Degradation and toxicity depletion of RB19 anthraquinone dye in water by ozone-based technologies

María E. Lovato, María L. Fiasconaro and Carlos A. Martín

ABSTRACT

This research investigated the discoloration and mineralization of Reactive Blue 19 (RB19) anthraquinone dye by single ozonation, single UV radiation and ozonation jointed with UV radiation (O_3/UV). The problem was approached from two points of view: with the objective of color removal or the mineralization of solution. In each case, the optimum operating conditions were different. Ozonation was the most effective treatment for color removal, while the combined O_3/UV treatment was for mineralization. Major intermediates of the dye degradation were identified by gas chromatography/mass spectrometry and a degradation pathway was proposed. In addition, a clear decrease of the toxicity of the dye was achieved at the end of the experiments. The effect of initial dye concentration, pH, ozone dose, and UV radiation on the degradation of the dye and decrease of total organic carbon was investigated, in order to establish the optimal operating conditions to achieve discoloration, mineralization or a combination of both.

Key words | degradation pathway, ozonation, Reactive Blue 19, toxicity, UV radiation

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INTRODUCTION

Textile wastewaters have different dye types and concentrations. Dyes are responsible for the presence of color in textile wastewater, impairing light penetration and compromising ecosystems in the receiving water media (Franca *et al.* 2015; Polat *et al.* 2015). These industrial wastes are considered as harmful pollutants, which are released into the natural water resources or wastewater treatment systems (Rondon *et al.* 2015).

Industrial textile wastewaters have a relatively low ratio between biological oxygen demand and chemical oxygen demand which shows that conventional biological treatment methods are not effective enough (Khandegar & Saroha 2013). This high non-biodegradability of textile effluents requires other alternative treatments in order to meet the discharge standards of the treated wastewaters.

Ozone appears as a promising chemical oxidant used for color removal from dye wastewaters. Molecular ozone is a strong oxidant which exhibits high reactivity and selectivity towards organic pollutants. During ozonation in water, both molecular O_3 and hydroxyl (•OH) radical coexist, having different reactivity and selectivity. •OH

production is usually promoted at high pH, with the addition of H_2O_2 or UV irradiation (Beltrán 2003).

Based on the color index, handling and mode of application on the substrate, dyes are categorized as acidic, basic, direct, disperse, mordant, reactive, solvent and vat dyes. In each of these categories, dyes can be furthermore classified as azoic, anthraquinonic and heteropolyaromatic, among others (Vinu *et al.* 2010).

Anthraquinone reactive dyes are sparingly biodegradable due to their merged aromatic structures (Deng *et al.* 2008). Also, they may cause toxicity or even potential carcinogenic and mutagenic effects on exposed aquatic organisms (Novotny *et al.* 2006). Consequently, anthraquinone dyes require attention from the toxicological and environmental viewpoints, especially given the current increase in their applications. Up to the present, numerous studies have identified the ozonation by-products of azo reactive dyes (Kusic *et al.* 2011; Venkatesh *et al.* 2015). In contrast, there is a limited amount of research studies focused on ozonation and degradation mechanism of anthraquinone reactive dyes (He *et al.* 2008; Chen *et al.* 2009; Fanchiang & Tseng 2009).

Recent studies (Patil & Shukla 2015; Polat et al. 2015; Venkatesh et al. 2015) reported ozonation as an effective process to accomplish discoloration and mineralization of textile and dyeing effluents. Throughout ozonation of a colored effluent, ozone initially attacks unsaturated bonds of chromophores, giving a fast elimination of color; nevertheless, single ozonation often is not sufficient for complete removal of the oxidation by-products (Soares et al. 2000). When oxidation processes are utilized to degrade organic pollutants, the partial oxidation may result in the production of intermediates even more persistent and toxic than the parent contaminants, disturbing the environmental water parameters (Chang et al. 2009). The knowledge of the reaction mechanism and the oxidation products, as well as the examination of the solution biotoxicity during treatment, is then required. From the environmental point of view, degradation of the dye should be evaluated as an overall process, involving removal of both the parent dye and its intermediates and products. Consequently, the most practical resource for estimating this overall process is to monitor the mineralization of the solution (He et al. 2008).

The intention of this study was to investigate the feasibility of discoloration and mineralization of a representative anthraquinone dye, Reactive Blue 19 (RB19), by an ozone-based process. Although several reports described the oxidation of RB19 solutions through ozonation processes, most of them focused on the discoloration efficiency and color removal kinetics (Tehrani-Bagha et al. 2010), or described the effect of operating parameters on mineralization (He et al. 2008), but there are no reports where the study of discoloration and mineralization processes are carried out systematically and simultaneously. Among the reports there are large discrepancies regarding the most appropriate experimental conditions required to achieve discoloration or mineralization. For example, concerning pH effect, Chen et al. (2009) established that pH 3 is the most suitable pH to achieve RB19 decolorization, while Tehrani-Bagha et al. (2010) proposed pH 10 as the best option, and Fanchiang & Tseng (2009) reported optimal pH between 3 and 5. Thus, the need to find the most suitable conditions for discoloration, mineralization or a combination of both arises.

In this report, the effects of operational parameters, including pH, initial dye concentration, O_3 dose, and the effect of UV radiation were investigated, in order to establish the appropriate conditions for the discoloration and/or mineralization of the dye. Additionally, a decrease of the toxicity of the solution was accomplished and a degradation pathway was proposed.

