for these pH values were determined to be $0.183 \pm 0.004\ \text{mmol}^{0.5}\,\text{L}^{-0.5}\,\text{min}^{-1}$. This indicated that there was little difference in the decolorization rate at either pH value, which is similar to the observation by Lall et al. [15] and Zhang et al. [20]. Basically, ozone oxidizes organic pollutants via two pathways: by direct oxidation with ozone molecules and by the generation of free-radical intermediates, such as $^{\bullet}OH$ radical, a powerful, effective, non-selective oxidizing agent [39]. At higher pH value, hydroxyl radical would be generated from ozone decomposition in the presence of hydroxide ion. Therefore ozonation process may proceed via free radical pathway.

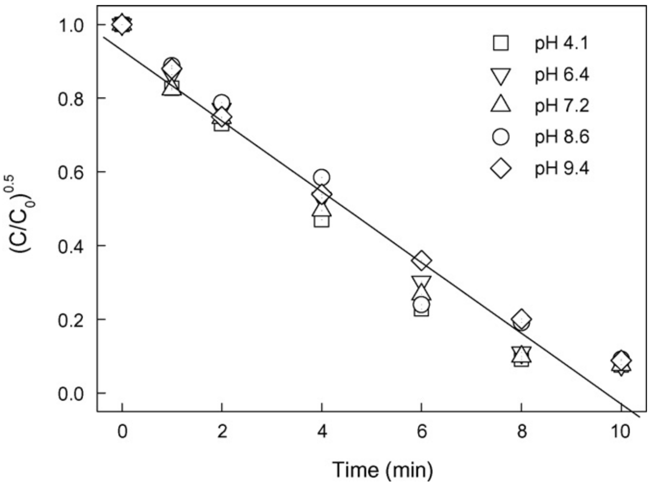

Fig. 5. The effect of pH on the decolorization ($C_0 = 0.91$ mmol/L, $[O_3]_g = 0.81$ mmol/L, $Q = 833$ mL/min, $P = 201$ W/L).

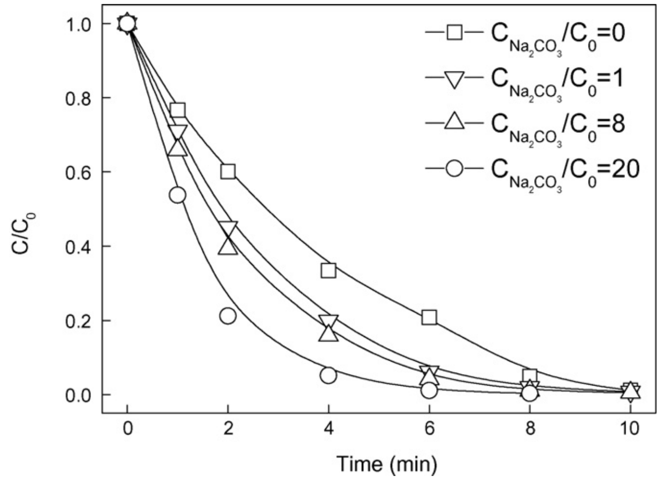

Fig. 7. The effect of sodium carbonate on the decolorization ($C_0 = 0.91$ mmol/L, $[O_3]_g = 0.80$ mmol/L, $Q = 833$ mL/min, pH_0 9.3, $P = 201$ W/L).

