

Ozonation of textile effluents and dye solutions under continuous operation: Influence of operating parameters

Olívia Salomé G.P. Soares^a, José J.M. Órfão^a, Dionísia Portela^b, António Vieira^b,
Manuel Fernando R. Pereira^{a,*}

^a *Laboratório de Catálise e Materiais, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

^b *CITEVE-Centro Tecnológico das Indústrias Têxtil e do Vestuário de Portugal, Quinta da Maia, Rua Fernando Mesquita, No. 2785, 4760-034 Vila Nova de Famalicão, Portugal*

Received 13 February 2006; received in revised form 28 April 2006; accepted 2 May 2006
Available online 7 May 2006

Abstract

Ozonation experiments were carried out under continuous operation in a bubble column. The effect of several parameters (inlet dye concentration, applied ozone dose, pH and conductivity) in colour and TOC removal of an acid dye solution was investigated with the aim to optimize the operation conditions. The ozone consumption was measured in each experiment. Ozonation was found to be effective for decolourisation of an acid dye; however, it only has a slight effect on TOC removal. Increasing the inlet dye concentration leads to a decrease in the decolourisation efficiency and an increase in the ozone consumption. The decolourisation increases with the applied ozone dose. Colour removal efficiencies for different ozone doses were between 76 and 100%. In the pH range 5–9, the decolourisation efficiency decreases with pH only when buffered solutions were used. The presence of salt decreases the decolourisation efficiency.

Several dyes of different classes were also studied and ozonation was found to be effective for decolourisation but considerably less efficient for TOC removal. Under the conditions tested, only the disperse and sulphur dyes presented a colour removal lower than 86%.

Practical application of this process was validated by treating two industrial textile effluents collected after two different biological treatments. © 2006 Elsevier B.V. All rights reserved.

Keywords: Ozonation; Continuous operation; Decolourisation; Dyes; Textile effluent

1. Introduction

Textile industry uses and rejects high amounts of water, its wastewaters being the main way by which dyes are discharged into the environment. Textile effluents have high concentrations of organic and inorganic compounds and strong colour, caused by residual dyes that were not fixed to the fibers in the dyeing process, and present as main characteristics high variations of flow and composition, large amount of non-biodegradable compounds, presence of toxic substances, high temperature and high pH value [1].

Colour is one of the main contaminants of textile wastewaters. In addition, there are many different types of dyes and differ-

ent dyeing manufacture processes, making difficult that only a single treatment process answers satisfactorily to the treatment requirements in all situations.

The conventional treatment usually consists of the removal of suspended solids of higher dimensions, oils and fats (primary treatment), followed by a biological treatment (secondary treatment) to remove the dissolved or colloidal organic matter, the conventional activated sludge being the most commonly used. The biological treatment significantly decreases the organic matter content, but the resultant effluent is still quite coloured. Depending on the destination of the treated effluent, this process can be completed with a tertiary treatment to remove colour, detergents and/or salinity. This refining treatment may allow the reutilization of the treated water [1].

In industry, the technologies that have already been applied in decolourisation of effluents are [2]: oxidation with ozone; oxidation with Fenton's reagent; UV oxidation; membranes filtration

* Corresponding author. Tel.: +351 225 081 468; fax: +351 225 081 449.
E-mail address: fpereira@fe.up.pt (M.F.R. Pereira).

processes; activated carbon adsorption; ion exchange resins; coagulation/flocculation or coagulation/flotation (fluctuation); and electrochemical methods.

Ozonation is one of the most attractive alternatives for solving the problem of colour in textile effluents. Ozone is an extremely strong oxidant ($E^\circ = 2.07 \text{ V}$) and reacts rapidly with most of organic compounds [2]. It is now widely accepted that ozone reacts in aqueous solution with various organic and inorganic compounds, either by a direct reaction of molecular ozone or through a radical type reaction involving the hydroxyl radical produced by the ozone decomposition in water [3,4]. Ozone and hydroxyl radicals generated in aqueous solution are able to open the aromatic rings [5]. Ozone molecule is selective and attacks preferentially the unsaturated bonds of chromophores. For this reason, colour removal by action of ozone is fast, but the mineralization is low. Typically, ozonation rarely originates complete mineralization to carbon dioxide and water, but leads to partial oxidation sub-products such as organic acids, aldehydes and ketones. The solution pH alters the chemical composition of ozone: for example, hydroxyl radicals are formed from ozone decomposition at high pH, while the molecular ozone remains as the main oxidant at low pH [5].