METHODS

Equipment and chemicals

Ozone was generated from dried oxygen with purity of 99.99% (Air Liquide Argentina) via corona discharge using an ozone generator (Fischer 503). The photoreactor was a cylinder having flat, quartz windows irradiated with two monochromatic germicidal lamps (Heraeus NNI 40/20) with emission at 253.7 nm and nominal power of 40 W, placed at the focal axis of two parabolic reflectors. The system included a counter-current operation packed bed column, a centrifugal pump, a sampling valve and a heat exchanger to maintain isothermal conditions (20 °C). Absence of reactant and/or reaction products stripping was carefully verified with blank runs. The total recirculating fluid volume was 1,700 cm³.

A detailed description of the experimental setup can be found in the Appendix (Figure A1, available with the online version of this paper) and in a previous work (Lovato et al. 2015). The stock RB19 (Sigma-Aldrich) dye solution of 1,000 mg was dissolved in distilled water (Osmoion) and diluted to 1,000 mL. The standard dye solutions were prepared from stock solution. The initial concentration of the dye (230 ± 1.5 mg L^{-1}) was chosen in order to quantify simultaneously the discoloration and mineralization of the solution within the studied operating conditions. To study the initial dye concentration effects, one set of experimental runs was made with initial RB19 concentrations of 111 and 466 mg L^{-1}. The natural pH of the solution was 6 ± 0.3. In order to study the pH effects, additional experimental runs were performed at pH 3, 7 and 10, where the solution pH was maintained constant using NaH_2PO_4/Na_2HPO_4 buffer. MarvinSketch™ software was used to estimate the pK_a (logarithmic acid dissociation constant) of the dye.

Analyses

Analytical determinations (triplicated) were made without delay after sample collection. The concentration of dye RB19 was detected by UV–visible spectrophotometry (Perkin Elmer) with appropriate calibrations at precise wavelength ($\lambda = 592$ nm). Since anthraquinone and other aromatic intermediates do not absorb radiation at that specific wavelength, absence of interferences was guaranteed. The oxygen inlet flow rate was controlled via a mass flow controller

(Aalborg GFC17) at 1 L min^{-1}. The inlet and outlet gaseous ozone concentrations were measured via an ozone analyzer (Teledyne 454) and expressed as mg L^{-1} NTP (normal temperature and pressure). The mineralization of the solution was determined by total organic carbon (TOC) analysis (Shimadzu TOC-5000A). We did blank essays (120 min) in the absence of ozone, in the dark, verifying the nonexistence of both discoloration and mineralization.

The biotoxicity evolution of the treated solution was examined at 15 °C using the *Vibrio fischeri* acute toxicity test (Microtox®). *Vibrio fischeri* (lyophilized) was reconstituted in a salt solution and then 1 mL of water sample was added to 100 µL of the reconstituted bacteria. Luminescence readings (490 nm) were taken prior to adding the drinking water and then at 5 and 15 minutes after the addition. Results were displayed as absolute light units, and the inhibition percentage was calculated.

In order to identify reaction intermediates, they were extracted from the liquid samples using solid phase microextraction technique with a polydimethylsiloxane 100 µm fiber. Analyses were carried out on a Perkin Elmer GC Clarus 600 coupled with a Perkin Elmer Clarus 600-T mass spectrometer. The analytical column was an Elite-5 phenyl methyl silicone column and helium was used as carrier gas.

RESULTS AND DISCUSSION

Influence of initial RB19 concentration

The conversion of RB19 at a given time decreases when elevating the initial concentration of the dye. Initial RB19 concentrations of 111, 235 and 466 mg L^{-1} were degraded in absence of UV radiation, using an inlet ozone concentration of $C_{O3}^{G,i} = 99.1$ mg L^{-1} NTP. Figure 1(a) shows that, after 1 min of reaction, the achieved conversions are 59%, 40% and 32%; and after 5 min of reaction, they are 100%, 96% and 90%, respectively. Figure 1(b) depicts that, for dye initial concentrations of 111, 235 and 466 mg L^{-1}, with corresponding TOC initial concentrations of 46.7, 99 and 196.4 mg L^{-1}, after 120 minutes of reaction the corresponding TOC conversions were 82%, 48% and 34%, and the mineralized TOC concentrations were 38.21, 47.17 and 66.67 mg L^{-1} respectively, which indicates that a sufficient number of ozone molecules were present to oxidize the dye molecules, even using the higher concentrations. The reason for the decrease in the mineralization rate could be that (1) under the studied conditions the ratio of ozone/dye molecules decreases with the increase of the
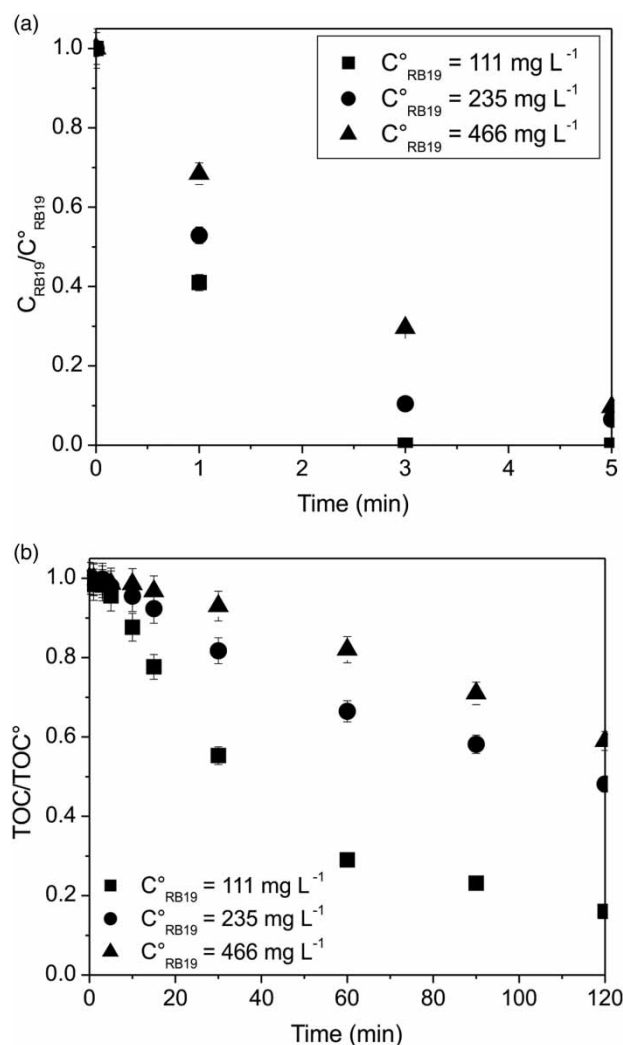

