



Application of electrochemically generated ozone to the discoloration and degradation of solutions containing the dye Reactive Orange 122

Mário H.P. Santana^{b,1}, Leonardo M. Da Silva^a, Admildo C. Freitas^{b,1}, Julien F.C. Boodts^{b,1}, Karla C. Fernandes^{b,1}, Luiz A. De Faria^{b,*}

^a Department of Chemistry - UFVJM, Laboratory of Environmental Electrochemistry, Rua da Glória 187, 39100-000 Diamantina, MG, Brazil

^b Institute of Chemistry - UFU, Laboratory of Electrochemistry, Campus Santa Mônica, Av. João Naves de Ávila 2160, 38400-902 Uberlândia, MG, Brazil

ARTICLE INFO

Article history:

Received 24 January 2008

Received in revised form 9 July 2008

Accepted 25 July 2008

Available online 5 August 2008

Keywords:

Ozone

Electrochemistry

Discoloration kinetics

Textile dye degradation

ABSTRACT

Aqueous solutions containing the commercial azo dye Reactive Orange 122 (RO122) were ozonated in acid and alkaline conditions. Ozone was electrochemically generated using a laboratory-made electrochemical reactor and applied using semi-batch conditions and a column bubble reactor. A constant ozone application rate of 0.25 g h^{-1} was used throughout. Color removal and degradation efficiency were evaluated as function of ozonation time, pH and initial dye concentration by means of discoloration kinetics and COD–TOC removal. Experimental findings revealed that pH affects both discoloration kinetics and COD–TOC removal. A single pseudo-first-order kinetic rate constant, k_{obs} , for discoloration was found for ozonation carried out in alkaline solutions, contrary to acidic solutions where k_{obs} depends on ozonation time. COD–TOC removal supports degradation of RO122 is more pronounced for alkaline conditions. Evaluation of the oxidation feasibility by means of the COD/TOC ratio indicates that the ozonation process in both acid and alkaline conditions leads to a reduction in recalcitrance of the soluble organic matter.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Ozonation comprises an important coadjutant process for treatment of different effluents containing a high load of recalcitrant compounds [1–7]. As previously discussed by Da Silva and Jardim [2], textile effluents are very difficult to treat satisfactorily because they contain several recalcitrant compounds while the wastewaters generated at the various stages of the dyeing process considerably differ in composition. The high-pollution load is mainly caused by: spent dyeing baths (unreacted dye; dispersing agents (surfactants); salts and organics washed out of the material which undergoes dyeing [8–17]. According to the EPA's toxics release inventory [18], approximately 2200 ton of four hazardous dyes are discharged annually into public owned treatment works.

Classical methods used for treating textile wastewaters include different combinations of biological (activated sludge), physical and

chemical processes [19,20]. Since dye molecules are highly structured [17], they are very difficult to be broken down biologically and cannot be treated efficiently by an activated sludge process or combinations of biological, chemical coagulation and physical methods [2,8,17,21]. Besides, the main drawback of these processes is the generation of a large amount of sludge or solid waste, resulting in high operational costs for sludge treatment and disposal [22,23].

Alternative technologies based on advanced oxidation processes (AOP) can be used in combination with the classical ones in order to provide an efficient discoloration and COD–TOC reduction of textile wastewater [2,23]. Degradation of textile dyes using AOP has been reported in the literature [8–16,21,23,24].

As a rule, AOP efficiency depends on the chemical nature of the effluent to be treated: pH, turbidity, COD–TOC and the presence of radical scavengers. A project aiming at the evaluation of the economic viability of AOP for an acceptable level of contaminants was described by Luck et al. [25].

In the special case of ozonation, the AOP efficiency depends on the TOC of the effluent [2]. For low strength dye waste effluents, ozonation alone is sufficient to totally eliminate the color and reduce turbidity. However, for medium and high strength waste effluents, ozonation is found to be adequate to reduce the color, but not enough to reduce the turbidity. Hence, coagulation using aluminum sulphate ($\sim 60 \text{ mg dm}^{-3}$) or especially designed polymers is necessary [26,27]. Tzitzis et al. [27] reported that ozonation

Abbreviations: RO122, reactive orange 122; EOP, electrochemical ozone production; TPCBP, transient persistent colored by-products; ITP, integrated treatment process; COD, chemical oxygen demand; TOC, total organic carbon; AOP, advanced oxidation process.

* Corresponding author. Tel.: +55 34 32394143; fax: +55 34 32394208.

E-mail address: lafaria@ufu.br (L.A. De Faria).

¹ Tel.: +55 34 32394143; fax: +55 34 32394208.

Nomenclature

[D]	initial dye concentration (mg dm^{-3})
E	enhancement factor
G_A	volumetric flow rate of the anodic gases ($\text{dm}^3 \text{s}^{-1}$)
G_E	volumetric flow rate of the electrolyte ($\text{dm}^3 \text{h}^{-1}$)
$k_{L,A}$	volumetric mass transfer coefficient for ozone (min^{-1})
k_{obs}	pseudo-first-order rate constant for discoloration (min^{-1})
$k_{\text{obs-1}}$	pseudo-first-order rate constant for initial ozonation times (min^{-1})
$k_{\text{obs-2}}$	pseudo-first-order rate constant for longer ozonation times (min^{-1})
$[\text{O}_3]_S$	dissolved ozone concentration (mg dm^{-3})
$[\text{O}_3]_S^*$	saturated ozone concentration (mg dm^{-3})
t_d	total discoloration time (min)

Greek letter

γ	susceptibility of oxidation of the soluble organic matter
ν_{EOP}	ozone application rate (g h^{-1})

of wastewater after applying a coagulation–precipitation process exhibited more efficient discoloration (>90%) and COD reduction (>30%), while biodegradability was found to increase, permitting effective degradation by the activated sludge process [2,4,7]. Thus, the combination of ozonation with proper chemical coagulation and an activated sludge process is a promising alternative technology for dealing with textile industry effluent, which reduces sludge disposal [2,21,23].

Ozone production cost has dropped by 50% in the last two decades and, therefore, a great number of new industrial applications have appeared in recent years [2,21]. Because ozone is unstable and cannot be stored over an extended period of time, it has to be generated on site [1–3]. Ozone can be generated “in situ” using the following technologies [1,28]: (i) Photochemistry (UV-radiation); (ii) Corona (silent electric discharge) and (iii) Electrochemistry (electrolysis of aqueous solutions or pure water).