Ozonation is a promising process for colour removal by the following reasons [5]: no chemical sludge is left in the treated effluent; has the potential to accomplish both colour removal and organic reduction in one step; little space is required and it is easily installed on site; less harmful than the other oxidative processes, since no stock hydrogen peroxide or other chemicals are required on site; it is easily operated; and all residual ozone can be easily decomposed to oxygen.

In the recent literature, the ozonation process has been suggested as a potential alternative for decolourisation [6–12] and improvement of biological degradation of textile effluents [13,14]. High values of decolourisation but low mineralization have been observed. Several studies have been carried out with the aim to confirm the effectiveness of ozone in decolourisation of effluents and to optimize the experimental ozonation conditions, such as pH, concentration and applied ozone dose

[13,15–18]. However, most of these reports were carried out in batch or semi-batch conditions. The aim of the present work is to study the ozonation of different dye solutions in a bubble column under continuous operation. Different parameters, namely: inlet dye concentration, ozone concentration, liquid and gas flow rate, pH, conductivity and influence of dyes chemical structure, were studied in order to optimize the working conditions. The effects of those operating parameters on decolourisation, TOC removal and ozone consumption were analyzed. In order to evaluate the practical application of this process, the ozonation of an industrial textile effluent after two different biological treatments was also carried out.

2. Experimental

2.1. Experimental set-up

A scheme of the experimental set-up is shown in Fig. 1. All the experiments were carried out in a continuous mode in an acrylic cylindrical column, perfectly isolated, with 2.5 cm internal diameter and 30 cm height. The height of the liquid inside the column was kept at 15 cm. The oxygen/ozone mixture was continuously introduced into the column through a porous plate placed at the bottom. The liquid flow was continuously introduced using a peristaltic pump in a lateral entrance at the bottom of the column.

Ozone was produced from pure oxygen, in a BMT 802X commercial ozone generator. The oxygen flow rate was controlled using a mass flow controller. Ozone in the gas phase leaving the generator was conducted by a system of three-way valves to one of the following options: bubble column; gas washing bottle, which is a by-pass to the column; BMT 964 commercial ozone analyzer, which allows the measurement of the ozone generated.

A needle valve was placed before the column to control the ozone flow rate, the flow in excess being removed in a gas washing bottle. After the column, there was a three-way valve which allows the gas flow to go to the ozone analyzer (to measure ozone that was not consumed in the column) or to a gas washing bottle.

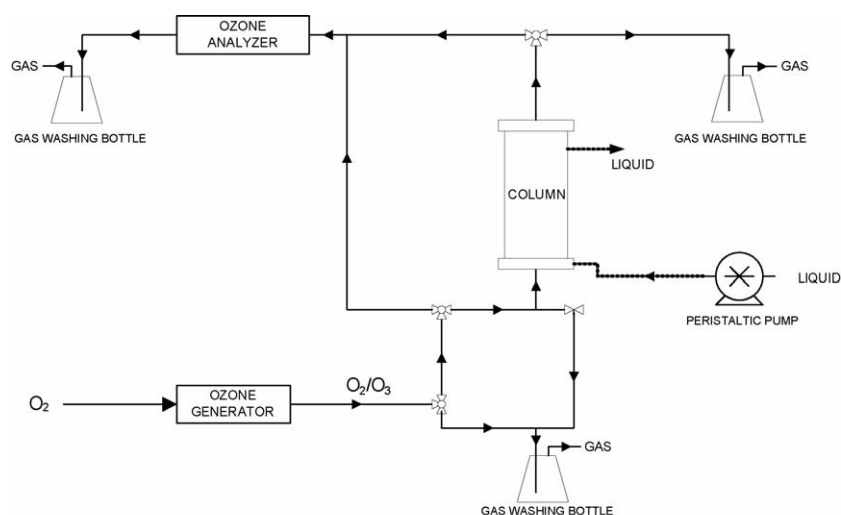


Fig. 1. Scheme of the experimental set-up.

Ozone in the gas phase leaving the ozone analyzer was removed in a series of gas washing bottles filled with a 2% potassium iodide (KI) solution.