However, the radical contribution to the decolorization of azo dyes could be neglected during ozonation in combination with ultrasonic irradiation because azo dyes present in their structure functional groups and double bonds very prone to the direct ozone attack [45]. It was also observed that ozone in aqueous phase would tend to react with azo dyes rather than free radicals in UV enhanced ozonation process [43] as well as US enhanced ozonation process [20]. To prove this point, some of the decolorization reactions in the coupled US/O_3 system were carried out in the presence of chloride, a kind of hydroxyl radical scavenger [46]. Sodium chloride to dye molar ratios investigated were 1, 8 and 20, respectively when the dye concentration was 0.91 mmol/L, ozone concentration was 0.83 mmol/L, the ozone gas flow rate was 833 mL/min, initial pH was 4.7, and power density was 201 W/L. The results showed that the presence of chloride had no significant effect on the decolorization rate when sodium chloride to dye molar ratio ranged from 1 to 20 (see Fig. 6). It is known that the lifetimes of cavitation bubble is longer at lower frequencies (3×10^{-5} s at 20 kHz as compared to 3×10^{-7} s at 514 kHz), hence hydroxyl radicals have less opportunity to escape the cavitation bubble before undergoing any reaction or recombination [31]. Therefore the primary mechanism of decolorization is direct decomposition by ozone instead of the reaction involved in radicals formed in the ultrasound-enhanced ozonation process. To reconfirm this point, another kind of hydroxyl radical scavenger, sodium carbonate, was employed for the decolorization reactions in the combined US/O_3 system. As illustrated in Fig. 7, the presence of sodium bicarbonate accelerated decolorization instead of hindering decolorization, and the decolorization rate increased with carbonate to dye molar ratio.

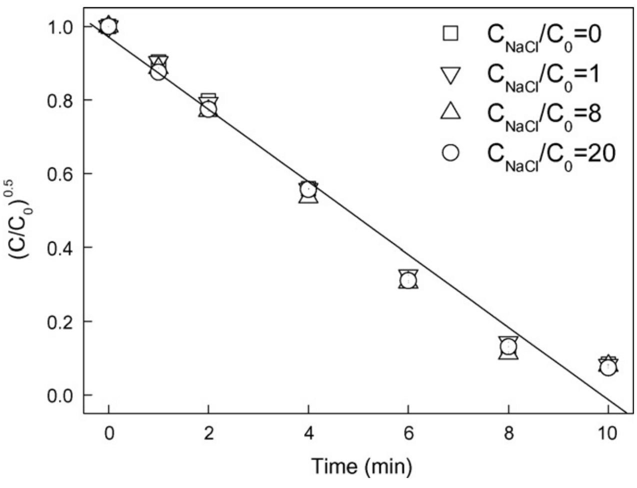

Fig. 6. The effect of sodium chloride on the decolorization ($C_0 = 0.91$ mmol/L, $[O_3]_g = 0.83$ mmol/L, $Q = 833$ mL/min, pH_0 4.7, $P = 201$ W/L).

Inorganic salts were found to reduce bubble coalescence which leads to the increase of mass transfer rate by enlarging the contact surface [47]. The ability of electrolytes to prevent bubble coalescence is due to their ionic strength: electric charge accumulated on the surface of bubbles produces a repulsive force, preventing them from approaching each other [48]. In addition, the dissolved salts may strengthen the electrostatic bonds between water molecules and make the film separating bubble stronger [49]. The inhibiting effect on bubble coalescence is pronounced above a critical concentration range of electrolyte, the so-called transition concentration [50]. Generally the transition concentration of the electrolytes depends on the valency, i.e., a more highly charged salt would effectively inhibit coalescence at a lower concentration [50,51]. For example, the transition concentration of sodium chloride was reported as high as 0. 175 mol/L [52], which was much higher than the concentration used in this study. Therefore, it was expected that sodium chloride had little effect on the direct ozonation of C.I. Acid Orange 7 when sodium chloride to dye molar ratio ranged from 1 to 20. To our knowledge, there was no report on the transition concentration of sodium carbonate. Only Cui et al. [53] observed that 1% sodium carbonate could prevent coalescence of vapor bubbles and enhance heat transfer accordingly.

In the presence of carbonate, the apparent decolorization kinetics deviated from pseudo-half behavior. When carbonate to dye molar ratio were 1, 8 and 20, respectively, the R^2 values

