DOI: 10.1590/S1413-41522019179346

Technical Article

Factors and mass ratio analyses for Reactive Blue 19 dye decolorization using ozone: an experimental and analytical modelling approach

Análises de atributos e taxa mássica da descolorização do corante Azul Reativo 19 usando ozônio: modelagem experimental e analítica

Mayara Sakamoto Lopes[1], Rodrigo Braga Moruzzi[1]*, Fabiano Tomazini Conceição[1], Mariana Scicia Gabriel Silva[1], Maria Lucia Pereira Antunes[1]

ABSTRACT

Dyes highly reduce sunlight penetration into the stream, and consequently affect photosynthesis and oxygen transfer into water bodies. An experimental and analytical modelling approach to Reactive Blue 19 (RB19) removal using ozone was carried out. For this purpose, factors and mass ratio analyses were assessed based on batch assays experiments. Removal efficiency increased from 64 to 94% when the dosage increased from 38.4 to 153.6 mg $O_3.L^{-1}$. Results showed that RB19 is more efficiently removed when initial pH is 7. The rate of RB19 removal decreased as the initial dye concentration increased. Kinetic studies showed that the ozonation of RB19 was a pseudo first-order reaction with respect to the dye, and the apparent rate constant declined logarithmically with the initial dye concentration. Mass ratio studies showed that, for the empirical analysis, the power law equation was adequate to describe mass ratio over time and the analytical analysis suggests that the process is influenced by mass transfer in the liquid film as well as in the bulk fluid.

Keywords: reactive dye; ozone; decolorization factors; kinetics and mass ratio.

RESUMO

Os corantes reduzem significativamente a penetração da luz solar no corpo d'água e, consequentemente, afetam a fotossíntese e a transferência de oxigênio. Realizaram-se modelagens experimental e analítica da remoção do azul reativo 19 por ozônio. Para isso, avaliaram-se os atributos e a taxa mássica por ensaios em batelada. A eficiência de remoção foi de 64 para 94% quando a dose de ozônio aumentou de 38,4 para 153,6 mg $O_3.L^{-1}$. Os resultados mostraram que o azul reativo 19 é removido mais eficientemente em pH inicial da solução de 7. A taxa de remoção do azul reativo 19 reduziu à medida que a sua concentração inicial aumentou. Os estudos cinéticos mostraram que a ozonização do azul reativo 19 é uma reação de pseudoprimeira ordem em relação ao corante e a constante cinética aparente decai logaritmicamente com a concentração inicial de corante. A análise empírica indica que a taxa mássica ao longo do tempo pode ser descrita adequadamente por uma equação de potência, e os estudos analíticos sugerem que o processo é influenciado pela transferência de massa tanto no filme líquido quanto na massa líquida.

Palavras-chave: corante reativo; ozônio; atributos de descolorização; cinética e taxa mássica.

INTRODUCTION

Dyes are organic compounds that consist of chromophores and auxochrome structures, which are responsible for the color of the dye and the intensity of the color, respectively (CHRISTIE, 2015). They are classified according to their chemical structure (azo, anthraquinone, phthalocyanine, triarylmethane, among others), their dissociation in an aqueous solution (anionic, cationic and non-ionic) and the method of application onto fabric (acidic, basic, direct, reactive, disperse and metal-complex), wherein acidic, direct and reactive dyes are anionic, basic dyes are cationic, and disperse dyes are non-ionic (MOUSSAVI & MAHMOUDI, 2009; ASGHER, 2012). Anionic and non-ionic dyes usually have azo and anthraquinone chromophore groups, constituting approximately 70 and 15% of the reactive dyes, respectively (MOUSSAVI & MAHMOUDI, 2009). Anthraquinone dyes are characterized by their wide range of colors, good adhesion and durability due to their fused aromatic structures, which decreases biodegradability (FANCHIANG & TSENG, 2009b; ASGHER, 2012).

---

[1]Universidade Estadual Paulista "Júlio de Mesquita Filho" – Bauru (SP), Brazil.
***Corresponding author:** rmoruzzi@rc.unesp.br

Received: 05/02/2017 – **Accepted:** 09/19/2017 – **Reg ABES**: 179346

Dyes are also highly visible in water, even at low concentrations (RAGHUVANSHI *et al.*, 2005; GAO *et al.*, 2014), damaging the aesthetic nature of water and reducing light penetration through the water's surface (TURHAN & OZTURKCAN, 2013; JESUS *et al.*, 2014). Thereby, photosynthesis and the oxygen transfer into water bodies are affected (SIDDIQUE *et al.*, 2009; TURHAN *et al.*, 2012). In addition, they are chemically stable, poorly biodegradable (ASGHER, 2012) and are generally more toxic than acid or direct dyes (RAGHUVANSHI *et al.*, 2005). It has been estimated that approximately 10–15% of dyes are wasted by dispersion into the environment upon completion of their use in the dyeing unit (MOUSSAVI & MAHMOUDI, 2009).

Synthetic dyes are extensively used in the cosmetic, food, leather, paper, pharmaceutical, plastic, printing, rubber and textile industries (MOUSSAVI & MAHMOUDI, 2009; GAO *et al.*, 2014). Reactive dyes are widely used to color the cellulosic fibers of the fabric due to the presence of reactive groups in their molecules, which bind to the fibers through covalent bonds (SIDDIQUE *et al.*, 2011; ASGHER, 2012). However, reactive dyes are water soluble and have low affinity for fabrics, being thus released into effluents (WEBER & STICKNEY, 1993; SIDDIQUE *et al.*, 2011). Textile effluents are characterized by extremes and by the fluctuation of pH and temperature, high levels of color, high chemical oxygen demand, and high concentrations of suspended solids and dissolved organics (RAGHUVANSHI *et al.*, 2005). They can also be associated with chelating agents, surfactants and heavy metals (WU & WANG, 2001), which are recalcitrant and toxic.