Figure 1 | Effect of initial dye concentration on (a) RB19 decolorization, (b) RB19 mineralization. $C_{O3}^{G,i} = 99.1$ mg L^{-1} NTP, pH = 6, no UV radiation.

dye initial concentration and (2) higher initial dye concentrations resulted in generation of more inorganic anions, which competed with organic matter for reaction with •OH radicals (He *et al.* 2008; Tehrani-Bagha *et al.* 2010).

Effect of ozone dosage

Results of RB19 decolorization for different inlet ozone concentrations ($C_{O3}^{G,i} = 56.1$, 71.1 and 99.1 mg L^{-1} NTP; oxygen flow rate $F_{O2} = 1$ L min^{-1}) are illustrated in Figure 2(a). The ozone dose is a parameter defined as $[(C_{O3}^{G,i}) \times (F^{O2})]$ and represents the ozone incorporated at the system per unit time. For the different experimental ($C_{O3}^{G,i}$), the ozone doses were 3.73, 4.27 and 5.47 g h^{-1}, respectively. In addition, the parameter 'ozone consumption' (OC) represents the total
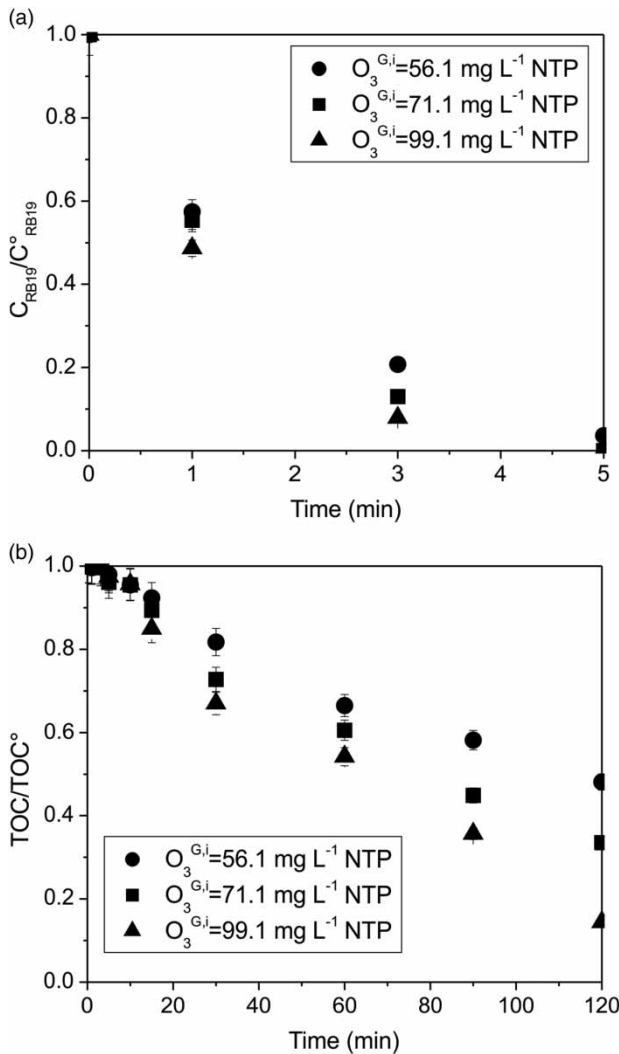
Figure 2 | Effect of inlet ozone concentration on (a) decolorization of RB19, (b) mineralization of RB19. $C_{RB19}^\circ = 230 \pm 2$ mg L^{-1}, pH = 6, no UV radiation.

ozone transferred per unit of liquid phase throughout a given reaction time. Using Equation (1):

$$\frac{d(OC)}{dt} = \frac{F_{O_2}}{V_L}[C_{O_3}^{g,i} - C_{O_3}^{g,o}(t)] \tag{1}$$

OC was computed for reaction times of 10, 30, 60 and 120 min). In Equation (1) V_L is the liquid volume (L), $C_{O_3}^{G,i}$ is the inlet ozone concentration (constant over time) and $C_{O_3}^{G,o}$ is the outlet ozone concentration (varies along the reaction time). Table 1 compiles the ozone dose, ozone consumption, RB19 decolorization and TOC depletion effectiveness throughout time at different O_3 concentrations. RB19 decolorization and TOC depletion efficiencies increased with time and $C_{O_3}^{G,i}$.