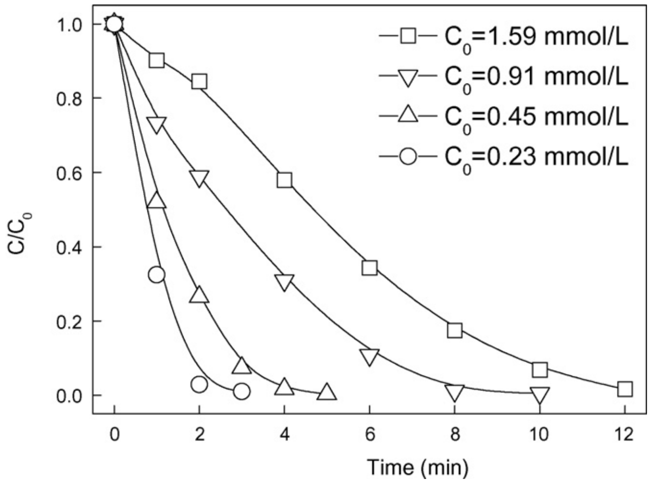

Fig. 8. The effect of initial dye concentration on the decolorization ($[O_3]_g = 0.85$ mmol/L, $Q = 833$ mL/min, pH_0 4.6, $P = 201$ W/L).

were only 0.9440, 0.9236 and 0.8680. The change of apparent kinetics may due to the transition of absorption regime when carbonate was applied into the system.

3.5. Effect of initial dye concentration on the decolorization of C.I. Acid Orange 7

Fig. 8 showed the decolorization of C.I. Acid Orange 7 in the combined US/O_3 system at different initial dye concentration when ozone concentration was 0.85 mmol/L, the gas flow rate was 833 mL/min, ultrasonic power density was 201 W/L and the initial pH was 4.6. The R^2 values were 0.9950, 0.9794, and 0.9673, and 0.9282 when initial dye concentrations were 1.59, 0.91, 0.45 and 0.23 mmol/L, respectively. This indicated that the apparent decolorization kinetics deviated from pseudo-half behavior with the decrease of the initial dye concentration. According to the film theory [41], the absorption regime is dependent on Hatta number, which is the function of dye concentration as defined in Eq. (6). The decrease of initial dye concentration would lead to the decrease of Hatta number, and the absorption regime would change accordingly.

As can be seen in Fig. 8, the decolorization rate decreased with initial dye concentration. Combining Eqs. (4) and (5), we have,

$$-\frac{dC}{dt} = zEk_{L}a[O_3]^{*} \tag{10}$$

Rewriting the above equation,

$$-\left.\frac{d(C/C_0)}{dt}\right|_{t=0} = zk_{L}a[O_3]^{*}\frac{E}{C_0} \tag{11}$$

The values of z, k_L a, and $[O_3]^*$ are fixed at different initial dye concentration. Although the enhancement factor E increases with dye concentration, it is not proportional to dye concentration [54]. Therefore, the initial decolorization rate in terms of normalized dye concentration C/C_0 decreased with initial dye concentration. In particular, when initial dye concentrations were 1.59 and 0.91 respectively, the higher R^2 values indicated the decolorization followed the apparent pseudo-half order kinetics. Then the apparent rate constant $k_{0.5}$ would be constant based on Eq. (9). Specifically, the $k_{0.5}$ values were 0.191 and 0.186 $mmol^{0.5}\,L^{-0.5}\,min^{-1}$ when initial dye concentrations were 1.59 and 0.91 $mmol\,L^{-1}$ respectively. Then rewriting Eq. (3),

$$-\left.\frac{d(C/C_0)}{dt}\right|_{t=0} = \frac{k_{0.5}}{\sqrt{C_0}} \tag{11}$$

The above equation indicated that the initial decolorization rate in terms of normalized dye concentration would be higher at the lower initial dye concentration.

3.6. Mineralization of C.I. Acid Orange 7 in different systems

To investigate the enhancement of sonication on the mineralization of C.I. Acid Orange 7 by ozonation, experiments were performed at the constant temperature of 29 °C with ozonation alone, ultrasound alone and the combined US/O_3 system, respectively. The dye concentration was 0.91 mmol/L, initial pH was 4.5, and the gas flow rate was 833 mL/min (oxygen instead of ozone was bubbled into the reactor in the run of ultrasound alone). Ozone concentration was 0.81 mmol/L in ozonation alone and the combined US/O_3 system, whereas ultrasonic power density was 201 W/L in ultrasound alone and the combined US/O_3 system. As shown in Fig. 9, C.I. Acid Orange 7 was continuously mineralized in ozonation alone system as well as the combined US/O_3 system. Ultrasound had no effect on either the decolorization or the mineralization (data not shown), since the production of $^{\bullet}OH$ radicals in the bulk liquid at 20 kHz frequency was too low to affect the degradation of C.I. Acid Orange 7 [55]. Although a little higher TOC removal rate was achieved by the combined US/O_3 system during the first 40 min of reaction, the difference of TOC removal between ozone alone and the combined US/O_3 system became insignificant after 40 min.