Because dyes are very stable and resistant to conventional biological wastewater treatment, a range of technologies has been developed and used for the removal of dye contaminants from wastewater. These methods include adsorption, advanced oxidation, chemical precipitation, coagulation/flocculation, electrochemical degradation, ion exchange, membrane filtration, ozonation, photocatalytic degradation, etc. (ADAMS & GORG, 2002; SOUZA *et al.*, 2013; GAO *et al.*, 2014; JESUS *et al.*, 2014). Among these treatment methods, ozonation has been found to be effective to decolorize dye-colored wastewater and to degrade several dyes (WU & WANG, 2001; WU; DOAN; UPRETI, 2008; TURHAN *et al.*, 2012; TURHAN & OZTURKCAN, 2013). Ozone is an excellent agent in the decomposition of aromatic covalent compounds, and hence it is good for the decolorization of the dyestuff wastewater (TURHAN *et al.*, 2012). In addition to the potential to efficiently accomplish both color removal and organic reduction in one step, ozonation has the following advantages: the aerobic biodegradability of dyes is increased, there is no solid waste, less space is required, it is easily operated, and all residual ozone can easily be decomposed to oxygen and water (CHU & MA, 2000).

Reactive Blue 19 (RB19) is one of the most widely used textile dyes. However, more research is needed to assess the role of kinetics and mass ratio relationship on dye decolorization. Adams and Gorg (2002) presented the results of a laboratory study on the effects of pH (2, 5 and 9) and gas-phase ozone concentration (1, 7 and 11 wt%) on the decolorization efficiency via ozonation for seven common textile dyes, including RB19; the authors concluded that higher gas-phase ozone concentrations resulted in higher decolorization rates, and that lower pH levels were often more efficient to decolorize dyes. Fanchiang and Tseng (2009a) concluded that ozonation is efficient to decolorize and to eliminate RB19, though complete mineralization does not occur. It has also been reported by Fanchiang and Tseng (2009b) that the degradation of RB19 by ozonation involves the destruction of dye chromophore components, anthraquinone rings and their functional groups. In addition, authors performed essays to find intermediate products, thus indicating that non-toxic products were generated after 7 minutes of oxidation.

Mathews and Panda (2012) developed a novel electrode design for the *in situ* generation of ozone and proposed that the fast RB19 decolorization reaction occurs partly in the liquid film and partly in the bulk fluid, depending on the reaction velocity, as defined by Charpentier (1981).

Thus, the aim of the present study is to present an experimental and analytical approach to Reactive Blue 19 (RB19) removal using ozone based on mass ratio analysis over time. Assays to investigate which factors (i.e. ozone dose, pH and initial dye concentration) affect the decolorization of RB19 in an aqueous solution by ozone were carried out. Furthermore, the pH in which the experiments were developed was also chosen taking into account viable application in wastewater treatment plants (WWTP); this approach diverges from previous studies, since they have focused on pH values far from the usual in WWTP. It is expected that results may assist practitioners and provide new insights into the understanding of the decomposition rate of this important textile dye by ozone.

METHODOLOGY

RB19 and experimental setup

Reactive Blue 19 (RB19) is an anthraquinone-based vinyl sulphone dye (SIDDIQUE; FAROOQ; SHAHEEN, 2011), with molar mass equal to 626.54 g.mol^{-1} (JESUS *et al.*, 2014) and solubility in water of 100 g.L^{-1} (WEBER & STICKNEY, 1993; CHU & MA, 2000). Its molecular formula is $C_{22}H_{16}N_2O_{11}S_3Na_2$, and the molecular structure is shown in Figure 1. RB19 solutions were prepared by dissolving the dye in Milli-Q water (18.2 MΩ cm) at different concentrations (150, 200, 250 and 300 mg.L^{-1}).

Ozone was generated from pure oxygen by a Model O&L 1.5 RM (Ozone & Life, São José dos Campos, São Paulo, Brazil), which is able to operate at variable nominal power (10 to 60 W). The experimental setup (Figure 2) consists of an oxygen cylinder, an ozone generator, a column reactor equipped with a porous gas diffuser and two washing bottles containing a 2% potassium iodide (KI) solution to absorb unused ozone. Ozone production and the off-gas ozone concentration were measured by 2% KI solution using the titrimetric method described in *Standard Methods for Examination of Water and Wastewater* (APHA; AWWA; WEF, 2012). Thus, it is possible to establish a relationship between oxygen flow, nominal power and ozone production. The gas flow rate was controlled by a needle valve and was measured by a flow meter, which is able to measure from 30 to 4,000 mL.min^{-1}. Specific to the mass ratio assays, the ozone production was kept constant at 53 mg O_3.h^{-1}.