The highest OC was registered for the higher inlet ozone concentration studied, which suggests an effective use of the supplied ozone (Cortez et al. 2010). Figure 2(a) shows clearly that the decolorization of RB19 was more pronounced with higher ozone doses. The mineralization of organic compounds is shown in Figure 2(b). At a reaction time of 10 min, more than 99% conversion was achieved for RB19 but 95% of the initial TOC still remains in solution, indicating that many organic intermediates of the reaction still persist. After a longer reaction time (120 min), TOC conversions were 52%, 66% and 86% for ozone inlet concentrations of 56.1, 71.1 and 99.1 mg L^{-1} NTP, respectively. Consequently, an increase in the ozone dose has a positive effect on mineralization rate. He et al. (2008) reported that an increment in ozone dosage is projected to correspond with an enhancement in the production of •OH radicals. Additionally, the augmented ozone concentration in the gas bubbles (O$_2$/O$_3$), which carry the O$_3$

Table 1 | O$_3$ dose, O$_3$ consumption (OC), RB19 decolorization and TOC depletion throughout time at different O$_3$ concentrations

		Reaction time (min)			
Ozone concentration	Parameter	10	30	60	120
56.1 mg L^{-1} NTP	OC (g L^{-1} liquid)	8.08×10^{-3}	1.18×10^{-2}	1.67×10^{-2}	3.31×10^{-2}
O$_3$ dose = 3.37 g h^{-1}	RB19 removal (%)	99	100	100	100
	TOC depletion (%)	5	18	34	52
71.1 mg L^{-1} NTP	OC (g L^{-1} liquid)	4.67×10^{-3}	9.69×10^{-3}	1.70×10^{-2}	3.29×10^{-2}
O$_3$ dose = 4.27 g h^{-1}	RB19 removal (%)	100	100	100	100
	TOC depletion (%)	5	27	39	66
99.1 mg L^{-1} NTP	OC (g L^{-1} liquid)	5.51×10^{-3}	1.34×10^{-2}	2.23×10^{-2}	3.66×10^{-2}
O$_3$ dose = 5.47 g h^{-1}	RB19 removal (%)	100	100	100	100
	TOC depletion (%)	5	33	46	86

molecules, should enhance the driving force for the mass transfer of ozone from the gas phase into the aqueous solution. This results in an increased concentration of O_3 in the liquid phase and a higher pseudo first-order rate constant (Sevimli & Sarikaya 2002).

Effect of pH

Based on the estimated pK_a values, only one predominant unhydrolyzed RB19 species exists between the pH values of 3 and 10. The dye molecule speciation and the major microspecies distribution can be found in the Appendix (Figure A2, Table A1, available with the online version of this paper). The absorption spectrum of the dye solution was the same at different pH values confirming that the dye solutions exhibit good stability against pH changes in the range of 3 to 10 (Figure A3).

Figure 3(a) illustrates the effect of pH on color removal of dye RB19 under constant ozone dosage. It can be observed that the highest discoloration rate for RB19 took place at pH 3. Since ozone can react via a direct reaction pathway or by an indirect way involving various highly reactive intermediates (Beltrán 2003), two different oxidation pathways simultaneously exist. At pH 3, due to the slower decomposition rate of ozone, the main oxidant species is molecular O_3 rather than •OH radicals (Lovato et al. 2009). Our results are in agreement with Chen et al. (2009) who found that the discoloration of RB19 was higher at low pH, in agreement with Liu et al. (2004), who reported that the discoloration ability of O_3 was higher at low pH for specific dyes.

The effect of pH on RB19 mineralization is shown in Figure 3(b). It can be observed that the higher TOC removals are those corresponding to pH 10. This observation can be explained since under alkaline conditions (pH 10) an elevated number of O_3 molecules are degraded to generate OH^- and finally •OH radicals throw radical chain reaction steps, which are the main responsible species in indirect oxidation reactions, favoring the dye mineralization (Beltrán 2003).

Effect of UV incident radiation at the reactor windows

The decolorization of 230 ± 1.5 mg L^{-1} of RB19 at a pH of 6.0 and ozone inlet concentration of 50 ± 2 mg L^{-1} NTP, feed of 4.8 g h^{-1}, was measured for the different studied processes: UV photolysis, ozonation, and UV/O_3 system. Figure 4(a) shows the corresponding decrease in the dye concentration. Direct UV photolysis of RB19 was negligible
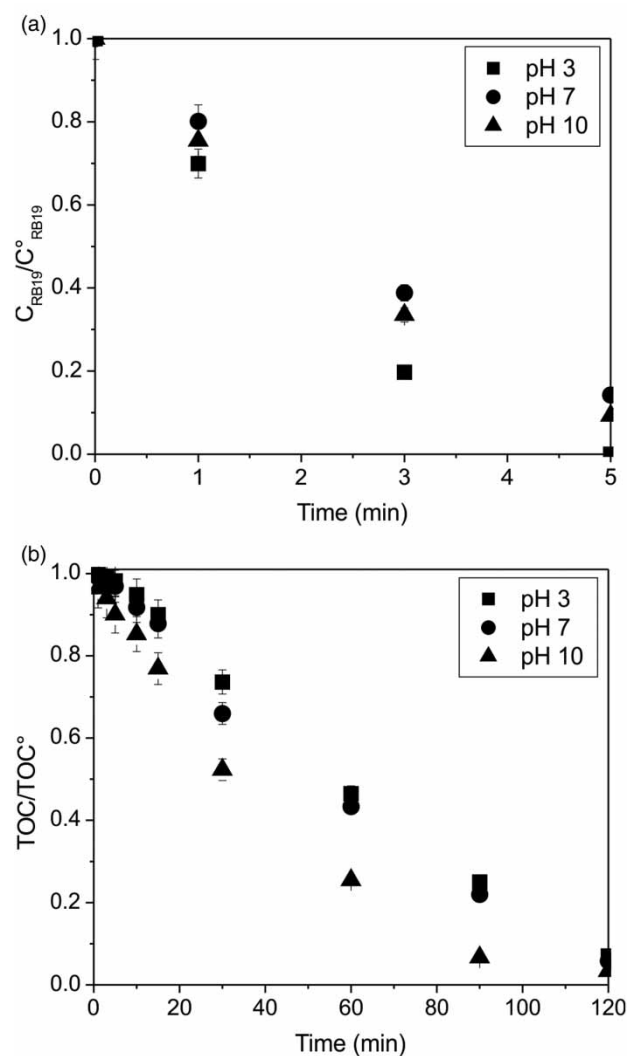

Figure 3 | Effect of pH on (a) RB19 decolorization, (b) RB19 mineralization. $C^\circ_{RB19} = 230 \pm 1.5$ mg L^{-1}, $C^{G,i}_{O3} = 52$ mg L^{-1} NTP.

as previously reported (Guimarães et al. 2012) and ozonation was more effective than UV/O_3 processes. For a reaction time of 1 min, the corresponding dye degradations are 0%, 46% and 30% employing direct photolysis, O_3 alone and the combined process O_3/UV, respectively. These results are in agreement with our results regarding the pH effect: molecular ozone is more effective for decolorization of RB19 than •OH radicals, as reported by Chen et al. (2009).

