Ozonation of acid yellow 17 dye in a semi-batch bubble column

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Abstract

A semi-batch bubble column was used to evaluate the effect of ozonation on the removal of acid yellow 17 dye from water. Results indicate that ozonation is very effective at removing acid yellow 17 dye from synthetic textile wastewater. The ozone consumed to apparent dye removal ratio ranged from 2 to 15,000 mg ozone per mg of dye decolorized and was dependent on both ozonation time and apparent dye concentration. The biodegradability of the dye wastewater was evaluated by monitoring changes in 5-day biochemical oxygen demand (BOD_5) with respect to chemical oxygen demand (COD). Results indicate that the wastewater biodegradability increased with an increase in ozonation time. Film theory was used to kinetically model the gas–liquid reactions occurring in the reactor. Modeling results indicated that during the first 10–15 min of ozonation, the system could be characterized by a fast, pseudo-first-order regime. With continued ozonation, system kinetics transitioned through a moderate then to a slow regime. Successful modeling of this period required use of a kinetic equation corresponding to a more inclusive condition. Model results are presented.
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1. Introduction

A renewed interest in the treatment of textile wastewaters has occurred due to the promulgation of more stringent industrial effluent regulations. Textile plants consume large quantities of water and conventional treatment results in an effluent with high chemical oxygen demand (COD), low biochemical oxygen demand (BOD), and high color concentrations. Wastewater containing color poses a variety of issues to receiving streams including the introduction of toxic compounds or compounds that are recalcitrant to the native microbial consortium, and a decrease in Secchi disc depth causing an impact on algae viability and therefore dissolved oxygen concentration. Ozonation is a common treatment for color containing wastewater as it has been shown to decrease color [1,2], COD [3,4] and increase the biodegradability (BOD_5:COD) of the wastewater [3,5,6]. Color reduction in wastewater by ozonation can be primarily related to the amount of ozone utilized [3,5,7,8] and it has also been shown

to be a function of several additional process variables including initial system pH, temperature, and COD, color and solids concentrations [3,9]. Acid yellow 17 dye is a common additive found in ordinary household products such as shampoo, bubble bath, shower gel, liquid soap, multi-purpose cleanser, dishwashing liquid and alcohol-based perfumes. As regulations associated with dyestuff are tightened, associated industries are faced with finding economically viable water treatment solutions.

Traditionally, mass transfer and associated reactions are modeled in terms of the two-film theory where the rates of reaction and mass transfer vary from one extreme to the other and are characterized by different "regimes". Most typically, such reactions are described as either "slow" or "fast" because relatively simple solutions exist for these regimes. For example, if the reaction is characterized by a dimensionless Hatta number (Ha; mathematically represented in kinetic modeling section below) greater than three, the reaction is assumed to proceed in the "fast" regime and the assumption is made that all reactions occur within the film. For an instantaneous, reversible reaction, film-theory provides an analytical solution. If the reaction is characterized as "slow" ($Ha < 0.3$), it is assumed that the reaction occurs within the bulk fluid and the reaction rate can be determined from standard kinetic theory. Unfortunately, there is no rigorous method available to describe the reaction characterized as moderate or as

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the "transition" regime when $0.3 < Ha < 3$. Approximate methods have been developed by Danckwerts [10], van Krevelen and Hoftijzer [11] and Schluter and Schulzke [12].

This study was undertaken to evaluate the effect of ozone on the removal of acid yellow 17 dye. Furthermore, a kinetic model based on film theory was developed to describe the removal of COD by ozonation in the semi-batch bubble column.

2. Materials and methods

All experiments were conducted in a semi-batch bubble column. The column was fabricated from clear 7.62 cm (3 in.) schedule 40 PVC pipe. The column was 2.44 m (8 ft) in height and contained six sample ports equally spaced along the length of the reactor. The gas feed was sparged through three stainless steel filters with 10 um porosity. The sparging system entered the side of the reactor 15.24 cm (0.5 ft) from the bottom of the column. Ozone was generated with the Ozotech, Inc. OZ2BTUSL. The air feeding the ozone generator was conditioned using the Power Prep Model Titan (Ozotech, Inc.). The carrier gas flow rate was maintained at a constant of 3.78 L/min (8 scfh) resulting in a uniform ozone introduction to the system of 79.2 mg O_3/min. Fig. 1 shows a schematic of the equipment utilized.