Factors affecting the decolorization of RB19

To evaluate the effect of ozone dosage on RB19 removal, assays were carried out at dosages of 38.4, 57.5, 76.7, 115.1 and 153.6 mg O_3.L^{-1} at a pH of 7, with initial dye concentration (C_0) of 300 mg.L^{-1}. Ozone doses were chosen considering operation limits of equipment and preliminary investigation in this study; and the initial dye concentration was equal to 300 mg.L^{-1} to increase the accuracy of the analytical method. In these conditions, ozone was not detected in any off-gas samples, showing that all ozone was indeed consumed via RB19 degradation. To detect the effect of the initial pH on the removal of RB19, dye samples of 161 mL (300 mg.L^{-1}) were submitted to 38.4 mg O_3.L^{-1} at different pH levels (2, 4, 6, 7, 8, 10 and 12). Diluted sodium hydroxide (1 M) and hydrochloric acid (1 M) were used to adjust the different initial pH values, and the pH of samples were measured by an Orion 710 Aplus pH meter (Thermo Electron Corporation, Waltham, Massachusetts, USA). The combined electrode was calibrated using the following high purity standards at pH levels of 4.00 (4.00 ± 0.01 at 25°C ± 0.2°C) and 7.00 (7.00 ± 0.01 at 25°C ± 0.2°C). Both assays were initiated immediately after the admission of ozone gas, and oxidation lasted 7 minutes. In addition, the effect of different RB19 concentrations (150, 200, 250 and 300 mg.L^{-1}) on the removal of RB19 was also tested at pH 7 and with an ozone dose of 38.4 mg O_3.L^{-1}. For spectrophotometric investigation, assays were carried out with an ozone dose of 38.4 mg O_3.L^{-1} at a pH of 7, with a C_0 equal to 300 mg L^{-1}, at different oxidation times (0, 9, 12 and 15 minutes). Then, the concentrations of RB19 solutions were determined indirectly by absorbance, which was measured using the variable wavelength Spectrophotometer DR 2800 (Hach Company, Loveland, Colorado, USA) at its maximum absorption wavelength (592 nm), regardless of the pH range. During all experiments, the temperature was fixed at 22 ± 1 °C. All experiments were performed in triplicate, and the results are presented as their average with error bars.

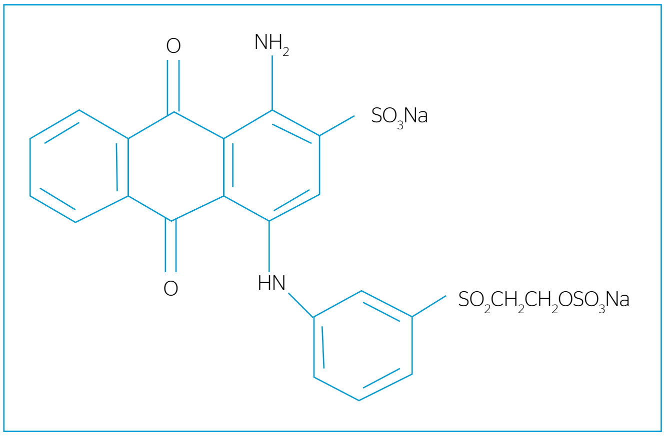

Figure 1 – Molecular structure of RB19.

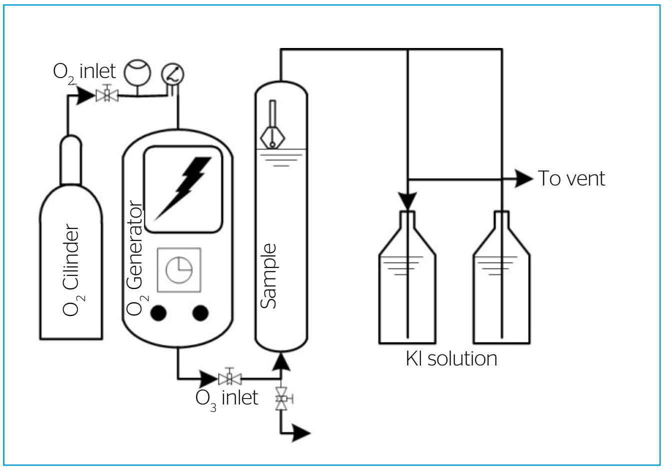

Figure 2 – Schematic of the experimental setup.

RB19 ozonation kinetics

Theoretically, ozonation kinetics should depend on both ozone and RB19 concentration, following Equation 1 (LANGLAIS; RECKHOW; BRINK, 1991).

$$-\frac{dC_{dye}}{dt}=k'C_{dye}C_{ozone} \tag{1}$$

In which:

C_{dye} = the dye concentration (mg.L^{-1});
C_{ozone} = the ozone concentration (mg.L^{-1});
k' = the second-order rate constant (L.(mg.min^{-1})).

However, if the ozone concentration is constant, which is the case in this study, the reaction can be assumed to be pseudo first-order with respect to the RB19 (Equation 2) (CHU & MA, 2000; SEVIMLI & SARIKAYA, 2002; DEMIREV & NENOV, 2005; TURHAN *et al.*, 2012).

$$-\frac{dC_{dye}}{dt}=kC_{dye} \tag{2}$$

In which:

k = the decolorization kinetic constant (min^{-1}).

By integrating Equation (2) between t = 0 and t = t, it is possible to write Equation (3).

$$\ln C_{dye} = -kt + \text{Ln } C_0 \tag{3}$$

In which:

C_0 = the initial dye concentration (mg.L^{-1}).

Mass ratio (z) over time

In this study, the mass ratio (*z*) over time was investigated using an empirical equation and an analytical formulation. The empirical relationship follows power law decay, while the analytical relationship was analyzed according to the liquid film theory. Thus, assuming that all ozone is consumed only via RB19 degradation, it is possible to suppose that ozone decay may be expressed by means of *z* (mg of ozone per mg of RB19) over time, which can be followed by an equation similar to the one presented by film theory. The stoichiometric ratio *z* of the reaction between ozone and RB19 was calculated using Equation (4) to obtain the ozone consumption per unit amount of RB19 reacted in the decolorization step. Though this model is not very realistic, it has the advantage of simplicity. Furthermore, predictions based on this model are often similar to those based on sophisticated models (CHARPENTIER, 1981); thus, it may assist designers and operators in both project and operational interventions.

$$z = \frac{C_{A,o}}{C_{B,o} - C_B} \tag{4}$$

In which:

$C_{A,0}$ = the initial dissolved ozone concentration (mg O_3.L^{-1});

$C_{B,0}$ = the initial RB19 concentration (mg RB19.L^{-1});

C_B = the remaining RB19 concentration in the solution (mg RB19.L^{-1}).