Figure 4(b) shows the mineralization of the dye. The TOC removal corresponding to UV photolysis was insignificant. Our results show that the combination O_3/UV resulted in a higher mineralization rate. After 120 min, the TOC decrease in the UV, O_3, and UV/O_3 treatments was 0%, 52%, and 94%, respectively. The addition of UV radiation to the system leads to O_3 photolysis, producing
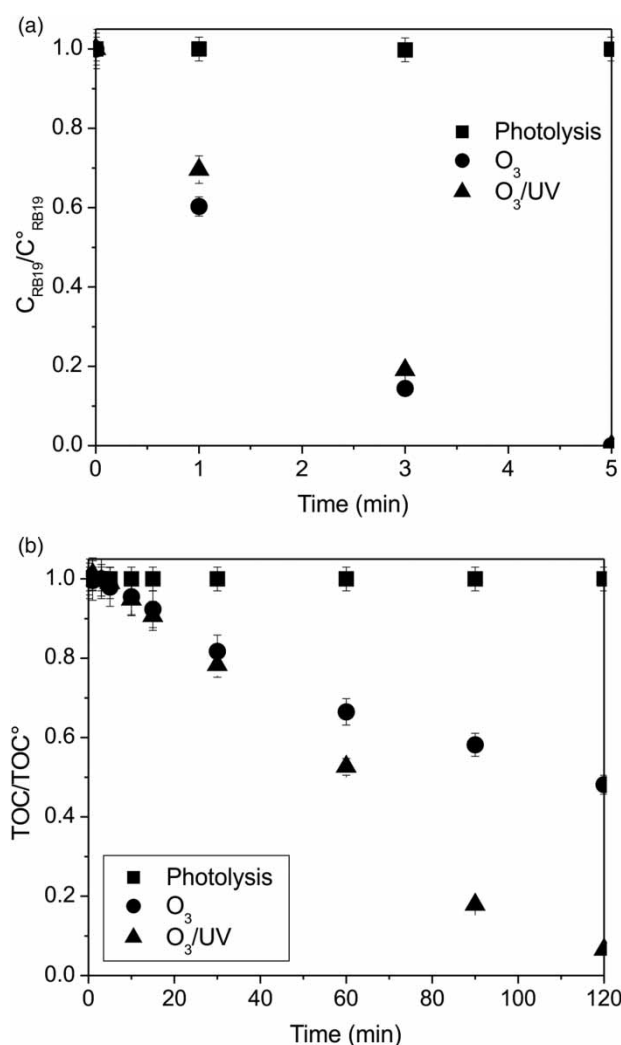
Figure 4 | Comparison of UV, O_3, and UV/O_3 for (a) RB19 decolorization, (b) RB19 mineralization. $C^{\circ}_{RB19} = 230 \pm 2$ mg L^{-1}. $C^{G.i}_{O_3} = 52$ mg L^{-1} NTP, pH = 6, UV power 40 W.

H_2O_2, which could react with O_3 via hydroperoxide ion or could be photolyzed, producing •OH radicals in both cases (Beltrán 2003). Consequently, the UV/O_3 system produces additional •OH radicals, which therefore enhance the ozonation process (Gilliard et al. 2013).

Kinetic studies

The plot of ln ($C_{RB19}/C^{\circ}_{RB19}$) versus reaction time was a straight line (integrating Equation (2)), in agreement with a typical pseudo first-order reaction. The slope of the straight line gives the apparent rate constant. The results are compiled in Table 2.

$$\frac{dC_{RB19}}{dt} = -kC_{RB19} \qquad (2)$$

The calculated k values of RB19 under acid pH are higher than those corresponding to neutral and alkaline conditions. Nevertheless, the variation in k values between acid and neutral pH and between neutral and caustic conditions was around 20% in both cases.

These findings are in accordance with the discussion regarding the effect of pH, confirming that the O_3 molecule is more effective than •OH radicals toward the specific chromophoric group of RB19. The regression coefficient R^2 obtained for the different studied conditions shows that the discoloration reaction of RB19 follows first-order kinetics.

