

Decolorization of methyl orange by ozonation in combination with ultrasonic irradiation

Hui Zhang^{a,*}, Lijie Duan^b, Daobin Zhang^a

^a Department of Environmental Engineering, Wuhan University, P.O. Box C319 Luoyu Road 129#, Wuhan 430079, China

^b Department of Environmental Science, Wuhan University, P.O. Box C319 Luoyu Road 129#, Wuhan 430079, China

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Abstract

The combination of ultrasound and ozone for the decolorization of azo dye, methyl orange, was studied. The effect of ultrasonic power, ozone gas flow rate, gaseous ozone concentration, initial dye concentration, pH and hydroxyl radical scavenger on the decolorization of methyl orange was investigated. The results showed that the synergistic effect was achieved by combining ozone with ultrasonic irradiation for the decolorization of methyl orange. The synergistic effect was more significant when the system temperature was raised due to the heat effect of ultrasonic irradiation. The decolorization of methyl orange fits the pseudo first order kinetic model. The decolorization rate increased with the increase of ultrasonic power, ozone gas flow rate, gaseous ozone concentration. However, the decolorization rate decreased with the increasing initial dye concentration. Either pH or sodium carbonate has little effect on the decolorization rate, indicating that the low frequency ultrasound enhanced ozonation process for the decolorization of methyl orange is mainly a direct reaction rather than radical reaction.

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1. Introduction

Azo dyes are widely used in a variety of industries from textile to paper [1]. The major sources of dyes in the environment are effluents from the textile industry [2]. The disposal of dye wastewater 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 [3]. 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 normal treatment process as they are designed to resist chemical and photochemical degradation [4].

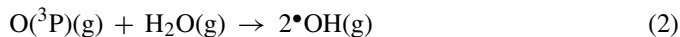
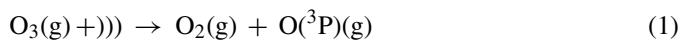
Ultrasonic irradiation has been investigated for the destruction of aqueous organic and inorganic pollutants [5–7]. The substrate molecules can undergo degradation by two different main pathways depending on their chemical nature: pyrolytic reactions inside the cavitation bubbles or oxidation by hydroxyl

radical in the bulk medium [2]. 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 [8]. 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 [9]. 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 [10]. Research on dyestuff degradation by ultrasonic irradiation alone is scarce due to the nonvolatile nature of the azo dyes, and the complete decolorization was achieved after long exposure to ultrasound [1,2,11,12].

Ozone has been used for the treatment of industrial wastewater such as textile industry wastewater [13]. However, industrial applications of ozonation have been limited by the high production cost of ozone and the low ozone utilization due to poor mass transfer rate of ozone [14]. One method of enhancing ozonation reaction is through the use of ultrasound [15]. This combined technology is also more advantageous than ultrasound alone in effectively degrading recalcitrant contaminants [16]. The cou-

* Corresponding author. Tel.: +86 27 68775837; fax: +86 27 68778893.
E-mail address: eeng@whu.edu.cn (H. Zhang).

pling of ultrasonic irradiation with ozonation (US/O₃) may provide a possible advanced oxidation process (AOP). Ozone is decomposed thermolytically in the vapor phase of a cavitation bubble by sonolysis [17]:



where the symbol “ $\xrightarrow{\text{US}}$ ” 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 [5]. In addition, ultrasonic irradiation has been demonstrated to increase the mass transfer of ozone to solution by means of increasing volumetric mass transfer coefficient [8,15,18,19]. The coupled US/O₃ process has been widely used for the destruction of aqueous pollutants [4,5,8,15,19–30].

The system temperature during sonolysis could 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 [10]. However, Sierka [20] reported that the removal rates of both TNT and TOC increased directly with increases in reaction temperature in the coupled US/O₃ process, and Lall et al. [15] also observed the decolorization rate increased with the increasing temperature. The combined US/O₃ process was more efficient for decolorization than ozonation alone [15]. This is opposite to the results of Martins et al. [30] who observed that ozonation of parosaniline dye was more efficient than ozonation combined with ultrasonic irradiation when no reactor cooling was provided. If the increase in temperature is favorable for decolorization, the cooling water would not be needed and the operation cost for cooling water would be saved. Therefore, in this study, methyl orange, as a model azo dye, was treated by the coupled US/O₃ process. The decolorization of methyl orange with and without reactor cooling was first investigated, and then the effects of operating conditions such as initial pH, hydroxyl

radical scavenger, ultrasonic power, gaseous ozone concentration, ozone gas flow rate and initial dye concentration on the decolorization efficacy were investigated at the favorable temperature condition.