The attempt to analytically describe the behavior of *z* over time was based on the film theory, whereas the reaction is slow and occurs mostly in the bulk. Therefore, decay can be described by Equation 5.

$$\frac{dz}{dt} = -\, k'_{ap}\,(z - z^*) \tag{5}$$

In which:

k'_{ap} = the apparent decay constant (min^{-1});

z = the stoichiometric ratio (mg O_3.mg RB19^{-1});

z^* = the equilibrium stoichiometric ratio (mg O_3.mg RB19^{-1}).

RESULTS AND DISCUSSION

Spectrophotometric investigation

The decolorization of RB19 at different oxidation times is illustrated in Figure 3.

Absorption peak occurs at a wavelength (λ) of 592 nm. According to Fanchiang and Tseng (2009b), RB19 has two major characteristic absorption bands, one in the UV region of 310 nm, characterizing the chromophore components of the dye molecules (anthraquinone), and the other in the visible region of 592 nm, which corresponds to the color blue. It is clear from Figure 3 that absorption intensity decreased as reaction time increased at every wavelength investigated, indicating that ozone is able to degrade (by destroying the chromophore structure) and decolorize the dye. Additionally, the decrease in the absorption peak by over 80% in the visible region suggests a rapid decolorization of RB19 by ozone.

Effect of ozone dose on the removal of RB19

The effect of the ozone dose on the removal of RB19 is shown in Figure 4.

It is noticeable that efficiency increases when the ozone dose increases. The residual RB19 decreases from 107 to 18 mg.L^{-1} when the dosage increases from 38.4 to 153.6 mg O_3.L^{-1}. This result is consistent with other studies (ADAMS & GORG, 2002; TURHAN *et al.*, 2012; TURHAN & OZTURKCAN, 2013) and occurs because increasing ozone concentration in air bubbles enhances the driving force for the transfer of ozone from the gas phase into the dye solution. Consequently, there is more ozone dissolved in the solution, and the rate of dye oxidation is higher (SEVIMLI & SARIKAYA, 2002; RAGHUVANSHI *et al.*, 2005; HE *et al.*, 2008; TURHAN *et al.*, 2012).

It has been reported that the RB19 is only partially oxidized by ozone, without complete mineralization (CHU & MA, 2000; FANCHIANG & TSENG, 2009a; 2009b). However, according to Fanchiang and Tseng

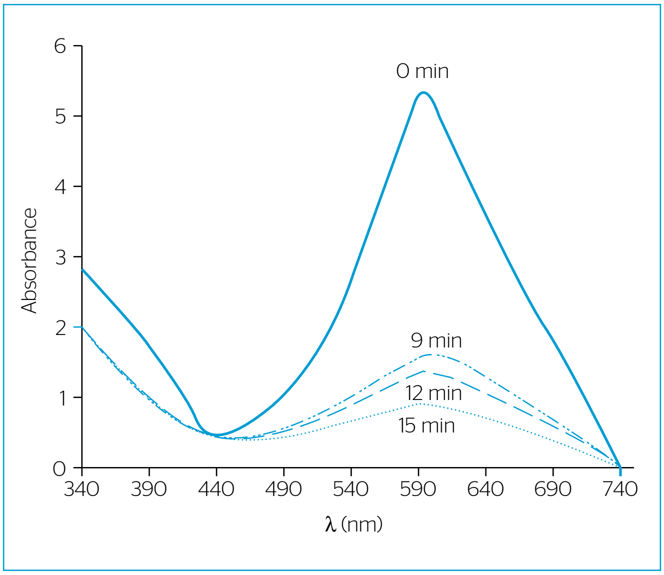

Figure 3 – Absorption spectrum of RB19 (300 mg.L^{-1}) with ozone (38.4 mg O_3.L^{-1}) at initial pH of 7 after different reaction time.

(2009b), it is possible to enhance the RB19 mineralization by increasing the ozone dose or the reaction time.

Effect of initial pH on the removal of RB19

The efficiency of dye removal as a pH function is shown in Figure 5.

Results show that RB19 is more efficiently removed when initial pH is 7, value within the operating pH range of WWTP. The pH affects the ozonation process by affecting the rate of ozone decomposition and ozonation kinetics (ELOVITZ & GUNTEN, 1999). In the case of neutral pH, reactions can be mediated by both molecular ozone and hydroxyl radicals. Chu and Ma (2000) also noticed that the increase of pH does not necessarily improve the decolorization of anthraquinone dyes. In addition, Chu and Ma (2000) and Adams and Gorg (2002) concluded that, with respect to the decolorization efficiency, ozonation at a low pH is more efficient than at higher pH levels, probably because selective direct ozone reactions target unsaturated chromophoric bonds in the dyes.