It should be noted that, in order to study the effect of pH on the global kinetics, the experimental runs were performed at constant pH, using phosphate buffer. Since these species act as a radical scavenger, even maintaining constant the other experimental conditions, the reaction

Table 2 | Pseudo first-order rate constants at different operation conditions for RB19 discoloration

pH	C_{RB19} (mg L^{-1})	O_3 dose (g h^{-1})	UV radiation	Pseudo first-order constant k (min^{-1})	Std error of k	R^2	Sum of squared residuals
3 (with buffer)	230	3.37	0	0.554	0.068	0.985	0.022
7 (with buffer)	230	3.37	0	0.318	0.013	0.998	0.001
10 (with buffer)	230	3.37	0	0.375	0.053	0.981	0.013
6	230	3.37	0	0.576	0.024	0.998	0.003
6	230	4.27	0	0.686	0.033	0.998	0.005
6	230	5.47	0	0.854	0.046	0.997	0.010
6	230	3.37	40 W	0.522	0.059	0.987	0.017
6	230	0	40 W	0	–	–	–
6	111	3.37	0	0.900	0.002	0.999	2.1×10^{-5}
6	466	3.37	0	0.409	0.010	0.999	4.7×10^{-4}

rates for the experimental runs with and without phosphate buffers with hydroxyl radicals were different. For pH values of 2.8–4.5 the reaction rate of ·OH with phosphate species would be low. Conversely, at alkaline conditions more radical scavengers such as CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} react with ·OH leading to a decrease of the radical concentration (He et al. 2008). Our results are very close to those found by Chen et al. (2009). With an O_3 dose of $4.00\ g\ h^{-1}$ the authors calculated first-order decay constants of 0.79, 0.37 and $0.44\ min^{-1}$. Pirgalioglu & Ozbelge (2009), using an O_3 dose of $6.9\ g\ h^{-1}$ (double that used in this study), reported pseudo first-order constants of 0.72, 0.64 and $0.77\ min^{-1}$ for pH 3, 7 and 10, respectively.

The pseudo first-order rate constants increased as the initial dye concentration decreased. This result is consistent with reported data (Chen et al. 2009; Siddique et al. 2011). A modification of C°_{RB19} from 230 ppm to 111 ppm leads to an increase in the apparent reaction rate of 36%.

As shown in the previous section, an increase in the O_3 dosage enhances the discoloration rate, with a difference in the apparent reaction rates between the experiments with the higher and lower inlet O_3 concentrations of 33%. The results are consistent with those found by Chen et al. (2009) using an O_3 dose of $4.00\ g\ h^{-1}$.

The incorporation of UV radiation to the ozonation system leads to a decrease of 9% in the apparent reaction rate, in agreement with the results shown above and the outcome about pH effects (molecular O_3 is more effective for degrading the chromophore molecule of RB19 than are ·OH radicals).

Biotoxicity test

The marine bacterium *V. fischeri* was used as biotoxicity indicator, using the acute test and estimating the inhibition of *V. fischeri* at 15 min of time exposure. The sample pH was set to 7, while the osmotic pressure was adjusted in order to obtain salinity of 2%. The progress of the biotoxicity of the solution is shown in Table 3, together with the RB19 and TOC conversion, for an experimental run conducted with the higher RB19 concentration, and the lower ozone dose in absence of UV radiation, i.e. the less favorable conditions.

It can be observed that toxicity reaches a maximum for a reaction time of 10 min, and then decreases. This indicates that there were toxic intermediates present in the treated solution, as found by He et al. (2008) who utilized an ozonation–sonolysis process to degrade RB19 and reported toxic intermediates like aniline and phenol. In this study phenol was also detected, as discussed in the next section.

Table 3 | Mineralization and toxicity evaluation of the treated dye solution. $C^{\circ}_{RB19} = 435\ mg\ L^{-1}$, $C^{G,i}_{O3} = 55.8\ mg\ L^{-1}$ NTP, pH = 6, no UV radiation

Reaction time (min)	RB19 conversion (%)	TOC conversion (%)	Inhibition (%)
0	0	0	60
10	100	2	95
30	100	12	64
60	100	67	39
120	100	94	16

Identification of RB19 intermediates and final products

Using gas chromatography coupled with mass spectrometry (GC/MS) analyses, the following compounds were identified: anthraquinone, isobenzofuran-1,3-dione (phthalic anhydride), isoindoline-1,3-dione (phthalimide); phthalic acid, benzoic acid, maleic acid, benzyl alcohol, benzaldehyde, phenol, aniline, oxalic acid, acetic acid. The results are in agreement with different reference data (Fanchiang & Tseng 2009; Siddique et al. 2011) which correspond to the degradation of RB19 using sonolytic ozonation, ozonation and ultrasound-assisted electrochemical processes, respectively. The identified intermediates and products and their MS spectra are shown in the Appendix (Table A2, available with the online version of this paper).

Assessing the toxicity of reactive intermediates and products, some of the identified degradation products are more toxic than RB19 ($\cong$90% inhibition), indicating that the moment of finalization of the oxidation process should be carefully established, if complete mineralization is not the objective.