2. Materials and methods

2.1. Materials

Methyl orange (C.I. acid orange 52, analytical grade) was purchased from Tanjin Chemical Reagent Co., Inc. (China) and used as received. Ozone was generated onsite by electric discharge using 99.9% oxygen.

2.2. Methods

Stock solution of methyl orange was prepared in distilled water before each run. H₂SO₄ or NaOH was used to adjust the pH of the dye solution. The stock solution was fed into a 180 mL glass reactor. 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 3 cm into the liquid layer. The sonication was administered in pulses with a 50% duty cycle. The reactor was immersed into a water bath to keep the temperature around 16 °C if necessary (see Fig. 1). A magnetic stirrer provided complete mixing of the solution in the reactor. Ozone was bubbled into the solution using an ozone generator (XFZ-5QI, China). The ozone gas flow rate Q was determined with a bubble flow meter. The gaseous ozone concentration [O₃]_g was monitored by the iodometric method with potassium iodide solution [31]. A predetermined amount of aliquot was removed with syringe at different intervals. It was diluted with distilled water and the pH was adjusted to 5.5. Then the sample was measured using a Shimadzu UV-1600 spectrophotometer at maximum absorption wavelength of 465 nm to monitor the effect of the oxidation on the decolorization of methyl orange.

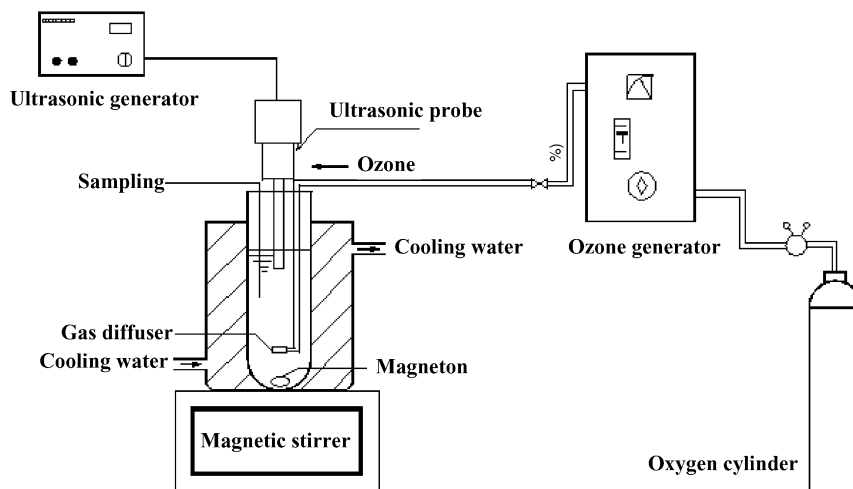


Fig. 1. The experimental set up.

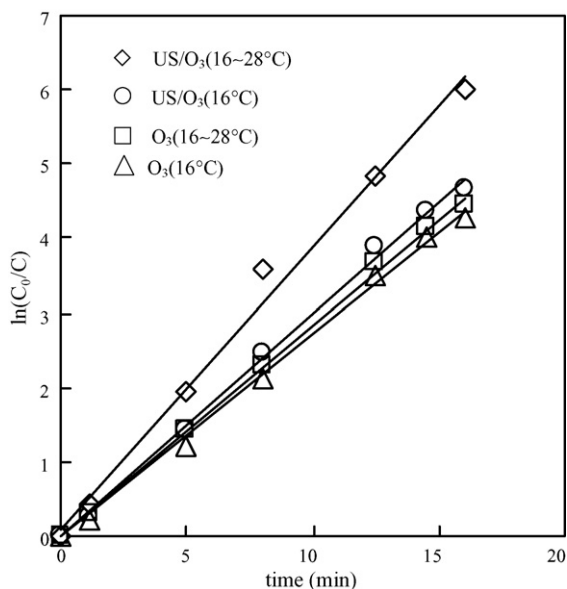


Fig. 2. Decolorization of methyl orange by ozonation with/without sonolysis ($C_0 = 400$ mg/L, $[O_3]_g = 113.5$ mg/L, $Q = 100$ mL/min, pH 5.5, $P = 200$ W).