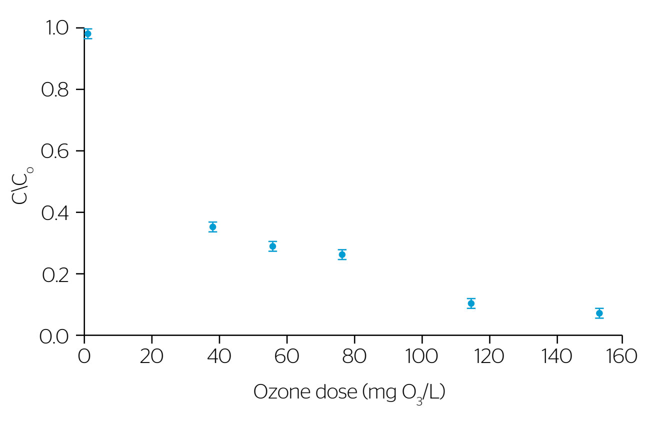

Figure 4 – Effect of ozone dose on removal of RB19 (300 mg.L^{-1}) at a pH of 7 during ozonation for 7 minutes.

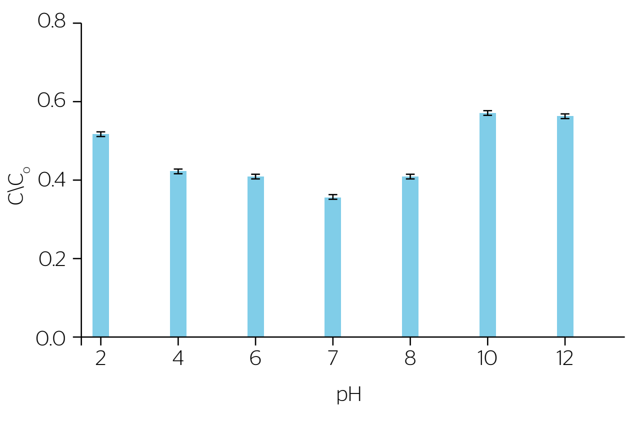

Figure 5 – Effect of initial pH on removal of RB19 (300 mg.L^{-1}) during 7 minutes of ozonation (38.4 mg O$_3$.L^{-1}).

Effect of initial dye concentrations on the removal of RB19

The impact of various initial dye concentrations (150, 200, 250 and 300 mg.L^{-1}) on the removal of RB19 at a pH of 7 and ozone dose of 38.4 mg O$_3$.L^{-1} is illustrated in Figure 6.

It is evident that the rate of RB19 removal decreased as the initial dye concentration increased. The rate of dye removal was higher at the beginning and decreased over time, as previously mentioned by Turhan *et al.* (2012) and Turhan and Ozturkcan (2013).

Decolorization kinetics

Pseudo first-order trends of decolorization were observed in all the experimental runs. The same behavior was also reported in Chu and Ma (2000), Sevimli and Kinaci (2002), Demirev and Nenov (2005), Turhan *et al.* (2012) and Turhan and Ozturkcan (2013).

According to Equation 3, a plot of the first term *versus* oxidation time (Figure 7) should lead to a straight line for each experiment, whose graphic slope defines the rate constant k.

Results show that the decolorization kinetic constant declines with the initial dye concentration. The effect of the initial dye concentration on the apparent rate constant k_{ap} (min^{-1}) at an applied ozone dose of 38.4 mg O$_3$.L^{-1}, pH 7, was investigated using equation $ln\ k = f(ln\ C_0)$, as shown in Figure 8.

It is observed from Figure 8 that k_{ap} decreases logarithmically with an increase in the initial dye concentration, as in Equation 6.

$$k_{ap} = 128.7 \cdot C_0^{-1.28} \tag{6}$$

The logarithmic relationship between k_{ap} and C_0 derived in this study is in agreement with the relationships observed by other

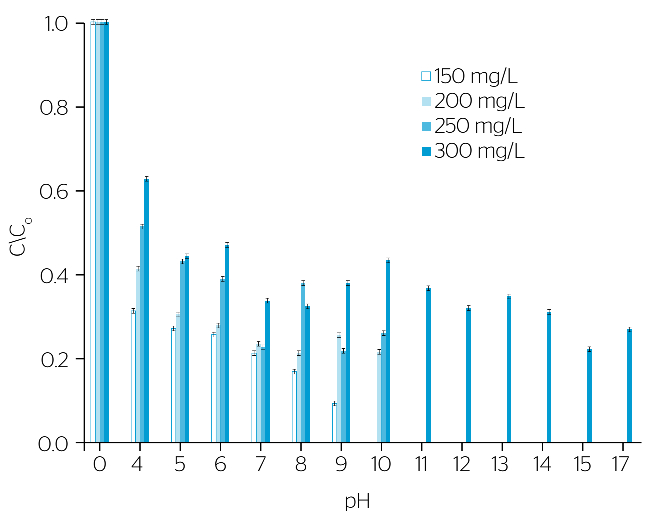

Figure 6 - Concentration time data for different RB19 initial concentration at a pH of 7 during ozonation (38.4 mg O$_3$.L^{-1}).

authors (WU; EITEMAN; LAW, 1998; WU & WANG, 2001; SEVIMLI & SARIKAYA, 2002; DEMIREV & NENOV, 2005; WU; DOAN; UPRETI, 2008; TURHAN *et al.*, 2012; TURHAN & OZTURKCAN, 2013). Wu, Eiteman and Law (1998), Sevimli and Sarikaya (2002) and Wu, Doan and Upreti (2008) affirm that k_{ap} decreases with an increase in C_0 because more intermediate compounds are generated. These intermediates also consume ozone, implying lower concentration of ozone with higher C_0. The linearity between ln (k) and ln (C_0) seems valid for the ozonation of azo and reactive dyes, regardless of the co-existence of other components (WU & WANG, 2001; WU; DOAN; UPRETI, 2008).