Ozone exiting the reactor was trapped in a potassium iodide solution and quantified according to Standard Methods 2350 E, a titration method, utilizing a 0.005N sodium thiosulfate solution. COD was quantified colorimetrically by HACH method 8000 utilizing the HACH DR/2000 spectrophotometer. An accumet® pH meter and probe were used to monitor the pH of the synthetic wastewater samples. Color concentration was measured spectrophotometrically using a Spectronic

20D+ at a wavelength of 400 nm. A standard curve was generated that predicted the following linear relationship between absorbance and dye concentration: Acid yellow 17 dye concentration (mg/L) = 27.9 × absorbance at 400 nm ($R^2 = 0.99$).

The synthetic wastewater was prepared by adding acid yellow 17 dye ($C_{16}H_{10}C_{12}N_4Na_2O_7S_2$) to 8 L of tap water (City of Macon, Georgia). Acid yellow 17 dye concentration, COD, and the quantity of ozone captured in the off-gas were measured as a function of time. Experiments were conducted at an initial pH of 7 and the dye concentration was varied between 1 and 250 mg/L. A standard curve was prepared showing the absorbance versus concentration of acid yellow 17 dye. A separate experiment was performed to determine the correlation between BOD and COD. BOD analyses were performed in accordance to Standard Methods [13], Section 5210.

3. Results and discussion

3.1. Influence of operational parameters on performance

The initial concentration of acid yellow 17 dye was varied from 1 to 245 mg/L in an effort to determine the effect of ozone on the decolorization of the dye and the system COD concentration. The decolorization effect was monitored spectrophotometrically and reported as a change in absorbance at 400 nm. These data are plotted in Fig. 2. Notice that the ordinate is portrayed on a base 10 logarithmic scale. In all cases, color decreased exponentially with respect to time. When the initial concentration was 245 mg/L, the dye concentration was reduced by greater than three orders of magnitude to 0.20 mg/L in 40 min. A similar reduction was observed when the initial con-
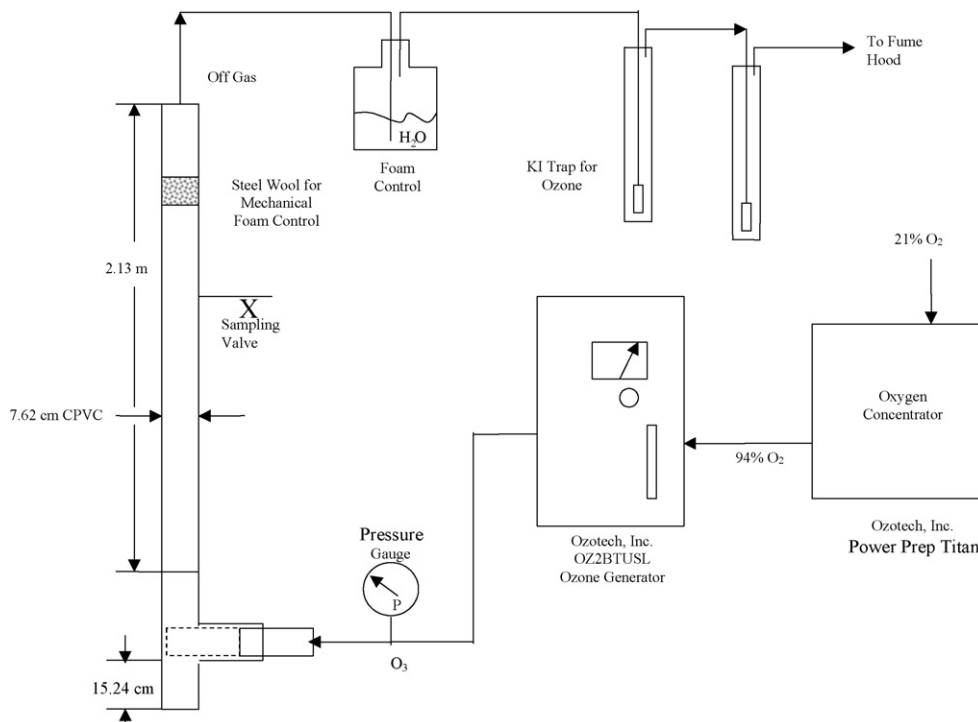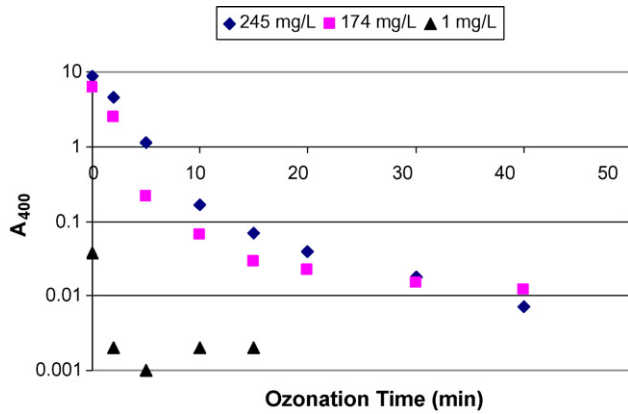