3. Results and discussion

3.1. Decolorization of methyl orange in different systems

Experiments were performed at the constant temperature of $T = 16^\circ\text{C}$ with ozonation alone, ultrasound alone and the combined US/O₃ system, respectively, to investigate the enhancement of sonication on the decolorization by ozonation. The dye concentration C_0 was fixed at 400 mg/L with the initial pH of 5.5 and the gas flow rate was 100 mL/min (oxygen instead of ozone was bubbled into the reactor in the run of ultrasound alone). Ozone concentration was 113.5 mg/L for ozonation alone and the combined US/O₃ system, whereas ultrasonic power P was 200 W for ultrasound alone and the combined US/O₃ system. As shown in Fig. 2, the decolorization of methyl orange by ozonation with/without ultrasonic irradiation follows apparent pseudo-first-order kinetics. This is in agreement with other works when azo dyes were degraded by ozonation as well as US enhanced ozonation [3,15,28,29]. The apparent pseudo-first-order rate constant k_1 was 0.30 min^{-1} in the coupled US/O₃ system, which was a little higher than 0.27 min^{-1} of rate constant achieved in ozonation alone. Ultrasound had no effect on the decolorization (data not shown), which is similar to the work by Tao et al. [32] who reported the decolorization efficiency was very small when methyl orange was degraded by 28 kHz ultrasonic irradiation.

The system temperature during sonolysis could be raised due to the heat effect of ultrasonic irradiation, and some authors observe that an increase in the ambient temperature can result in an overall decrease in the sonochemical effect [10]. This observation is contrary to chemical reactions in general. In addition, the temperature increase during ultrasonic irradiation may decrease the decolorization rate due to the greater decomposition of ozone and reduction of its solubility in water [30]. Therefore, all three runs mentioned above were operated at the

constant temperature of 16°C . As the synergistic effect was not greatly significant, the decolorization in the combined US/O₃ system was tested without using cooling water to keep temperature constant. The temperature in the system rose from 16 to 28°C ($\Delta T = 12^\circ\text{C}$) and rate constant was achieved as high as 0.39 min^{-1} .

The ozonation of azo dyes in water was observed to be in mass transfer limited region [33], and the controlling resistance of mass transfer is in liquid film [34]. When gas bubbles containing ozone enter the ultrasonic reactor, the greater mixing due to ultrasonic irradiation leads to the turbulence [8], which reduces the liquid film thickness [15]. According to the two-film theory, mass transfer coefficient k_L is inverse proportionally 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 [8], which lead to the larger specific surface area a . Therefore, volumetric mass transfer coefficient $k_L a$ would increase in the presence of ultrasonic irradiation.

However, the enhancement of ultrasound is more pronounced when the system temperature is not controlled. One more run was tested to investigate whether the difference was attributed to the temperature effect when only ozone was supplied to the reactor and the system temperature was raised from 16 to 28°C . As shown in Fig. 2, the decolorization rate was still lower than the coupled US/O₃ system whether the temperature was controlled or not, though the decolorization rate was a little higher than ozonation at the fixed temperature of 16°C . This indicates that there are other mechanisms leading to the enhancement of decolorization rate apart from the mechanical and temperature effects of ultrasound.

Ince and Tezcanlı [28] thought that one mechanism of the enhancement by 520 kHz ultrasound was the fragmentation of the azo links by immediate hydroxyl radical attack produced through reactions (1) and (2). However, the radical type reaction was not significant with 20 kHz ultrasonic irradiation in this study according to the investigations of pH and radical scavenger effects mentioned in the following sections.

As the synergistic effect was more significant in the combined US/O₃ system without the adjustment of system temperature, cooling water was not provided to keep temperature constant in the following experiments.