Proposal of reaction scheme

Samples at different intervals were collected during ozonation of $230\ mg\ L^{-1}$ RB19 at pH 6 and $C^{G,i}_{O3} = 55.1\ mg\ L^{-1}$ NTP. The proposed degradation pathway is illustrated in Figure 5. In this process the C(2)—C(3), C(10)—C(11), C(3)—C(4), C(9)—C(10), C(5)—N, C(6)—S, C(8)—N, C(16)—S, C(15)—N bonds have a tendency to be cleaved (Siddique et al. 2011). The reaction pathway is based on the identified products: phthalimide (formed through cleavage of C(3)—C(4) and C(9)—C(10) bonds and rearrangements), anthraquinone (formed after the cleavage of C(5)—N, C(6)—S and C(8)—N bonds), aniline and phenol (formed after the cleavage of C(8)—N, C(16)—S and subsequent oxidation of the amino group). Through cleavage of C(3)—C(4) and C(9)—C(10) anthraquinone was degraded into benzyl
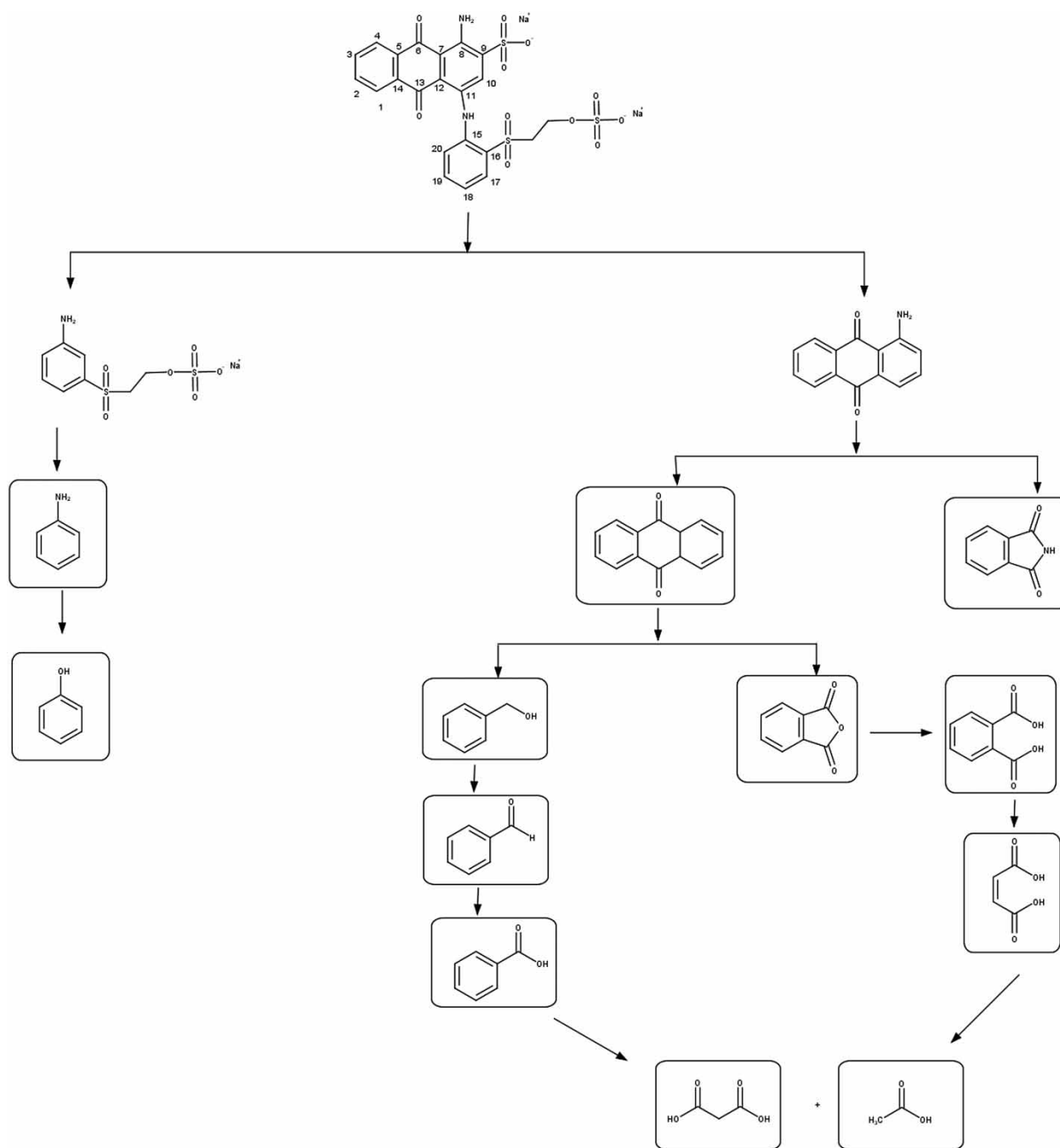
Figure 5 | Proposed degradation pathway of RB19 by O_3. $C_{O3}^{G,i} = 52$ mg L^{-1} NTP, pH $= 6$, $C_{RB19}^{o} = 230$ mg L^{-1}. Boxed compounds: identified by GC/MS in this study.

alcohol and phthalic anhydride. Benzyl alcohol was further oxidized to benzaldehyde and then to benzoic acid. Phthalic anhydride was further oxidized to phthalic acid and then to maleic acid. Under oxidation conditions, maleic acid and benzoic acid would be degraded into smaller molecules, such as oxalic and acetic acid and then mineralized into CO_2 and H_2O.

CONCLUSIONS

Discoloration and mineralization rates of RB19 were affected by initial dye concentration, pH, O_3 dose, and UV radiation. UV radiation alone gave negligible results, but O_3/UV treatment yielded a higher mineralization rate compared with ozonation alone, due to the enhanced •OH

radical formation. Based on these results, the appropriate conditions for dye discoloration and/or mineralization can be established. Molecular O_3 proved to be the most effective treatment for color removal. Our results show that the most suitable experimental conditions to achieve RB19 discoloration are pH 3 and absence of UV radiation. On the other hand, •OH radicals, whose production is favored at high pH values and UV radiation (Beltrán 2003), were more effective than molecular O_3 for RB19 mineralization. The major TOC decreases were achieved at pH 10 with the combined AOP O_3/UV. Both discoloration and mineralization processes are improved by increasing the inlet O_3 concentration. Several intermediates and products were identified using GC/MS. The Microtox® assay showed that the biotoxicity of the reacting mixture reaches a maximum value and then was significantly reduced after 30 minutes of treatment. These results present ozonation as a suitable alternative for treatment of wastewater with a high content of recalcitrant reactive dyes and allows determination of the operating conditions to achieve the desired results.

ACKNOWLEDGEMENTS

REFERENCES

Beltrán, F. 2003 *Ozone Reaction Kinetics for Water and Wastewater Systems.* Lewis Publishers, New York.

Chang, S., Chuang, S., Li, H., Liang, H. & Huang, L. 2009 Comparative study on the degradation of I.C. Remazol Brilliant Blue R and I.C. Acid Black 1 by Fenton oxidation and Fe 0/air process and toxicity evaluation. *Journal of Hazardous Materials* **166**, 1279–1288.