Fig. 1. Schematic of ozonation system.

Fig. 2. Effect of initial dye concentration on the rate of dye decolorization represented as the absorbance at 400 nm. The initial concentration of acid yellow 17 dye was varied from 1 to 245 mg/L. The system was unbuffered.

centration was 174 mg/L as the final concentration after 40 min of ozonation was 0.33 mg/L. When the initial dye concentration was 1 mg/L, no dye was detected after 20 min as the spectrophotometric detection limit (concentration was less than the detection limit approximated as 0.01 mg/L) was reached. During the ozonation process, the pH was observed to drop in the unbuffered system at a rate relative to the initial concentration. With relatively high initial concentrations, 245 and 174 mg/L, the pH dropped from 7.5 to 2.9 and 7.2 to 3.3, respectively. When the initial concentration was only 1 mg/L, the pH drop was less dramatic from 7.1 to 5.9. This drop in solution pH was not surprising, as literature suggests that organic acid formation is common during the ozonation of complex organic compounds [5].

Fig. 3 summarizes the ozone demand by plotting the mg of ozone consumed per mg of dye decolorized as a function of the apparent system dye concentrations. Results from experiments conducted with initial concentrations of 245 and 174 mg/L are presented. In both instances, the demand for ozone increased as the concentration of dye decreased. Notice that as system dye concentrations decreased from over 100 mg/L to less than

1 mg/L the ozone required to decolorize a mg of dye increased by four orders of magnitude. This result suggests that the ozonation process produced decolorized breakdown products that continue to consume ozone prior to complete mineralization and that these reactions compete with the decolorization process. Data indicate that as the color causing dye compound became less available within the system, the reactions between ozone and the reaction by-products dominated resulting in the observed dramatic increase in the ozone dose required to decolorize the remaining dye in the system [5].

3.2. Affect of ozonation on biochemical oxygen demand of dye

The biodegradability of the dye wastewater was evaluated by monitoring changes in BOD_5 with respect to COD [17]. Fig. 4 shows results obtained in an unbuffered system having initial dye and COD concentrations of 33.8 and 180 mg/L, respectively. Total time of ozonation was 40 min. The initial BOD_5:COD ratio was 0.0083 and over time increased by an order of magnitude to a maximum ratio of 0.126 at 30 min. Such results indicate that the wastewater biodegradability increased with an increase in ozonation time. These data suggest that partial oxidation of the dye occurred, not total mineralization, resulting in lower molecular weight compounds that were more amenable to microbial oxidation [6,14,15,18,19]. These results are consistent with our previous observations from experiments conducted in an unbuffered system that showed the pH drop throughout the ozonation process indicating that smaller, more biodegradable, organic acids are being produced. Note that at 40 min there is some indication, shown by the drop in BOD_5:COD ratio, that the more simple, biodegradable products are being converted through the ozonation process to carbon dioxide and water.