The most common technology for ozone production is the Corona process, where a dry gas, either air or pure oxygen, is subjected to a silent electrical discharge [1,21,28]. Electrochemistry is a promising alternative technology for “in situ” ozone generation [1–3,21,24] presenting some features that are not achieved with the Corona process, thus making it an interesting alternative for several ozone applications [2,21].

Electrolytic ozonizers based on the solid polymer electrolyte technology, which operate in electrolyte-free water and under ambient temperature conditions ($\sim 30^\circ\text{C}$), permit ozone application directly into water streams permitting various oxidizing and/or disinfectant applications [21,29]. In this case the total energy demand is minimized, since O_3 -production is conducted at ambient temperature (no energy spent with refrigeration) while the high ozone mass transfer rate avoids the use of accessories such as gas diffusers and pumping systems [21].

Another EOP technology is based on the use of specially designed electrolytes [30,31] taking advantage of the reduction of oxygen as the cathodic process. As a result, the specific energy demand becomes very close to a conventional Corona device [30]. This technology furnishes a very high efficiency ($\geq 35 \text{ wt}\%$), making this electrochemical ozonizer competitive with the corona technology for applications where a high O_3 -concentration in the gaseous phase is necessary.

The objective of this paper is to investigate the application of electrochemically generated ozone to the discoloration and degradation, in acid and alkaline solutions, of the commercial reactive azo dye C.I. Reactive Orange 122 (RO122).

2. Experimental

2.1. Electrochemical ozone production

Electrochemical ozone generation and ozonation of aqueous solutions containing the textile dye RO122 were carried out using the experimental set-up presented in Fig. 1.

The electrochemical ozone reactor, developed by Da Silva et al. [24], presents an EOP current efficiency of up to 21 wt% (EOP rate of $\sim 5 \text{ g h}^{-1}$ and an EOP specific power consumption of 70 Wh g^{-1}). The gas mixture (O_2/O_3) leaving the anode compartment is separated from the circulating electrolyte using a gas separator flask and is introduced into the column bubble reactor (see Fig. 1). The electric current applied to the reactor and the electrolyte temperature were adjusted to provide a constant ozone application rate of 0.25 g h^{-1} . This value was chosen considering the geometric prop-

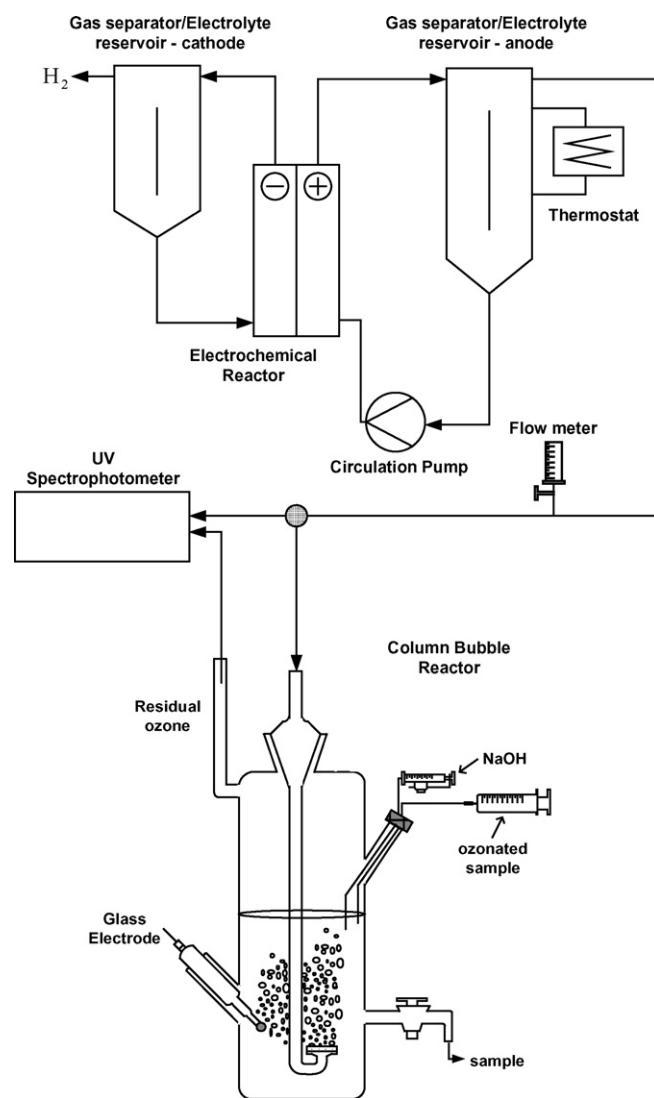


Fig. 1. Flow diagram representing the experimental set-up used for electrochemical ozone generation and ozonation under semi-batch conditions of aqueous solutions containing the textile dye RO122.

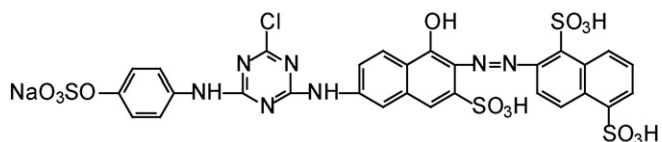


Fig. 2. Chemical structure of the textile dye RO122. λ_{\max} = 488 nm; solubility in water: 75 g dm^{-3} ; degree of purity: 80–85%.

erties of the column bubble reactor (liquid height, volume capacity and diameter of the porous coarse glass plate) in order to maximize ozone utilization efficiency during the treatment. The electrochemical reactor was powered by a 80 A/12 V dc current source. In all cases the electrolyte ($3.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 0.03 \text{ mol dm}^{-3} \text{ KPF}_6$) was circulated in the anodic compartment ($G_E = 60 \text{ dm}^3 \text{ h}^{-1}$) using a model 7018-21 MASTERFLEX peristaltic circulation pump (Cole-Parmer).

The linear velocity of the electrolyte was 1.30 cm s^{-1} and the space velocity 5.19 min^{-1} . The flow regime was turbulent ($Re > 3000$). Electrolyte temperature control (0°C) was achieved by means of a model FC55A01 FTS cooling system connected to the all-glass electrolyte reservoir/gas separator flask. The electrolyte temperature at the anode surface was monitored using a model 61 FLUKE digital thermocouple.

Ozone concentration in the gaseous phase was analyzed by UV absorption measurements at 254 nm, using a homemade quartz gas flow cell [24]. Absorbance was read after 15 min of cell polarization when steady-state conditions were observed. Ozone reproducibility is 2.0–2.5% while sensitivity is 0.0396 L mg^{-1} . At the wavelength of 254 nm no interference is observed.