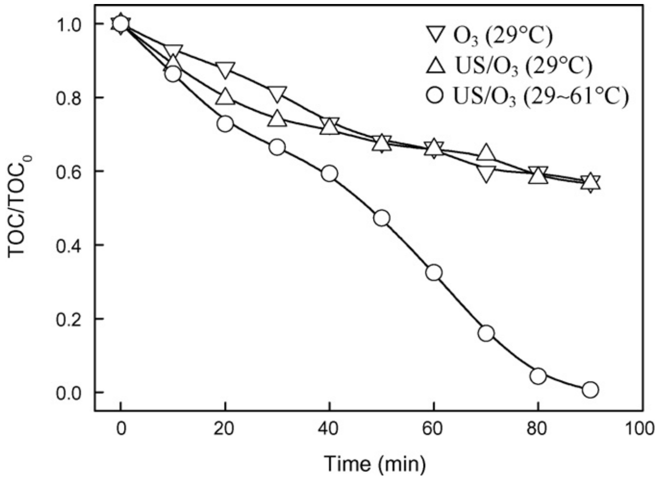

Fig. 9. Mineralization of C.I. Acid Orange 7 by ozonation with/without sonolysis ($C_0 = 0.91$ mmol/L, $[O_3]_g = 0.81$ mmol/L, $Q = 833$ mL/min, pH_0 4.5, $P = 201$ W/L).

The presence of ultrasonic irradiation would enhance mass transfer rate of ozone from gas phase to liquid phase. In addition, azo dyes are susceptible to direct ozone reactions [20,43]. This resulted in the higher TOC removal rate in the coupled US/O_3 system in the initial stage of the reaction. However, the subsequent reactions of ozone with the byproducts such as carboxylic acids were quite slow. At constant temperature of 29 °C, the production of hydroxyl radicals via reactions (1) and (2) was not pronounced. Therefore, TOC removal was not enhanced when ozonation byproducts was dominant. Tezcanli-Güyer and Ince [16] also observed that 520 kHz ultrasound could not enhance the mineralization of C.I. Acid Orange 7 by ozonation when the temperature was kept constant at 25 ± 1 °C.

When the mineralization in the combined US/O_3 system was tested without using cooling water to keep temperature constant, C.I. Acid Orange 7 was nearly mineralized completely after 90 min reaction when the temperature in the system rose from 29 to 61 °C. Sierka [56] also observed that compared with ozone alone system, 10% more TOC was destroyed when trinitrotoluene (TNT) was treated by the coupled US/O_3 process for 60 min and the reaction temperature increased from 26 to 41 °C. The presence of ultrasonic irradiation and the elevation of the temperature would improve mass transfer of ozone into solution and enhance the decomposition of ozone to free radicals. These radicals have oxidation potentials far in excess of ozone and should dramatically increase reaction rate between ozone and azo dyes as well as the intermediates such as carboxyl acids [56]. Therefore TOC removal rate would increase when the system temperature increased from 29 to 61 °C.

4. Conclusion

This study shows ozonation in combination with 20 kHz ultrasound irradiation has synergistic effect on the mineralization of C.I. Acid Orange 7 when reactor cooling was not provided to keep the constant reaction temperature. The decolorization of C.I. Acid Orange 7 fits the half order kinetic model for most operating conditions. The effect of pH on the decolorization was insignificant when pH ranged from 4.1 to 9.4. The presence of hydroxyl radical scavenger such as chloride had little influence on the decolorization rate, which indicates that the primary mechanism of decolorization is direct decomposition by ozone instead of the reaction involved in radicals formed in the US/O_3 process. The decolorization rate was enhanced in the presence of another hydroxyl radical scavenger, sodium carbonate. The decolorization rate increased with increasing power density, gas flow rate, and sodium carbonate to dye molar ratio, but decreased with the initial dye concentration.

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