3.3. Kinetic modeling for semi-batch bubble reactor

COD and apparent dye concentration removal rates can be directly related to the rate of ozone absorption/utilization rate [5]. The ozonation of acid yellow 17 dye was modeled as a second-order reaction typical of most organics with ozone
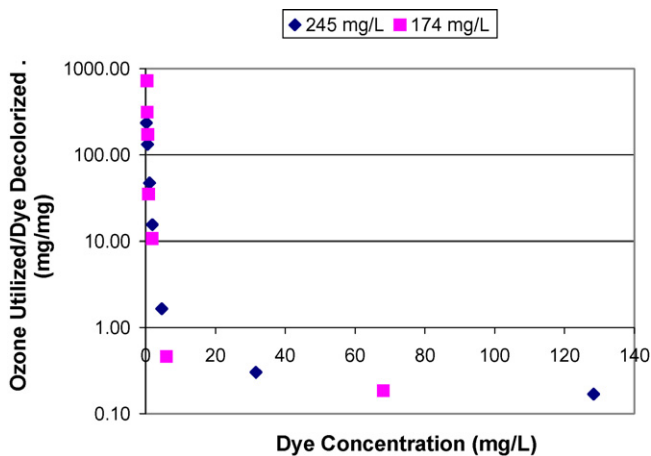

Fig. 3. Ozone demand associated with dye decolorization while operating at a range of dye concentrations between 0.20 and 245 mg/L. Results from experiments conducted with initial concentrations of 245 and 174 mg/L are presented.
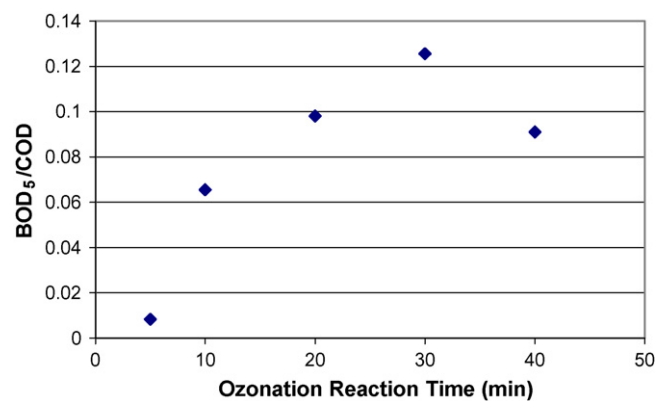

Fig. 4. Influence of ozonation reaction time on the biodegradability of the acid yellow 17 dye. The system was unbuffered and had initial dye and COD concentrations of 33.8 and 180 mg/L, respectively. Total time of ozonation was 40 min.

[9,20–22]. It was assumed that many different reactions were occurring in solution in addition to the most observable reaction, dye decolorization. To this end, the removal of system chemical oxygen demand (COD) was targeted and modeled as an irreversible, second-order reaction, $COD + zO_3 \rightarrow$ products, where z is the stoichiometric ratio defined as the moles of ozone consumed per mole of COD degraded. The local rate of reaction can be shown as $d[COD]/dt = k_d[O_3][COD]$, where k_d is the rate constant for the ozone–dye system. The stoichiometric ratio was calculated as $z = (C_{O_3,in} - C_{O_3,out})/([COD]_{in} - [COD]_t)$, where the numerator represents the molar change in the gas phase ozone concentration over a specified time period (i.e., ozone consumed during a measured time) and the denominator represents the change in COD concentration over the same time interval.

Film theory was used to model ozone absorption and its effect on the removal of COD in the system. In an effort to determine the overall rate constant, k_d, an ozone mole balance was performed around a differential volume of the bubble column reactor. Within the model, a variety of assumptions were made including:

1. Perfect mixing occurred in the reactor making the liquid phase homogenous throughout.
2. The plug flow assumption was made for the movement of ozone gas through the reactor.
3. Henry's Law applies.
4. Gas volumetric flow rate was assumed a constant for a given experiment.
5. The concentration of dissolved ozone in the bulk liquid phase was assumed to be negligible for the entire reaction period [15].