The ozone application rate, v_{EOP} , was calculated using the following equation [24]:

$$v_{\text{EOP}}(\text{g h}^{-1}) = \frac{3600(A G_A M)}{\varepsilon \cdot l} \quad (1)$$

where A = absorbance at 254 nm; G_A = volumetric flow rate of the anodic gases (O_2/O_3) ($\text{dm}^3 \text{ s}^{-1}$); $\varepsilon = 3024 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ is the ozone absorptivity at 254 nm in the gaseous phase [28]; l = optical path length (0.63 cm) and M = ozone molecular weight (48 g mol^{-1}).

2.2. Ozonation of the textile dye solutions

Samples in distilled water were prepared by dissolving the commercial azo dye C. I. Reactive Orange 122, RO122 (degree of purity: 80–85%), furnished by CERMATEX Textile Industry Ltd. (Americana, Brazil). The chemical structure of the textile dye RO122 is presented in Fig. 2.

2.2.1. Discoloration kinetics

Color removal was studied under semi-batch conditions ($V = 0.6 \text{ dm}^3$) using a column bubble reactor (see Fig. 1). The gas mixture (O_2/O_3) was bubbled using a porous plate diffuser (Schott #2 coarse glass frit; $A = 3.5 \text{ cm}^2$) placed at the bottom of the column bubble reactor.

In order to evaluate the influence of the ozone mass transfer on the discoloration process, the volumetric mass transfer coefficient, $k_{L,a}$, was determined applying the standard non steady-state method for the column bubble reactor containing 0.6 dm^3 of distilled water ($T = 25^\circ\text{C}$; $G_A = 2.1 \text{ dm}^3 \text{ h}^{-1}$; $v_{\text{EOP}} = 0.25 \text{ g h}^{-1}$). Since ozone presents a low solubility in water at 25°C [28], the resistance to mass transfer of ozone in the gas phase (inside the gas bubbles) is negligible when compared to the resistance of the ozone mass transfer across the liquid film formed at the gas (bubble)/solution interface [32–35]. The ozone concentration in the aqueous phase

was calculated at 258 nm ($\varepsilon = 2900 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) [28] as function of the ozonation time until the saturation condition was reached.

The discoloration kinetic study was carried out by measuring the absorbance at a fixed wavelength ($\lambda_{\max} = 488 \text{ nm}$ —determined for both acid and alkaline solutions) during the first 60 min of reaction, using a model OPTIZEN 2120UV PLUS Spectrophotometer from MECASYS. Ozonation was carried out in alkaline (initial pH adjusted for 12 by adding NaOH) and acid solutions (initial pH of 4.5—natural pH solution). All samples, presenting an initial dye concentration, $[D]$, of 150 or 300 mg dm^{-3} , were continuously ozonated during 1 h keeping the pH constant by adding 5.0 mol dm^{-3} NaOH solution. The pH was monitored using a combined glass electrode (see Fig. 1).

Discoloration was investigated using 0.6 dm^3 of dye solution. Ozonated samples (3 cm^3) were periodically withdrawn using a syringe for absorbance measurements and re-injected into the reactor flask after each measurement ($\sim 45 \text{ s}$) (see Fig. 1).

2.2.2. Degradation rate

TOC was determined using a model 5000A TOC analyzer from Shimadzu. COD measurements were carried out following the standard procedure [36]. The degradation of RO122 samples (0.6 dm^3 and $[D] = 300 \text{ mg dm}^{-3}$) was investigated, without periodic pH adjustment, by stopping the ozonation process in order to complete the treatment interval of 1 h. A total of 18 samples were taken to evaluate the degradation efficiency.

3. Results and discussion

3.1. Ozone mass transfer in the column bubble reactor

As recently reported [2,21], the global kinetic process concerning ozonation of long-chain organic compounds is very complex. Ozonation of aqueous solutions containing organic pollutants involves the ozone mass transfer process from the gas to the liquid phase, which is combined with ozone consumption (chemical reaction and/or O_3 self-degradation) at the liquid side of the gas/solution interface [21,32,33,35]. This combined process is normally described using the parameter denoted as enhancement factor, E , which describes the acceleration of ozone transfer across the liquid film caused by the chemical reaction on the solution side of the interface [33,35].

From a practical point of view, E is calculated based on the experimental determination of the volumetric mass transfer coefficient in the absence, $k_{L,a}$, and in the presence, $k_{L,a}^*$, of a chemical reaction ($E \equiv k_{L,a}^*/k_{L,a}$) using the non steady-state method [21,35]. This experimental approach is based on the analysis of the transient behavior presented by the ozone concentration in pure water (or aqueous solutions) until O_3 -saturation is reached for a given temperature [35].

Under semi-batch and saturation conditions the mass balance equation for ozone distribution in pure water is given by the next differential equation [32,33,35]:

$$\frac{d[\text{O}_3]_L}{dt} = k_{L,a}([\text{O}_3]_L^{\text{Sat.}} - [\text{O}_3]_L) - k_d[\text{O}_3]_L \quad (2)$$

where $[\text{O}_3]_L$ and $[\text{O}_3]_L^{\text{Sat.}}$ are the instantaneous and the stationary ozone concentration in pure water for a given temperature. The second term at the right side of Eq. (2) describes the O_3 self-degradation process in the aqueous phase, which is characterized by the kinetic rate constant k_d .

Considering stationary conditions prevail under ozone saturation and that the O_3 self-decomposition process is negligible

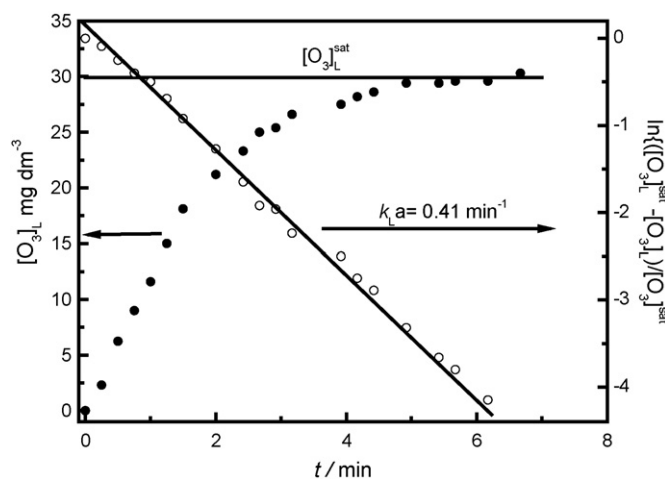


Fig. 3. Time behavior of dissolved ozone concentration in distilled water and the linear dependence predicted by Eq. (3). $G_A = 2.1 \text{ dm}^3 \text{ h}^{-1}$; $\nu_{EOP} = 0.25 \text{ g h}^{-1}$; $T = 25^\circ \text{C}$.