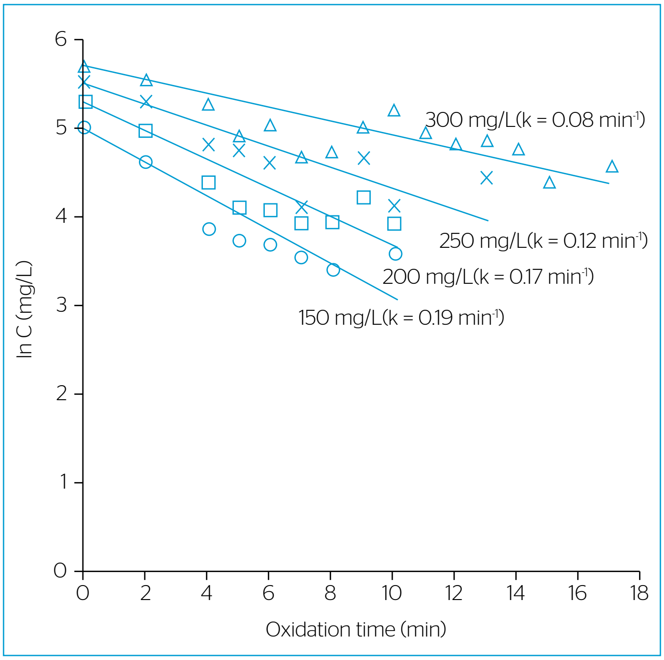

Figure 7 – Pseudo first-order decay rate constants for different RB19 initial concentration at a pH of 7 during ozonation (38.4 mg O_3.L^{-1}).

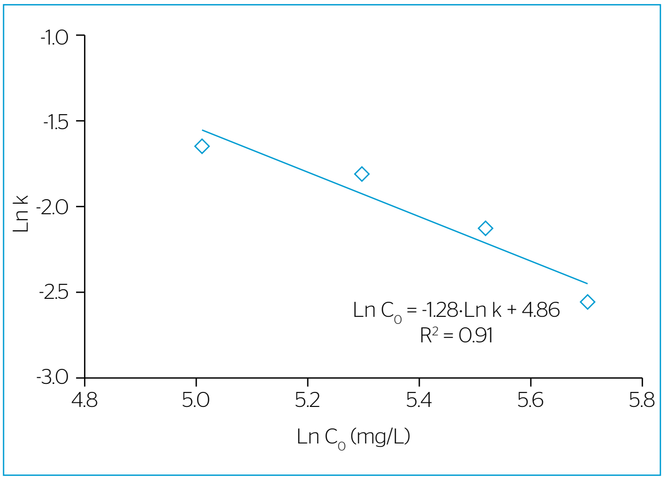

Figure 8 – Dependence of the apparent rate constant of decolorization k_{ap} on different initial RB19 concentration at a pH of 7 during ozonation (38.4 mg O_3.L^{-1}).

Mass ratio analyses

The experimental results and the power law empirical trend are shown in Figure 9.

Results showed that the mass ratio over time is slightly dependent on C_0 values. This behavior can be described by exponential decay, with a good fit in the empirical equation. The result suggests that the desired removal of RB19 can be achieved by simply controlling the consumed ozone.

For the analytical analyses, the obtained values of each parameter for different C_0 are shown in Table 1.

It is possible to conclude that the parameters used in Equation 5 followed a linear relationship with C_0, with low slope values and $R^2 >$ 0.87 (Table 2), thus reinforcing that RB19 is slightly dependent on C_0.

Figure 10 presents all the experimental results for several C_0 values that were fitted by the non-linear integrated form of Equation 5.

In general, it is possible to see that the analytical proposal can follow the trend of the experimental results. However, the spread of the

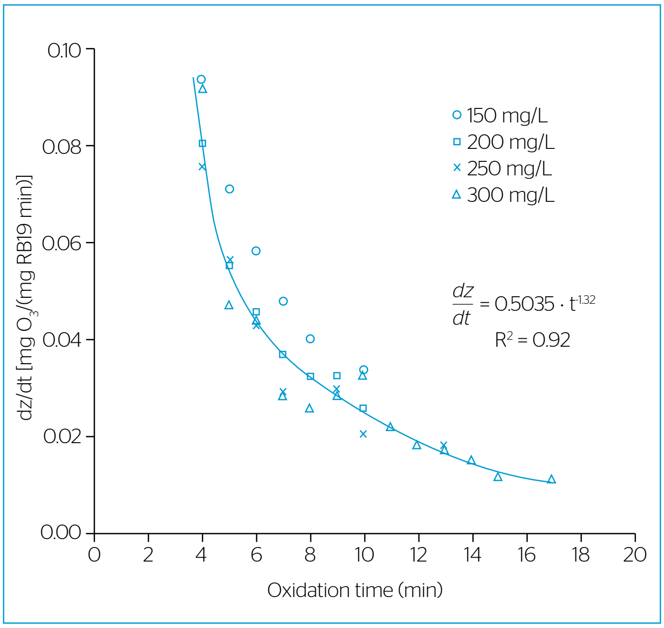

Figure 9 – Experimental data for empirical stoichiometric mass ratio over time.

Table 1 – Parameters of RB19 decay for analytical analyses.

Parameters	150 mg.L^{-1}	200 mg.L^{-1}	250 mg.L^{-1}	300 mg.L^{-1}
z	0.55	0.51	0.47	0.39
z*	0.32	0.22	0.20	0.17
k'_{ap}	0.39	0.27	0.26	0.14

Table 2 – Adjusted parameters of different C_0 for analytical analyses.