The ozone molar balance within the gas phase can be represented as follows

$$Q_g \, dC_{O_3,g} = N_{O_3} \, dV + \frac{dC_{O_3,g}}{dt} \, dV \tag{1}$$

where Q_g is the ozone gas flow rate (m³/s), $C_{O_3,g}$ the gas phase ozone concentration (mol/L), N_{O_3} the ozone absorption rate at the gas–liquid interface (mol/L s), and V is the reaction volume (m³).

Using film theory to model the ozone absorption rate [10], the ozone absorption rate was described as follows

$$N_{O_3} = k_L a E C_{O_3}^* \tag{2}$$

where E is the "enhancement factor" that describes the increase in absorption caused by the reaction occurring in the system and $C_{O_3}^*$ is the interfacial ozone concentration. The enhancement factor is characterized by the kinetic regime controlling the ozone absorption in the system. The coefficients, k_L (individual liquid phase mass transfer coefficient (m/s)) and a (specific interfacial area (m⁻¹)) are collectively referred to as the "volumetric liquid phase mass transfer coefficient." The interfacial area, a, was determined to be 162 m⁻¹ and calculated by assuming $a = 6\varepsilon/D_b$ [23]. The gas holdup, ε, was calculated by the volume expansion method such that $\varepsilon = \Delta H/(\Delta H + H_L)$, where H_L is the ungassed

liquid height and ΔH is the increase in liquid level after gas introduction. The bubble diameter, D_b was estimated as 0.20 cm [23]. The Calderbank equation was used to calculate the individual liquid phase mass transfer coefficient as $k_L = 1.36 \times 10^{-4}$ m/s. This value was checked using an equation developed by Zhou and Smith [5] and a similar value for k_L was obtained.

The ozone gas concentration leaving the reactor is assumed to be in equilibrium with the ozone concentration at the gas–water interface. Henry's Law can describe this relationship as follows

$$C_{O_3,out} = H C_{O_3}^* \tag{3}$$

As the dye concentrations in solution were high relative to the ozone concentrations, the reaction regime was initially assumed to be fast and of pseudo-first-order [8,10,24]. For the fast absorption regime with a pseudo-first-order reaction, film theory suggests that the enhancement factor, E is equal to the dimensionless Hatta number (Ha) defined as

$$Ha = \frac{\sqrt{COD \, D_{O_3} k_d}}{k_L} \tag{4}$$

where D_{O_3} is the ozone diffusivity in water, was considered a constant value of 1.3×10^{-9} m²/s [8,25]. The fast psuedo-first-order regime is satisfied when

$$3 \le Ha \le \frac{E_i}{2}, \quad E_i = 1 + \frac{D_{OM} \, COD}{z \, D_{O_3} \, C_{O_3}^*} \tag{5}$$

where E_i is the dimensionless "instantaneous reaction factor".

By considering the second term on the right (the accumulation term) in Eq. (1) negligible and solving by substituting Eqs. (2)–(4), the ozone molar balance simplifies to

$$\ln\left(\frac{C_{O_3,out}}{C_{O_3,in}}\right) = \alpha \sqrt{k_d} \sqrt{COD}, \quad \text{where } \alpha = \frac{aV}{Q_G H} \sqrt{D_{O_3}} \tag{6}$$