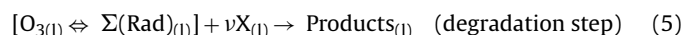
($k_d \cong 0$) during the experiment, integration of Eq. (2) furnishes Eq. (3):

$$\ln \left\{ \frac{[\text{O}_3]_L^{\text{Sat.}} - [\text{O}_3]_L}{[\text{O}_3]_L^{\text{Sat.}}} \right\} = -k_L a t \quad (3)$$

Fig. 3 shows the transient behavior presented by $[\text{O}_3]_L$ in distilled water and the linear dependence predicted by Eq. (3).

Analysis of the data presented in Fig. 3 shows that $k_L a = 0.41 \text{ min}^{-1}$ (25°C); a value in good agreement with literature reports for ozone dissolution in water using a porous plate diffuser and a moderate G_A -values [32–35].

Da Silva and Jardim [2] recently presented a simplified scheme to represent ozonation of organic pollutants (e.g., discoloration) at the gas/liquid interface. According to this scheme, ozone transfer to the liquid phase is followed by the irreversible degradation reaction, as follows:



where $\text{O}_{3(g)}$ and $\text{O}_{3(l)}$ represent ozone present in the gaseous and liquid phases, respectively; $[\text{O}_{3(l)} \rightleftharpoons \Sigma(\text{Rad})_{(l)}]$ describes the O_3 -decomposition that yields oxygenated free radicals (e.g., HO^\bullet); ν is the stoichiometric coefficient, and X is a given target organic compound.

The global ozonation process of organics can be treated using different theoretical approaches (Film, Penetration and Surface Renewal models) [28]. However, the film model is the most frequently used to represent ozonation of recalcitrant organics [32–35].

According to the film model, the mass transfer step (see Eq. (4)) at the gas/liquid interface is described by the enhancement factor, which represents the mass transfer acceleration caused by the degradation step (see Eq. (5)) [35]. Therefore, both pH (ozone self-degradation) and the presence of a chemical reaction can enhance mass transfer across the gas/liquid interface.

According to this theoretical approach, the global ozonation process can be classified as “slow” or “fast” [21,33]. If the “degradation step” is considered slow in comparison with the “mass transfer step”, the limiting case where $E=1$ is observed. In this case the ozonation process occurs in the more external region of the film and the overall reaction rate is governed by the chemical reaction [32–35]. If, however, the degradation step is fast ($E>1$), the ozone concentration is considerably depleted in the film region

and the overall reaction rate is now governed by the mass transfer step.

3.2. Influence of pH on the total discoloration of aqueous dye solutions

Discoloration of solutions containing the dye RO122 was carried out as function of the ozonation time, at different initial pH-values (12.0 or 4.5). Fig. 4 shows the dependence of the instantaneous pH-values and the absorbance decrease (color removal – Abs/Abs_0) on ozonation time, for both acid and alkaline conditions.

Fig. 4 clearly shows total discoloration (color removal >99%) is achieved, in both alkaline and acid conditions after a short ozonation time ($t < 15 \text{ min}$). These findings are in agreement with the literature reports [21,24,33,37,38], thus confirming that ozonation is a very efficient process for color removal. According to the literature [21,24,33], the discoloration process via ozonation is a rapid one in both alkaline and acid conditions. This behavior can be attributed to the electrophilic nature of the direct (attack by O_3 molecules) and the indirect (attack via HO^\bullet radicals) ozonation process, which considerably facilitates the reaction with the azo-groups (chromophore centers) [16,17,24,33]. Fig. 4 also shows the instantaneous pH suffers a decrease during the initial phase of the ozonation process ($t < 5 \text{ min}$). This behavior is a consequence of ozone degradation, which is initiated by the consumption of hydroxyl ions, and by the formation of organic and inorganic acids (ozonation by-products) [16,39,40]. Considering the O_3 self-degradation phenomenon in water [41,42], the pH-decrease observed in Fig. 4 is somewhat more important from a practical point of view in alkaline conditions. The hydroxyl production can be reduced considerably, thus increasing the $\text{O}_3/\text{HO}^\bullet$ -ratio in solution and, as a

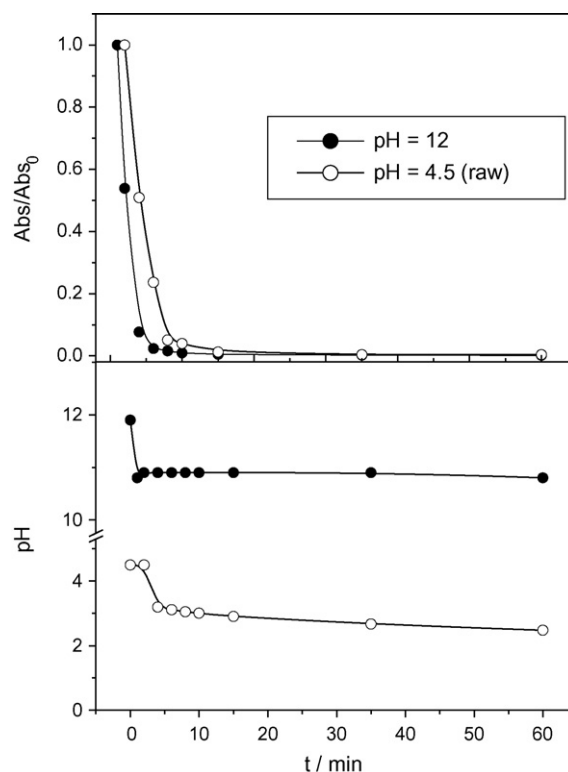


Fig. 4. Dependence of the instantaneous pH and the normalized absorbance (Abs/Abs_0) on ozonation time. $[\text{D}] = 300 \text{ mg dm}^{-3}$; initial pH values (before ozonation): 12.0 and 4.5; $\nu_{EOP} = 0.25 \text{ g h}^{-1}$; $T = 25^\circ \text{C}$.

consequence, leading to a reduction in the global ozonation efficiency.