Parameters	Slope	Intercept	R^2
z	-0.0010	0.714	0.97
z*	-0.0009	0.439	0.87
k'_{ap}	-0.0016	0.618	0.92

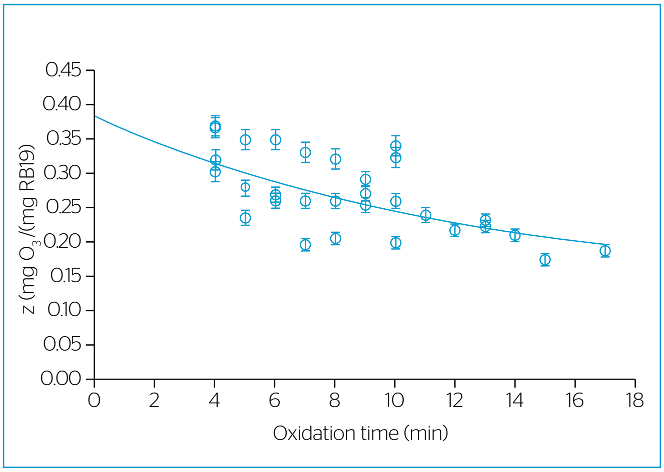

Figure 10 – Predicted and experimental *z* values for all investigated C_0 values over time for analytical model. $z = 0.38$ mg O_3.mg $RB19^{-1}$ (t = 0), $z^* = 0.13$ mg O_3.mg $RB19^{-1}$ and $k'_{ap} = 0.08$ min^{-1}.

data around the line that describes the analytical behavior suggests that mass transfer occurs both in liquid film and in bulk fluid.

CONCLUSIONS

The removal of RB19 by ozone demands an understanding of the decomposition rate. The main conclusions obtained in this study were as follows:

- the RB19 removal efficiency increased from 64 to 94% when the ozone dose increased from 38.4 to 153.6 mg $O_3.L^{-1}$;
- RB19 decolorization is more efficient at pH 7;
- the rate of RB19 removal decreased as the initial RB19 concentration increased;
- the ozonation of RB19 was a pseudo first-order reaction with respect to the dye;
- the apparent rate constant decreased logarithmically with the initial RB19 concentration;
- the experimental mass ratio obtained is independent of the initial RB19 concentration;
- power law decay is adequate to describe the mass ratio over time for the empirical analysis;
- the decolorization reaction is influenced by mass transfer in the liquid film as well as in the bulk fluid.

REFERENCES

ADAMS, C.D.; GORG, S. (2002) Effect of pH and gas-phase ozone concentration on the decolorization of common textile dyes. *Journal of Environmental Engineering*, v. 128, n. 3, p. 293-298. http://doi.org/10.1061/(ASCE)0733-9372(2002)128:3(293)

AMERICAN PUBLIC HEALTH ASSOCIATION (APHA); AMERICAN WATER WORKS ASSOCIATION (AWWA); WATER ENVIRONMENT FEDERATION (WEF). (2012) *Standard Methods for Examination of Water and Wastewater*. 22. ed. Washington, D.C.: American Public Health Association, American Water Works Association, Water Environment Federation.

ASGHER, M. (2012) Biosorption of reactive dyes: a review. *Water, Air and Soil Pollution*, v. 223, n. 5, p. 2417-2435. http://doi.org/10.1007/s11270-011-1034-z

CHARPENTIER, J.C. (1981) Mass-transfer Rates in Gas-liquid Absorbers and Reactors. *In*: _____ (Ed.). *Advances in chemical engineering*. New York: Academic, p. 3-133.

CHRISTIE, R.M. (2015) *Colour Chemistry*. 2. ed. Cambridge: The Royal Society of Chemistry. 332 p.

CHU, W.; MA, C.W. (2000) Quantitative prediction of direct and indirect dye ozonation kinetics. *Water Research*, v. 34, n. 12, p. 3153-3160. http://dx.doi.org/10.1016/S0043-1354(00)00043-9

DEMIREV, A.; NENOV, V. (2005) Ozonation of two acidic azo dyes with different substituents. *Ozone: Science and Engineering*, v. 27, n. 6, p. 475-485. http://dx.doi.org/10.1080/01919510500351834

ELOVITZ, M.S.; GUNTEN, U. (1999) Hydroxyl Radical/Ozone ratios during ozonation processes. I The R_{ct} Concept. *Ozone: Science and Engineering*, v. 21, n. 3, p. 239-260. http://dx.doi.org/10.1080/01919519908547239

FANCHIANG, J.M.; TSENG, D.H. (2009a) Decolorization and transformation of anthraquinone dye Reactive Blue 19 by ozonation. *Environmental Technology*, v. 30, n. 2, p. 161-172. http://dx.doi.org/10.1080/09593330802422886

FANCHIANG, J.M.; TSENG, D.H. (2009b) Degradation of anthraquinone dye C.I. Reactive Blue 19 in aqueous solution by ozonation. *Chemosphere*, v. 77, n. 2, p. 214-221. http://dx.doi.org/10.1016/j.chemosphere.2009.07.038

GAO, P.; LI, K.; LIU, Z.; LIU, B.; MA, C.; XUE, G.; ZHOU, M. (2014) Feather keratin deposits as biosorbent for the removal of Methylene Blue from aqueous solution: equilibrium, kinetics and thermodynamics studies. *Water, Air and Soil Pollution*, v. 225, p. 1946-1958. http://dx.doi.org/10.1007/s11270-014-1946-5

HE, Z.; LIN, L.; SONG, S.; XIA, M.; XU, L.; YING, H.; CHEN, J. (2008) Mineralization of C.I. Reactive Blue 19 by ozonation combined with sonolysis: performance optimization and degradation mechanism. *Separation and Purification Technology*, v. 62, n. 2, p. 376-381. http://dx.doi.org/10.1016/j.seppur.2008.02.005

JESUS, C.P.C.; ANTUNES, M.L.P.; CONCEIÇÃO, F.T.; NAVARRO, G.R.B.; MORUZZI, R.B. (2014) Removal of reactive dye from aqueous solution using thermally treated red mud. *Desalination and Water Treatment*, v. 55, n. 4, p. 1040-1047. http://dx.doi.org/10.1080/19443994.2014.922444

LANGLAIS, B.; RECKHOW, D.A.; BRINK, D.R. (1991) *Ozone in Water Treatment: Application and Engineering*. Boca Raton: Lewis Publishers. 569 p.