3.2. UV-vis spectra changes in the combined US/O₃ system

To clarify the changes of molecular and structural characteristics of methyl orange 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 methyl orange in water was characterized by one main band in the visible region, with its maximum absorption at 465 nm and by another band in the ultraviolet region located at 273 nm. The peak at 273 nm was associated with "benzene-like" structures in the molecule [28], and that at 465 nm was originated from an extended chromophore, comprising both aromatic rings, connected through the azo bond. The disappearance of the vis-

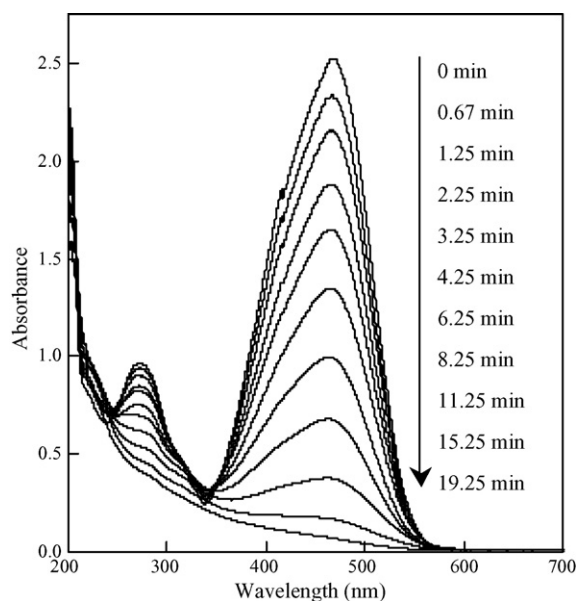


Fig. 3. UV-vis spectral changes with reaction time ($C_0 = 400$ mg/L, $[O_3]_g = 50.7$ mg/L, $Q = 100$ mL/min, pH 5.5, $P = 175$ W).

ible band with the time was due to the fragmentation of the azo links by direct ozone attack [35]. In addition to this rapid bleaching effect, the decay of the absorbance at 273 nm was considered as evidence of aromatic fragment degradation in the dye molecule and its intermediates [28]. The rates of abatement of the two absorption bands were shown in Fig. 4, both of which followed apparent pseudo-first-order kinetics [28,36]. The significantly faster rate of decay of the visible band was attributed to the priority of cleavage of the azo-links in the ozonation, resulting in the rapid disappearance of chromophores in the dye structure. The similar result was reported by Ince and Tezcanlı [28].

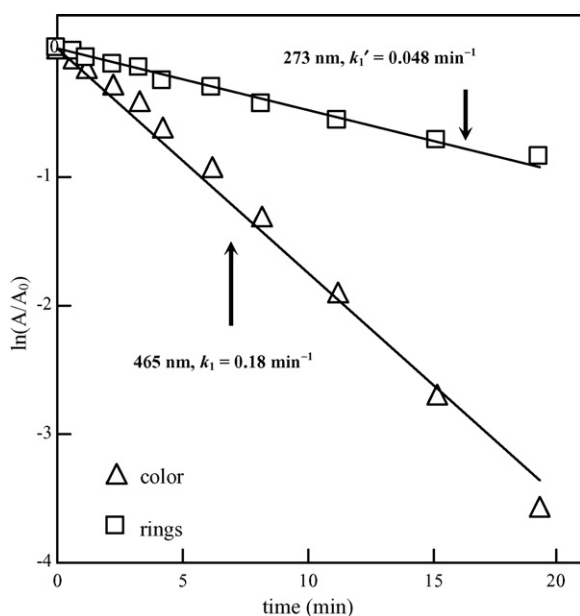


Fig. 4. The evolution of normalized absorbance at 465 and 273 nm with reaction time ($C_0 = 400$ mg/L, $[O_3]_g = 50.7$ mg/L, $Q = 100$ mL/min, pH 5.5, $P = 175$ W).