3.3. Discoloration kinetics in semi-batch conditions

Ozonation of organics depends on pH, chemical reaction (intrinsic kinetics), ozone mass transfer and ozone load in the gaseous phase [2,21,41,42]. As discussed by Wu and Wang [35], the driving force for ozone mass transfer, comprising the difference between the dissolved and the equilibrium ozone concentration at the gas/liquid interface, is system dependent.

The dependence of this driving force for ozone mass transfer on the wastewater characteristics results from the fact that the concentration of dissolved ozone varies considerably with the rate of O₃ self-degradation and the nature of the chemical reaction.

As previously discussed by Franco et al. [21], there is a difference between total discoloration of the dye solution and the total degradation (mineralization) of the dye molecules. In fact, the discoloration process via ozonation takes place when the chromophore bond(s) is(are) removed, while many colored by-products of the parent dye molecule may remain stable in solution [17,21]. Therefore, discoloration may be the initial step in the degradation route of a dye molecule, which is not necessarily accompanied by quantitative carbon removal (considerable degree of mineralization) [21,24,38]. From a practical point of view, discoloration via ozonation requires a lower oxidant load than mineralization, thus becoming an interesting pre-treatment step for the traditional biochemical process, which frequently presents a poor efficiency for color removal [2,17].

The experimental discoloration data reveal an exponential decay of the absorbance measured at a fixed wavelength (488 nm) as function of ozonation time. A rather good linear behavior ($r > 0.998$) was verified using the pseudo-first-order kinetic model.

A recent study by Peng and Fan [37] of the kinetic order of dye discoloration via ozonation under perfect mixing conditions, reports that the pseudo-first-order condition is actually achieved only when the ozone to dye molar ratio remains in the 5.57–9.31 interval. According to this study the reaction order may not be constant throughout the ozonation process, since it can change with the variation of the ozone to dye ratio during the progress of the ozonation process.

During the course of the ozonation reaction it is possible that daughter products (colored by-products) compete with the parental dye molecules for the oxidant (ozone and/or hydroxyl radical) [21]. In this case, the reaction order for the discoloration process (n) can be determined using a least square regression fit of the integrated form of the material balance expression [21,43]:

$$\frac{d[\text{cro}]}{dt} = k_{\text{obs}} [\text{cro}]^n \tag{6}$$

Considering the discoloration process follows a pseudo-first-order model ($n = 1$), integration of Eq. (6) furnishes next relation:

$$\ln \frac{[\text{cro}]}{[\text{cro}]_0} = -k_{\text{obs}} t \tag{7}$$

where $[\text{cro}]$ and $[\text{cro}]_0$ are the instantaneous and the initial chromophore concentrations, respectively [21].

Due to the complex nature of the ozonation process of long-chain organic molecules [28], the overall pseudo-first-order rate constant, k_{obs} , contains the effect of the intrinsic kinetics and may reflect more than one mass transfer-chemical regime [21,28,43], sometimes resulting in a rather complex expression for k_{obs} [43]:

$$k_{\text{obs}} = \alpha (\nu_{\text{EOP}})^x ([\text{HO}^-])^y ([\text{cro}]_0 [\text{HO}^\bullet])^z \tag{8}$$

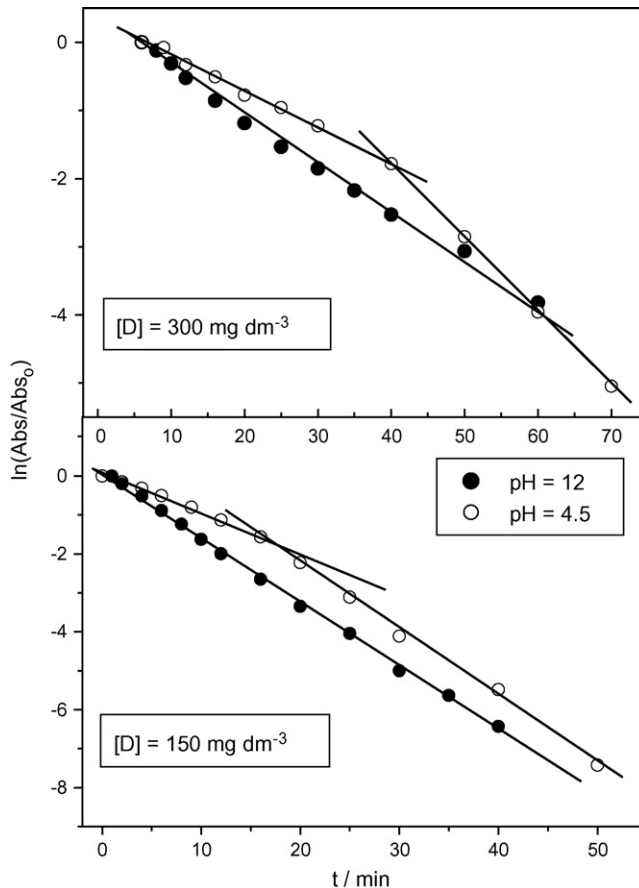


Fig. 5. Pseudo-first-order kinetic profiles for discoloration of the textile dye RO122 as functions of the pH solution and initial dye concentration [D].

where: ν_{EOP} = ozone application rate; $[\text{OH}^\bullet]$ = hydroxyl radical concentration and $[\text{OH}^-]$ = hydroxyl anion concentration. α , x , y and z are the empirical constants for the particular ozonation (discoloration) process. Considering $[\text{cro}]$ and $[\text{cro}]_0$ can be experimentally determined by UV-visible spectroscopy, applying Lambert-Beer's law to Eq. (7), discoloration kinetics can be experimentally investigated using next relation [21].

$$\ln \frac{A}{A_0} = -k_{\text{obs}} t \tag{9}$$

where the ratio A/A_0 represents the normalized absorbance measured at a fixed wavelength (488 nm for RO122).

Fig. 5 shows pseudo-first-order kinetic discoloration profiles while Table 1 gathers k_{obs} as function of pH, which was kept constant during ozonation, and [D]. Comparison of the data presented in Table 1 ($0.052 \text{ min}^{-1} \leq k_{\text{obs}} \leq 0.170 \text{ min}^{-1}$) with the experimental k_{La} -value ($=0.41 \text{ min}^{-1}$), indicates that the chemical discoloration reaction can be considered a slow process when compared with the ozone mass transfer process. In fact, according to the literature [38] the chemical discoloration reaction of azo dyes, in both alkaline and acid solutions, comprises the rate determining step of

Table 1
Dependence of k_{obs} on pH and [D] for the textile dye RO122

[D] (mg dm ⁻³)	pH 12.0	pH 4.5	
	(k_{obs} (min ⁻¹))	($k_{\text{obs-1}}$ (min ⁻¹))	($k_{\text{obs-2}}$ (min ⁻¹))
150	0.163	0.099	0.170
300	0.070	0.052	0.109

the global ozonation process even for cases where $k_{La} < 0.3 \text{ min}^{-1}$. Therefore, we can conclude that the chemical reaction between O_3 and/or HO^\bullet and the chromophore centers governs the global rate of the ozonation discoloration process.