MATHEWS, A.P.; PANDA, K.K. (2012) Analysis of absorption and reaction kinetics in the oxidation of organics in effluents using a porous electrode ozonator. *Chinese Journal of Chemical Engineering*, v. 20, n. 3, p. 417-425. https://doi.org/10.1016/S1004-9541(11)60148-1

MOUSSAVI, G.; MAHMOUDI, M. (2009) Removal of azo and anthraquinone reactive dyes from industrial wastewaters using MgO nanoparticles. *Journal of Hazardous Materials*, v. 168, n. 2-3, p. 806-812. https://doi.org/10.1016/j.jhazmat.2009.02.097

RAGHUVANSHI, S.P.; SINGH, R.; KAUSHIK, C.P.; RAGHAV, A.K. (2005) Removal of textile basic dye from aqueous solutions using sawdust as bio-adsorbent. *International Journal of Environmental Studies*, v. 62, n. 3, p. 329-339. https://doi.org/10.1080/0020723042000275150

SEVIMLI, M.F.; KINACI, C. (2002) Decolorization of textile wastewater by ozonation and Fenton's process. *Water Science and Technology*, v. 45, n. 12, p. 279-286. https://doi.org/10.2166/wst.2002.0436

SEVIMLI, M.F.; SARIKAYA, H.Z. (2002) Ozone treatment of textile effluents and dyes: effect of applied ozone dose, pH and dye concentration. *Journal of Chemical Technology and Biotechnology*, v. 77, n. 7, p. 842-850. https://doi.org/10.1002/jctb.644

SIDDIQUE, M.; FAROOQ, R.; KHALID, A.; FAROOQ, A.; MAHMOOD, Q.; FAROOQ, U.; RAJA, I.A.; SHAUKAT, S.F. (2009) Thermal-pressure-mediated hydrolysis of Reactive Blue 19 dye. *Journal of Hazardous Materials*, v. 172, n. 2-3, p. 1007-1012. https://doi.org/10.1016/j.jhazmat.2009.07.095

SIDDIQUE, M.; FAROOQ, R.; KHAN, Z.M.; KHAN, Z.; SHAUKAT, S.F. (2011) Enhanced decomposition of Reactive Blue 19 dye in ultrasound assisted electrochemical reactor. *Ultrasonics Sonochemistry*, v. 18, n. 1, p. 190-196. https://doi.org/10.1016/j.ultsonch.2010.05.004

SIDDIQUE, M.; FAROOQ, R.; SHAHEEN, A. (2011) Removal of Reactive Blue 19 from wastewaters by physicochemical and biological processes – a review. *Journal of the Chemical Society of Pakistan*, v. 33, n. 2, p. 284-293.

SOUZA, K.C.; ANTUNES, M.L.P.; COUPERTHWAITE, S.J.; CONCEIÇÃO, F.T.; BARROS, T.R.; FROST, R. (2013) Adsorption of reactive dye on seawater-neutralised bauxite refinery residue. *Journal of Colloid and Interface Science*, v. 396, p. 210-214. https://doi.org/10.1016/j.jcis.2013.01.011

TURHAN, K.; DURUKAN, I.; OZTURKCAN, S.A.; TURGUT, Z. (2012) Decolorization of textile basic dye in aqueous solution by ozone. *Dyes and Pigments*, v. 92, n. 3, p. 897-901. http://dx.doi.org/10.1016/j.dyepig.2011.07.012

TURHAN, K.; OZTURKCAN, S.A. (2013) Decolorization and degradation of reactive dye in aqueous solution by ozonation in a semi-batch bubble column reactor. *Water, Air and Soil Pollution*, v. 224, p. 1353-1365. http://dx.doi.org/10.1007/s11270-012-1353-8

WEBER, E.J.; STICKNEY, V.C. (1993) Hydrolysis kinetics of Reactive Blue 19-Vinyl sulfone. *Water Research*, v. 27, n. 1, p. 63-67. https://doi.org/10.1016/0043-1354(93)90195-N

WU, J.; DOAN, H.; UPRETI, S. (2008) Decolorization of aqueous textile reactive dye by ozone. *Chemical Engineering Journal*, v. 142, n. 2, p. 156-160. http://dx.doi.org/10.1016/j.cej.2007.11.019

WU, B.J.; EITEMAN, M.A.; LAW, S.E. (1998) Evaluation of membrane filtration and ozonation processes for treatment of reactive-dye wastewater. *Journal of Environmental Engineering*, v. 124, n. 3, p. 272-277. http://dx.doi.org/10.1061/(ASCE)0733-9372(1998)124:3(272)

WU, J.; WANG, T. (2001) Ozonation of aqueous azo dye in a semi-batch reactor. *Water Research*, v. 35, n. 4, p. 1093-1099. http://dx.doi.org/10.1016/S0043-1354(00)00330-4