Eq. (6) indicates that a plot of $\ln(C_{O_3,in}/C_{O_3,out})$ versus the $\sqrt{COD}$ should give a straight line for fast pseudo-first-order kinetics. Notice in Fig. 5 that such a plot does not produce a
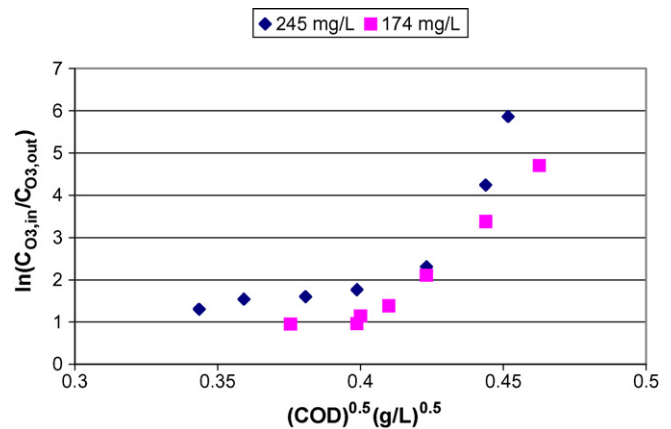

Fig. 5. Validation of modeling ozone absorption in fast, pseudo-first-order kinetic regime by plotting Eq. (6) for two independent experiments with varying initial COD concentrations.

Table 1
Assuming a fast, pseudo-first-order kinetic regime, the overall rate constant, Hatta number and the instantaneous reaction factor, E_i are presented for two experimental runs conducted in an unbuffered solution

Initial dye concentration (mg/L)	Ozonation reaction time (min)	Overall reaction rate constant, k_d ($m^3\ mol^{-1}\ s^{-1}$)	Ha	E_i
245	2	3117	8.85	76.8
	5	1794	6.4	8.57
	10	601	3.5	1.18
	30	361	2.3	1.0
174	2	1844	7.1	24.4
	5	1035	5.1	3.3
	10	445	3.2	1.02
	30	104	1.45	1.0

straight line for the entire ozonation period. Table 1 gives calculated values for the overall rate constant, k_d, as well as values for Ha and E_i. Notice that the fast, pseudo-first-order regime, and therefore overall rate constants calculated, are only valid for time periods less than approximately 10–15 min. A plot of A_{400}, COD and O_3 gas phase concentrations versus reaction time can establish further evidence that the fast pseudo-first-order kinetic regime does not hold throughout each experimental time period. Fig. 6 shows that during the ozonation process, the exiting ozone gas phase concentration was initially minimal (approximately 10 min) and then increased rapidly with time. The A_{400} and COD concentrations dropped quickly during the first 10–15 min and then asymptotically began an approach to some limiting value. Results from Figs. 5 and 6 combined with the numerical values given for Ha and E_i shown in Table 1 indicate that the reaction regime initially followed a fast, pseudo-first-order kinetics and then transitioned through a moderate to then a slow regime with increasing ozonation reaction time [4,26]. Given these conclusions, the fast regime was successfully used to model results obtained during the first 10–15 min of the reaction period.

A more general approach developed by van Krevelen and Hoftijzer [11] was used to determine k_d values for ozonation times greater than 15 min. According to the film theory-based
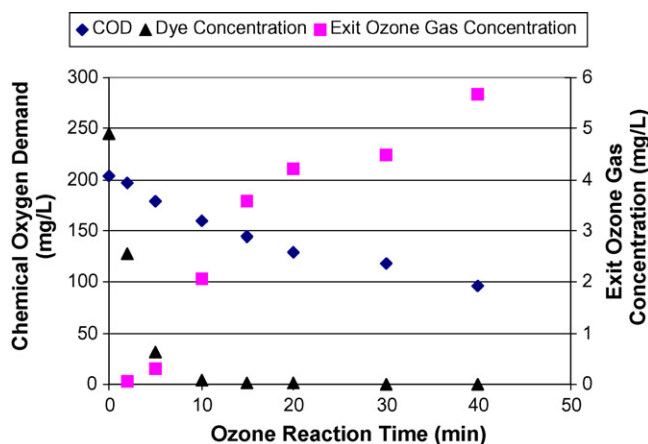