According to Chu et al. [38], the discoloration process is accompanied by an increase of the enhancement factor during the initial stage of ozonation comprising the primary ozone attack at the chromophore groups (azo link groups), while during the second stage of ozonation ($t > t_d$) the enhancement factor slightly decreases as a consequence of the recalcitrance nature of the reaction between ozone and/or HO^\bullet and the discoloration by-products.

Wu and Wang [35] proposed an empirical linear relation for the discoloration process which correlates, for a given temperature, the enhancement factor with the initial dye concentration and the ozone application rate. This relation is denoted as $E = x + y[D] + z(\nu_{EOP})$, where x , y and z are experimental parameters determined for each dye system. According to these authors [35], E increases with $[D]$ due to the chemical kinetics, since dye ozonation is first order with respect to O_3 and the dye. Therefore, the E -value should increase ($y > 0$) with the concentration of both the dye and dissolved ozone. However, keeping constant ν_{EOP} under semi-batch conditions, ozonation becomes pseudo-first-order with respect to the dye, and the E -parameter increases linearly only with $[D]$. Wu and Wang [35] also reported that increasing the ν_{EOP} -value the turbulence at the gas/liquid interface also increases, thus enhancing mass transfer ($z > 0$). The authors also reported the influence of $[D]$ and ν_{EOP} on k_{obs} and found that k_{obs} declines logarithmically with $[D]$. This behavior was described by the relation $k_{obs} = w[D]^{-m}$, where w and m are empirical constants. The study carried out by these authors revealed that the linear $\log(k_{obs}) - \log([D])$ relationship is always true for azo dyes regardless of the co-existence of other compounds.

Analysis of the data presented in Table 1 clearly supports k_{obs} -values depend on both $[D]$ and pH. However, the dependence of k_{obs} on ozonation time observed in acid solution reveals a more complex scenario for the discoloration process. These findings are in agreement with the literature [16,21], reporting k_{obs} depends on dye composition, $[D]$, pH and can present more than one value during the ozonation progress.

A comparison of the k_{obs} -values as functions of pH supports that both the direct and indirect oxidative pathways play a similar role during discoloration. This behavior can be understood considering that both O_3 and HO^\bullet present a strong electrophilic nature, which considerably facilitates the attack at the chromophore centers.

In the light of the discussion presented by Franco et al. [21], and considering that ν_{EOP} , $[\text{OH}^-]$ and $[\text{cro}]_0$ are constants for each case, one can propose that changes in k_{obs} -values as functions of the ozonation time, observed in acid medium, can be attributed to modifications suffered in the intrinsic kinetics between the oxidant (O_3 and/or HO^\bullet) and the chromophore centers.

The discoloration kinetics can be divided into three stages [21]: (i) primary attack: the discoloration process is governed by chemical reaction involving the oxidant (O_3 and/or HO^\bullet) and the more reactive chromophore centers of the parental molecule; (ii) secondary (transient) attack: color removal rate is influenced by changes in the intrinsic nature of the oxidation process as a consequence of the competition between the new chromophore centers present at the transient persistent colored by-products (TPCBP), which are formed after the primary attack; and (iii) tertiary attack (last stage of discoloration): color removal takes place via oxidation of the remaining chromophore centers present in TPCBP.

Considering the above discussion the changes in k_{obs} as functions of the ozonation time and $[D]$ (see Table 1), can be attributed to modifications in the $[\text{dye}]/[\text{TPCBP}]$ -ratio, causing a considerable modification in the intrinsic kinetics between the oxidant

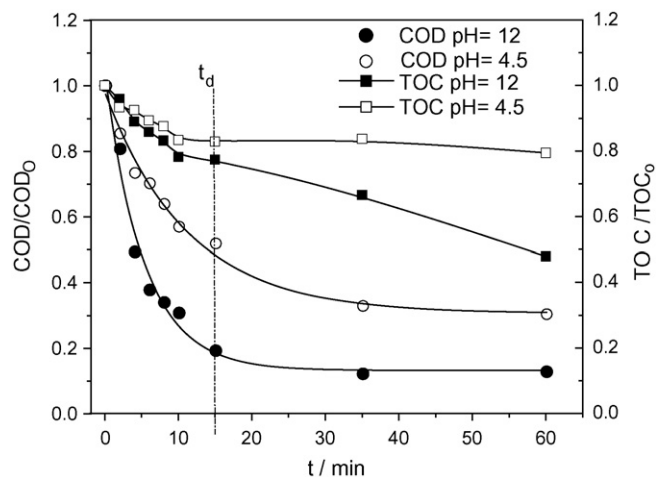


Fig. 6. Influence of the solution pH and ozonation time on COD-TOC removal. $[D] = 300 \text{ mg dm}^{-3}$; $\nu_{EOP} = 0.25 \text{ g h}^{-1}$.

(O_3 and/or HO^\bullet) and the chromophore centers [21]. A comparison of k_{obs-1} and k_{obs-2} indicates that the primary oxidation stage comprises the slow step for discoloration. Accordingly, these results also indicate that the chemical reaction between the oxidant and the TPCBP leading to discoloration is the easy step, thus revealing a decrease, during ozonation, in the recalcitrance nature of the chromophore centers present in TPCBP when compared to the centers present in RO122. From a theoretical point of view, this complex behavior presented by k_{obs} reflects the important influence of the intrinsic properties of the chromophore centers (electronic density) on discoloration kinetics.

3.4. Influence of the pH on degradation of RO122

The degradation rate of RO122 using electrochemically generated ozone was carried out measuring the TOC reduction. COD measurements were carried out in order to provide information about the susceptibility of the organic matter towards chemical oxidation [5]. Fig. 6 shows the influence of the solution pH on the COD-TOC removal, while Fig. 7 presents the feasibility of oxidation, γ , of the soluble organic matter during ozonation at different pH-values [5].