3.3. The effect of initial pH and hydroxyl radical scavenger on the decolorization of methyl orange

The initial pH values investigated for the coupled US/ O_3 system were 5.5, 6.3, 8.2 and 9.7, respectively when the dye concentration was 400 mg/L, ozone concentration was 58.4 mg/L, the ozone gas flow rate was 100 mL/min and ultrasonic power was 175 W. The apparent first-order rate constants for these pH values were determined to be 0.24 min^{-1} . This indicates that there is little difference in the decolorization rate at either pH value, which is similar to the observation by Lall et al. [15]. 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 [37]. 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. 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 [35]. Shu and Huang [33] also observed ozone in aqueous phase would tend to react with azo dyes rather than free radicals in UV enhanced ozonation process. To prove this point, some of the decolorization reactions in the coupled US/ O_3 systems were carried out in the presence of sodium carbonate, a kind of hydroxyl radical scavenger. Sodium carbonate concentrations investigated were 1.92, 6.36 and 18.9 mmol/L, respectively when the dye concentration was 400 mg/L, ozone concentration was 66.7 mg/L, the ozone gas flow rate was 100 mL/min, initial pH was 9.7 and ultrasonic power was 175 W. The results showed that there was no appreciable difference between data obtained in the absence and presence of sodium carbonate when the concentration ranged from 1.92 to 18.9 mmol/L. 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 [10]. Therefore, the primary mechanism of decolorization is not the reaction involved in radicals formed in the ultrasound-enhanced ozonation process but direct decomposition by ozone.

3.4. The effect of ultrasonic power on the decolorization of methyl orange

The decolorization of methyl orange in the coupled US/ O_3 system was investigated at different ultrasonic powers when the dye concentration was 400 mg/L, ozone concentration was 68.8 mg/L, the ozone gas flow rate was 100 mL/min and the initial pH was 5.5. It can be seen that the decolorization rate increased with the increasing ultrasonic power (see Table 1). The apparent rate constants were 0.24, 0.28, 0.31 and 0.33 min^{-1} when ultrasonic powers were 87.5, 112.5, 150 and 200 W, respectively. When ultrasound is introduced into the reactor, acoustic streaming is caused by an energy gradient in the direc-

Table 1
The apparent pseudo-first-order rate constants under various operating conditions (initial pH 5.5)

Run	C_0 (mg/L)	$[O_3]_g$ (mg/L)	Q (mL/min)	P (W)	ΔT ($^{\circ}C$)	k_1 (min^{-1})	R^2
P-1	400	68.8	100	87.5	6.5	0.24	0.9975
P-2	400	68.8	100	112.5	15.0	0.28	0.9954
P-3	400	68.8	100	150	22.0	0.31	0.9948
P-4	400	68.8	100	200	39.0	0.33	0.9975
O-1	400	25.4	100	175	– ^a	0.15	0.9742
O-2	400	56.4	100	175	– ^a	0.23	0.9939
O-3	400	80.5	100	175	21.0	0.30	0.9904
O-4	400	114.2	100	175	12.0	0.38	0.9894
Q-1	400	87.0	40	175	30.0	0.16	0.9872
Q-2	400	87.0	100	175	15.0	0.30	0.9877
Q-3	400	87.0	154	175	15.0	0.45	0.9845
Q-4	400	87.0	190	175	6.5	0.68	0.9822
C-1	67.63	70.3	100	175	15.0	0.62	0.9705
C-2	135.3	70.3	100	175	18.0	0.42	0.9888
C-3	405.8	70.3	100	175	16.5	0.32	0.9916
C-4	676.3	70.3	100	175	15.9	0.26	0.9810

^a Not available.

tion of propagation of the acoustic wave. The energy gradient corresponds to a force which when acting on a liquid causes the liquid to accelerate turbulence [19]. It is known that an increase in ultrasonic power increases turbulence, which reduces the liquid film thickness and, hence, increases the mass transfer rate of ozone in aqueous phase [15]. As discussed above, decolorization of azo dyes is a mass transfer controlled process, and the increase in the mass transfer rate would increase the decolorization rate.

3.5. The effect of gaseous ozone concentration on the decolorization of methyl orange

The decolorization of methyl orange in the combined US/O₃ system was investigated at different gaseous ozone concentrations when the dye concentration was 400 mg/L, ultrasonic power was 175 W, the ozone gas flow rate was 100 mL/min and the initial pH was 5.5. Higher ozone concentration led to higher decolorization rate, i.e., 0.15, 0.23, 0.30 and 0.38 min⁻¹ apparent rate constants when gaseous ozone concentration were 25.4, 56.4, 80.5 and 114.2 mg/L, respectively (see Table 1). The increase in the gaseous ozone concentration would increase the equilibrium ozone concentration in the aqueous phase and, hence, increase the mass transfer driving force. This leads to the increase of the volumetric mass transfer coefficient and then mass transfer rate of ozone from gas phase to liquid phase. Since the US enhanced ozonation process is mass transfer limited, the decolorization rate would increase with the increasing gaseous ozone concentration, as shown in Table 1.