Fig. 6. Typical plot showing behavior of COD, apparent dye concentration and outlet gas phase ozone concentrations during a single experiment.
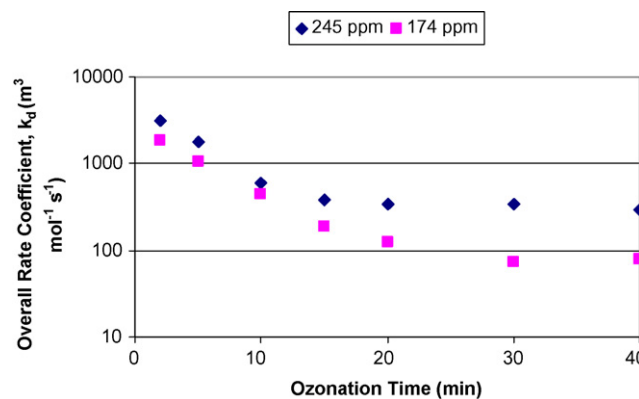

Fig. 7. Overall reaction rate coefficient, k_d, as it varied with time for different initial acid yellow dye concentrations.

model, the ozone absorption rate at the gas liquid interface can be represented as Eq. (7) when two simplifying assumptions that are appropriate for our ozonation system are made. Eq. (7) is valid when a sparingly soluble gas (as is ozone) is reacting with the liquid and when the concentration of the liquid phase reactant can be considered a constant throughout the liquid film:

$$N_{O_3} = k_L a C_{O_3}^* \frac{Ha}{\tanh(Ha)} \left[1 - \frac{k_L a\, Ha/\sinh(Ha)\cosh(Ha)}{k_d COD + (k_L a\, Ha/\tanh(Ha))} \right] \tag{7}$$

Substituting Eq. (7) into the gas phase ozone balance (Eq. (1)) and integrating yielded Eq. (8). By trial and error, k_d was obtained for ozonation time periods greater than 15 min:

$$\ln\left(\frac{C_{O_3,\text{out}}}{C_{O_3,\text{in}}}\right)$$
$$= \frac{Ha\, k_L a V}{\sinh(Ha) Q_g H}$$
$$\times \left[\cosh(Ha) - \frac{1}{(\sinh(Ha) Ha/D_{O_3} a) + \cosh(Ha)}\right] \tag{8}$$

Results are presented in Fig. 7. For the time period greater than 15 min, k_d values obtained by solving Eq. (8) were smaller than those values presented in Table 1 that were derived assuming the fast pseudo-first-order kinetics regime. For example, when the initial dye concentration was 245 mg/L the k_d values obtained by using Eq. (8) were 344, 345 and 289 $m^3\ mol^{-1}\ s^{-1}$ at reaction times of 20, 30 and 40 min, respectively. Similarly, when the initial dye concentration was 174 mg/L, k_d values obtained from the more general expression, Eq. (8), were determined as 124, 73 and 78 $m^3\ mol^{-1}\ s^{-1}$ at ozonation times of 20, 30 and 40 min, respectively. For time periods greater than 15 min, the Hatta number was found to be less than 3 in all cases analyzed.

4. Summary and conclusions

Ozonation experiments of water contaminated with acid yellow dye 17 were conducted in a 11.12 L bubble column to investigate the effect of process variables on system performance. Film theory was used to model the ozonation reaction

occurring. Initial dye concentration had significant effects on the pseudo-first-order rate constants observed in the batch system. Listed below are the major conclusions presented in this manuscript:

1. Results corroborate the findings of Yongqiang et al. [16] showing initial dye concentrations effect the rate of dye decolorization. Results indicated that with an increase in initial dye concentration, the rate of decolorization increased.
2. Results from this study indicate that apparent dye concentration affects the ozone demand required to decolorize the dye studied. The demand for ozone increased as the apparent dye concentration decreased such that as system dye concentrations decreased from over 100 mg/L to less than 1 mg/L the ozone required to degrade a mg of dye increased by four orders of magnitude.
3. Results from this study indicate that the stoichiometric ratio increased as the reaction time increased [27].
4. Results indicate that the first 15 min of ozonation reaction time can be successfully modeled assuming the reaction regime to be fast and of pseudo-first-order [8,24].
5. After approximately 15 min of ozonation, the fast, pseudo-first-order kinetics no longer accurately described the system and a more general approach to modeling must be employed.

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