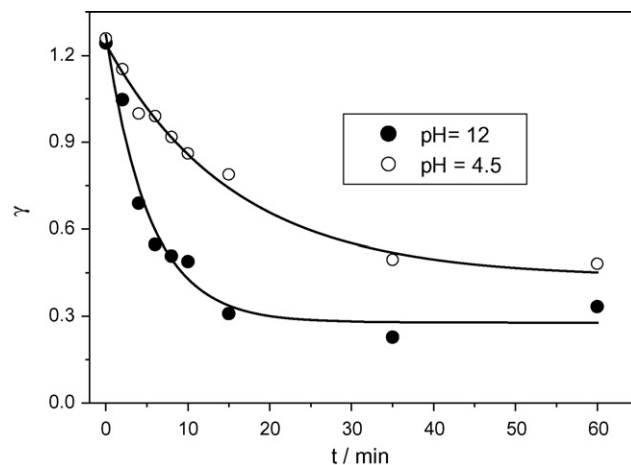


Fig. 7. Influence of ozonation, in acid and alkaline solutions, on the feasibility of oxidation ($\gamma = \text{COD}/\text{TOC}$) of the soluble organic matter. $[D] = 300 \text{ mg dm}^{-3}$.

Fig. 6 clearly shows that both TOC and COD removal rate are more pronounced, mainly in alkaline solution, during the initial stage of the ozonation process ($t < 5$ min). This behavior reveals that partial mineralization of RO122 is more pronounced when total color removal takes place. The fact that the TOC-removal rate is more pronounced when ozonation is carried out in alkaline solution is a consequence of the higher oxidation potential presented by the hydroxyl radical ($E^0 = 2.80$ V) when compared to ozone ($E^0 = 2.07$ V) [28].

Analysis of Fig. 6 reveals TOC-reduction in acid medium for the $t \geq t_d$ interval is not very pronounced, indicating the direct oxidative pathway via O_3 does not constitute an efficient process for further oxidation of the ozonation by-products. On the contrary, in alkaline conditions a considerable TOC-reduction takes place during the entire ozonation interval, thus revealing that the non-selective nature of the indirect oxidative process by HO^\bullet radical results in a continuous degradation of the ozonation by-products.

Fig. 7 clearly shows γ (\equiv COD/TOC) decreases with increasing ozonation time, especially in alkaline conditions, indicating ozonation leads to an increase in the oxidation feasibility of the soluble organic matter. As previously discussed by Franco et al. [21], this behavior is experimental evidence that ozonation can constitute, especially in alkaline medium, an efficient pre-treatment step for integrated treatment processes (ITP) devoted to wastewater treatment [2], where chemical oxidation and biologic processes are combined in order to provide an efficient and economical technology for remediation of recalcitrant pollutants.

4. Conclusions

This study investigating the application of electrochemically generated ozone on the discoloration and degradation of the dye RO122 supports the electrochemical technology as a promising alternative technology for ozone applications in environmental problems concerning the treatment of textile effluents.

The discoloration kinetic study and the analysis of the COD–TOC removal data as functions of ozonation time, carried out in acid and alkaline solutions, revealed that ozonation constitutes an efficient technology for both color and organic matter removal. Total discoloration was rapidly achieved in both acid and alkaline solution, thus revealing that both direct (O_3) and indirect (HO^\bullet) oxidative pathways are efficient for color removal, although an alkaline medium proved to be somewhat superior. Discoloration kinetics follow a pseudo-first-order model, where the apparent kinetic rate constant is influenced by the initial dye concentration and the solution pH. In the case of acid solutions, the apparent kinetic rate constant is also influenced by the ozonation time.

A considerable degree of mineralization ($\geq 70\%$) was achieved after 1 h of ozonation using a low ozone application rate (0.25 g h^{-1}). Besides, it was also found that ozonation, mainly in alkaline medium, promotes a considerable increase in the oxidation feasibility of the soluble organic matter.

Acknowledgements

Mário H.P. Santana wishes to thank the CNPq (Process No. 150156/2005–7) for a post-doctoral fellowship; Luiz A. De Faria wishes to thank financial support received from the CNPq (Process No. 473499/2004–5) and the FAPEMIG (Process No. CEX-834/04). L.M. Da Silva wishes to thank financial support received from the FAPEMIG (Process No. EDT-410/07). The authors wish to thank Dr. Adalgisa Andrade (FFCLRP/USP–Brazil) for providing the TOC data.