3.6. The effect of ozone gas flow rate on the decolorization of methyl orange

The decolorization of methyl orange in the coupled US/O₃ system was investigated at different ozone gas flow rate when the dye concentration was 400 mg/L, ozone concentration was 87.0 mg/L, ultrasonic power was 175 W and the initial pH was 5.5. It can be seen that the decolorization rate increased with

the increase of ozone gas flow rate (see Table 1). The apparent rate constants were 0.16, 0.30, 0.45 and 0.68 min⁻¹ when ozone gas flow rates were 40, 100, 154 and 190 mL/min, respectively. Increasing the flow rate corresponds to a larger net surface area for mass transfer of ozone to the aqueous phase [19], 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/O₃ system.

3.7. Effect of initial dye concentration on the decolorization of methyl orange

The decolorization of methyl orange in the combined US/O₃ system was investigated at different initial dye concentrations when ozone concentration was 70.3 mg/L, the ozone gas flow rate was 100 mL/min, ultrasonic power was 175 W and the initial pH was 5.5. Higher initial concentration corresponded to lower decolorization rate, i.e., 0.62, 0.42, 0.32 and 0.26 min⁻¹ apparent rate constants when initial concentration were 67.63, 135.3, 405.8 and 676.3 mg/L, respectively (see Table 1). Ozonation of methyl orange with ultrasonic irradiation can be regarded as a mass transfer process coupled with chemical reactions, i.e., gaseous ozone was absorbed into the aqueous phase and then reacted with in it dissolved methyl orange. The degradation rate was considered to be equal to the ozone absorption rate N_{Aa} [38],

$$-\frac{dC}{dt} = zN_{Aa} \quad (3)$$

where z is the stoichiometric ratio. Usually N_{Aa} was obtained at the initial time based on the assumption that ozone only reacted with the parent compound and the reactions with possible intermediates formed were negligible [39], i.e.,

$$-\left. \frac{dC}{dt} \right|_{t=0} = zN_{Aa} \quad (4)$$

And the ozone absorption rate can be expressed by the following equation [38],

$$N_A a = Ek_L a C_A^* \quad (5)$$

where C_A^* 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. Substituting in Eq. (3),

$$-\frac{dC}{dt} \Big|_{t=0} = zEk_L a C_A^* \quad (6)$$

Substituting the apparent pseudo-first-order kinetics in the above equation,

$$-\frac{dC}{dt} \Big|_{t=0} = k_1 C|_{t=0} = k_1 C_0 = zEk_L a C_A^* \quad (7)$$

Then k_1 can be expressed as,

$$k_1 = zEk_L a C_A^* \frac{E}{C_0} \quad (8)$$

The stoichiometric ratio z , volumetric mass transfer coefficient $k_L a$ and ozone equilibrium concentration C_A^* are all fixed when only the initial dye concentration changes. Although the enhancement factor E increases with dye concentration [40], it is not proportional to dye concentration. Therefore, the apparent first order rate constant k_1 decreased with initial dye concentration.

4. Conclusion

This study shows ozonation in combination with 20 kHz ultrasonic irradiation has synergistic effect on the decolorization of methyl orange and the synergistic effect is more pronounced when reactor cooling was not provided to keep the constant reaction temperature. The decolorization of methyl orange fits the first order kinetic model. The effect of pH on the decolorization was insignificant when pH ranged from 5.5 to 9.7. The presence of hydroxyl radical scavenger had little influence on the decolorization rate, which indicates that the primary mechanism is not the reaction involved in radicals formed in the ultrasound-enhanced ozonation process but direct decomposition by ozone. The decolorization rate increased with increasing ultrasonic power, ozone gas flow rate, and gaseous ozone concentration respectively due to consequently improved mass transfer under the experimental conditions in our work. However, the decolorization rate decreased with the increasing initial dye concentration. Future work would be focused on the mineralization of methyl orange in the ultrasound-enhanced ozonation.

Acknowledgments

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