Chen, T., Kao, C., Hong, A., Lin, C. & Liang, S. 2009 Application of ozone on the decolorization of reactive dyes – Orange-13 and Blue-19. *Desalination* **249**, 1238–1242.

Cortez, S., Teixeira, P., Oliveira, R. & Mota, M. 2010 Ozonation as polishing treatment of mature landfill leachate. *Journal of Hazardous Materials* **182**, 730–734.

Deng, D., Guo, J., Zeng, G. & Sun, G. 2008 Decolorization of anthraquinone, triphenylmethane and azo dyes by a new isolated *Bacillus cereus* strain DC11. *International Biodeterioration & Biodegradation* **62**, 263–269.

Fanchiang, J. & Tseng, D. 2009 Degradation of anthraquinone dye C.I. Reactive Blue 19 in aqueous solution by ozonation. *Chemosphere* **77**, 214–221.

Franca, R., Vieira, A., Mata, A., Carvalho, G., Pinheiro, H. & Lourenço, N. 2015 Effect of an azo dye on the performance of an aerobic granular sludge sequencing batch reactor treating a simulated textile wastewater. *Water Research* **85**, 327–336.

Gilliard, M., Martín, C., Cassano, A. & Lovato, M. 2013 Reaction kinetic model for 2,4-dichlorophenoxyacetic acid decomposition in aqueous media including direct photolysis, direct ozonation, ultraviolet C, and pH enhancement. *Industrial & Engineering Chemistry Research* **52**, 14034–14048.

Guimarães, J., Guedes Maniero, M. & Nogueira de Araújo, R. 2012 A comparative study on the degradation of RB-19 dye in an aqueous medium by advanced oxidation processes. *Journal of Environmental Management* **110**, 33–39.

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* **62**, 376–381.

Khandegar, V. & Saroha, A. 2013 Electrocoagulation for the treatment of textile industry effluent – a review. *Journal of Environmental Management* **128**, 49–963.

Kusic, H., Juretic, D., Koprivanac, N., Marin, V. & Bozic, A. 2011 Photooxidation processes for an azo dye in aqueous media: modeling of degradation kinetic and ecological parameters evaluation. *Journal of Hazardous Materials* **185**, 1558–1568.

Liu, B., Chou, M., Kao, C. & Huang, B. 2004 Evaluation of selected operational parameters for the decolorization of dye-finishing wastewater using UV/ozone. *Ozone: Science & Engineering* **26**, 239–245.

Lovato, M., Martin, C. & Cassano, A. 2009 A reaction kinetic model for ozone decomposition in aqueous media valid for neutral and acidic pH. *Chemical Engineering Journal* **146**, 486–497.

Lovato, M., Gilliard, M., Cassano, A. & Martín, C. 2015 Kinetics of the degradation of n-butyl benzyl phthalate using O_3/UV, direct photolysis, direct ozonation and UV effects. *Environmental Science and Pollution Research* **22**, 909–917.

Novotny, C., Dias, N., Kapanen, A., Malachova, K., Vandrovcova, M., Itavaara, M. & Lima, N. 2006 Comparative use of bacterial, algal and protozoan tests to study toxicity of azo- and anthraquinone dyes. *Chemosphere* **63**, 1436–1442.

Patil, N. & Shukla, S. 2015 Decolorization of reactive blue 171 dye using ozonation and UV/H_2O_2 and elucidation of the degradation mechanism. *Environmental Progress & Sustainable Energy* **34**, 1652–1661.

Pirgalioglu, S. & Ozbelge, T. 2009 Comparison of non-catalytic and catalytic ozonation processes of three different aqueous single dye solutions with respect to powder copper sulfide catalyst. *Applied Catalysis A: General* **363**, 157–163.

Polat, D., Balci, I. & Özbelge, T. 2015 Catalytic ozonation of an industrial textile wastewater in a heterogeneous continuous reactor. *Journal of Environmental Chemical Engineering* **3**, 1860–1871.

Rondon, H., El-Cheikh, W., Boluarte, I., Chang, C., Bagshaw, S., Farago, L., Jegatheesan, V. & Shu, L. 2015 Application of

enhanced membrane bioreactor (eMBR) to treat dye wastewater. *Bioresource Technology* **183**, 78–85.

Sevimli, M. & Sarikaya, H. 2002 Ozone treatment of textile effluents and dyes: effect of applied ozone dose, pH and dye concentration. *Journal of Chemical Technology and Biotechnology* **77**, 842–850.

Siddique, M., Farooq, R., Mehmood Khan, Z., Khan, Z. & Shaukat, S. 2011 Enhanced decomposition of reactive blue 19 dye in ultrasound assisted electrochemical reactor. *Ultrasonics Sonochemistry* **18**, 190–196.

Soares, O., Orfão, J., Portela, D., Vieira, A. & Pereira, M. 2000 Ozonation of textile effluents and dye solutions under continuous operation: influence of operating parameters. *Journal of Hazardous Materials* **137**, 1664–1673.

Tehrani-Bagha, A., Mahmoodi, N. & Menger, F. 2010 Degradation of a persistent organic dye from colored textile wastewater by ozonation. *Desalination* **260**, 34–38.

Venkatesh, S., Quaff, A., Pandey, N. & Venkatesh, K. 2015 Impact of ozonation on decolorization and mineralization of azo dyes: biodegradability enhancement, by-products formation, required energy and cost. *Ozone: Science & Engineering* **37**, 420–430.

Vinu, R., Akki, S. & Madras, G. 2010 Investigation of dye functional group on the photocatalytic degradation of dyes by nano-TiO$_2$. *Journal of Hazardous Materials* **176**, 765–773.