References

- [1] L.M. Da Silva, M.H.P. Santana, J.F.C. Boodts, Electrochemistry and green chemical processes: electrochemical ozone production, *Quim. Nova* 26 (6) (2003) 880–888.
- [2] L.M. Da Silva, W.F. Jardim, Trends strategies of ozone application in environmental problems, *Quim. Nova* 29 (2) (2006) 310–317.
- [3] L.M. Da Silva, L.A. de Faria, J.F.C. Boodts, Green processes for environmental application: electrochemical ozone production, *Pure Appl. Chem.* 73 (12) (2001) 1871–1884.
- [4] W.W. Eckenfelder Jr., *Industrial Water Pollution Control*, 2nd edition, McGraw-Hill, New York, 1989.
- [5] A. Marco, S. Esplugas, G. Saum, How and why combine chemical and biological processes for wastewater treatment, *Water Sci. Technol.* 35 (3) (1997) 321–325.
- [6] P. Anastas, J.C. Warner, *Green Chemistry Theory Practice*, 1st edition, Oxford University Press, Oxford, 1998.
- [7] E.W.J. Diaper, in: F.L. Evans (Ed.), *Ozone in Water and Wastewater Treatment*, Ann Arbor Science Publishers, Michigan, 1972.
- [8] L. Szpyrkowicz, C. Juzzolino, S.N. Kaul, A comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and Fenton reagent, *Water Res.* 35 (9) (2001) 2129–2136.
- [9] S. Meriç, D. Kapitan, T. Olmez, Colour and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process, *Chemosphere* 54 (3) (2004) 435–441.
- [10] J.H. Churchley, Ozone for dye waste colour removal: four years experience at Leek STW, *Ozone Sci. Eng.* 20 (2) (1998) 111–120.
- [11] H.Y. Shu, C.R. Huang, Degradation of commercial azo dyes in water using ozonation and UV enhanced ozonation processes, *Chemosphere* 31 (8) (1995) 3813–3825.
- [12] I. Arslan, I.A. Balcioglu, T. Tuhkanen, D.W. Bahnemann, $H_2O_2/UV-C$ and $Fe^{2+}/H_2O_2/UV-C$ vs. $TiO_2/UV-A$ treatment for reactive dye wastewater, *J. Environ. Eng.* 126 (3) (2000) 903–910.
- [13] F. Torrades, J.G. Montaño, J.A.G. Hortal, X. Domènech, J. Peral, Decolorization and mineralization of commercial reactive dyes under solar light assisted photo-Fenton conditions, *Sol. Energy* 77 (5) (2004) 573–581.
- [14] S. Meriç, H. Selçuk, V. Belgiorno, Acute toxicity removal in textile finishing wastewater by Fenton's oxidation, ozone and coagulation–flocculation processes, *Water Res.* 39 (6) (2005) 1147–1153.
- [15] A.H. Konsowa, Decolorization of wastewater containing direct dye by ozonation in a batch bubble column reactor, *Desalination* 158 (1) (2003) 233–240.
- [16] Y.C. Hsu, J.T. Chen, H.C. Yang, J.H. Chen, Decolorization of dyes using ozone in a gas-induced reactor, *AIChE J.* 47 (1) (2001) 169–176.
- [17] O.J. Hao, H. Kim, P.C. Chiang, Decolorization of wastewater, *Crit. Rev. Environ. Sci. Technol.* 30 (4) (2000) 449–505.
- [18] EPA, Toxics Release Inventory, Public Data Release, Office of Pollution Prevention and Toxics, US Environmental Protection Agency, Washington, DC, 1995.
- [19] S.H. Lin, M.L. Chen, Treatment of textile wastewater by chemical methods for reuse, *Water Res.* 31 (4) (1997) 868–876.
- [20] S.J.S. Masten, H.R. Davies, The use of ozonation to degrade organic contaminants in wastewaters, *Environ. Sci. Technol.* 28 (4) (1994) 181–185.
- [21] D.V. Franco, J.F.C. Boodts, W.F. Jardim, L.M. Da Silva, Electrochemical ozone production as an environmentally friendly technology for water treatment, *Clean Soil Air Water* 36 (1) (2008) 34–44.
- [22] W. Chu, C-W Ma, Quantitative prediction of direct and indirect dye ozonation kinetics, *Water Res.* 34 (12) (2000) 3153–3160.
- [23] P. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment II: hybrid methods, *Adv. Environ. Res.* 8 (3–4) (2004) 553–597.
- [24] L.M. Da Silva, D.V. Franco, J.C. Forti, W.F. Jardim, J.F.C. Boodts, Characterization of a laboratory electrochemical ozonation system and its application in advanced oxidation processes, *J. Appl. Electrochem.* 36 (3) (2006) 523–530.
- [25] F. Luck, M. Djafer, N.K. Vel Leitner, B. Gombert, B. Legube, Destruction of pollutants in industrial rinse water by advanced oxidation processes, *Water Sci. Technol.* 35 (4) (1997) 287–292.
- [26] H. Lin Sheng, M. Lin Chi, Treatment of textile waste effluents by ozonation and chemical coagulation, *Water Res.* 27 (12) (1993) 1743–1748.
- [27] M. Tzitzitzi, D.V. Vayenas, G. Lyberatos, Pretreatment of textile-industry wastewaters with ozone, *Water Sci. Technol.* 29 (9) (1994) 151–156.
- [28] J. Hoigné, Mechanisms, rates and selectivities of oxidation of organic compounds initiated by ozonation in water, in: R.G. Rice, A. Netzer (Eds.), *Handbook of Ozone Technology and Applications*, Ann Arbor Science Publishers, Inc., Michigan, 1982, p. 341.
- [29] K. Scott, *Electrochemical Processes for Clean Technology*, Hartnolls, Cornwall, UK, 1995.
- [30] P.C. Foller, G.H. Kelsall, Ozone generation via the electrolysis of fluoboric acid using glass carbon anodes and air depolarized cathodes, *J. Appl. Electrochem.* 23 (4) (1993) 996–1010.
- [31] P. Foller, M.L. Goodwin, The electrochemical generation of high concentration ozone for small-scale applications, *Ozone: Sci. Eng.* 6 (2) (1984) 29–36.
- [32] H. Benbelkacem, H. Debellefontaine, Modeling of a gas–liquid reactor in batch conditions. Study of the intermediate regime when part of the reaction occurs within the film and part within the bulk, *Chem. Eng. Proc.* 42 (3) (2003) 723–732.
- [33] A. López-López, J.S. Pic, H. Debellefontaine, Ozonation of azo dye in a semi-batch reactor: a determination of the molecular and radical contributions, *Chemosphere* 66 (3) (2007) 2120–2126.

- [34] M.T. Gao, M. Hirata, H. Takanashi, T. Hano, Ozone mass transfer in a new gas–liquid contactor–Karman contactor, *Sep. Purif. Technol.* 42 (3) (2005) 145–149.
- [35] J. Wu, T. Wang, Ozonation of aqueous azo dye in a semi-batch reactor, *Water Res.* 35 (4) (2001) 1093–1099.
- [36] American Public Health Association, *Standard Methods for the Examination of Water and Wastewater*, 17th Edition, APHA, Washington, DC, 1989.
- [37] R.Y. Peng, H.J. Fan, Ozonolytic kinetic order of dye decoloration in aqueous solution, *Dyes Pigm.* 67 (2) (2005) 153–159.
- [38] L.B. Chu, X.H. Xing, A.F. Yu, Y.N. Zhou, X.L. Sun, K. Jurcik, Enhanced ozonation of simulated dyestuff wastewater by microbubbles, *Chemosphere* 68 (1) (2007) 1854–1860.
- [39] M. Koch, A. Yediler, D. Lienert, G. Insel, A. Kettrup, Ozonation of hydrolysed azo dye reactive yellow 84 (Cl), *Chemosphere* 46 (3) (2002) 109–113.
- [40] L.C. Chen, Effects of factors and interacted factors on the optimal decolorization process of methyl orange by ozone, *Water Res.* 34 (1) (2000) 974–982.
- [41] B. Langlais, D.A. Reckhow, D.R. Brink, *Ozone in Water Treatment: Application and Engineering*, CRC, Boca Raton, 1991.
- [42] J. Hoigné, *The Chemistry of Ozone in Process Technologies for Water Treatment*, Plenum Press, New York, 1988.
- [43] J.E. Whitlow, J.A. Roth, Heterogeneous ozonation kinetics of pollutants in wastewater, *Environ. Prog.* 7 (1) (1988) 52–57.