2.2. Experimental conditions

Ozonation of an acid dye was carried out in co-current by varying gas flow rate, liquid flow rate, inlet dye concentration, ozone concentration, solution pH and conductivity. Dyes from other classes were also studied. All experiments were performed at room temperature, varying only one parameter in each situation. Evolution of each experiment was followed until the steady state was reached. All the experiments started with the column filled with distilled water. The following standard operation conditions were used: $Q_L = 10 \text{ cm}^3/\text{min}$; $\tau = 7.36 \text{ min}$; $C_{\text{dye},i} = 50 \text{ mg/L}$; $Q_G = 10 \text{ cm}^3/\text{min}$; $C_{\text{O}_3,i} = 40 \text{ g}/(\text{N m}^3)$; pH 7; $h = 15 \text{ cm}$. The effect of inlet dye concentration was studied varying dye concentration from 50 to 100 mg/L. The effect of applied ozone dose was investigated varying liquid flow rate from 5 to 20 cm^3/min , gas flow rate from 5 to 100 cm^3/min and ozone concentration from 30 to 60 $\text{g}/(\text{N m}^3)$. The study of the effect of initial pH was carried out by adjusting the pH solution from 3 to 11. The effect of buffered solutions with a phosphate buffer was also investigated. The effect of conductivity was studied by adding sodium chloride from 0 to 5 g/L.

In all experiments, the dye concentration, TOC, ozone concentration at the top of the column and pH were measured during ozonation time.

Ozonation of textile effluents was carried out in co-current changing the liquid flow rate, ozone concentration and solution pH. The UV–vis spectrum was recorded for all the collected samples. Decolourisation of the effluent was evaluated at three different wavelengths: 436, 525 and 620 nm. In addition, aromatic organic matter (roughly estimated by measuring the absorbance at 254 nm) and TOC removal were also studied.

A hydrodynamic study of the bubble column reactor was previously performed. The residence time distribution curves obtained under these operation conditions showed that the bubble column can be described as approximately one continuous-stirred tank reactor and the steady state is reached after a period of 3–4 residence times.

2.3. Materials

Nine dyes from different classes were selected for this study (Table 1) [19]. Taking into consideration that in textile effluents reactive dyes are in the hydrolysed state, a hydrolysed procedure was carried out in the corresponding experiments, as described elsewhere [20]. Dye solutions were prepared by dissolving the dye in distilled water and the initial pH of all solutions was adjusted to 7, with exception of the solutions used in the experiments where the effect of pH was evaluated. The pH was adjusted by adding HCl or NaOH 0.1 M solutions. The effect of pH was also evaluated using a phosphate buffer solution. To study the effect of conductivity, sodium chloride was added. For each dye solution the UV–vis spectrum was previously obtained and the maximum wavelength determined (Table 1).

2.4. Analytical methods

Absorbances were determined in a Jasco V-560 UV/Vis spectrophotometer. TOC was measured in a Shimadzu TOC 5000A analyzer. Ozone concentration in the gas phase was determined using a BMT 964 ozone analyzer.

3. Results and discussion

3.1. Chemical oxidation of an acid dye

Colour and TOC removal and ozone consumption are the most important parameters to evaluate the performance of the continuous decolourisation of textile effluents. The colour and TOC removal determine the possibility of effluent reutilization and the ozone consumption determines the economical advantage. These parameters depend on: contact time, applied ozone dose, inlet dye concentration, pH and conductivity. In order to study their effect, different experiments were carried out.

Applied ozone dose was calculated from Eq. (1):

$$\text{Applied O}_3 \text{ (g O}_3/\text{m}^3 \text{ liquid)} = \frac{C_{\text{O}_3,i} \times Q_G}{Q_L} \quad (1)$$

Colour and TOC removal and ozone consumption, at steady state, were determined by the following equations:

$$R_{\text{colour}} (\%) = \frac{C_{\text{dye},i} - C_{\text{dye},o}}{C_{\text{dye},i}} \times 100 \quad (2)$$

$$R_{\text{TOC}} (\%) = \frac{\text{TOC}_i - \text{TOC}_o}{\text{TOC}_i} \times 100 \quad (3)$$

$$\text{O}_3 \text{ consumed (g O}_3/\text{m}^3 \text{ liquid)} = (C_{\text{O}_3,i} - C_{\text{O}_3,o}) \times \frac{Q_G}{Q_L} \quad (4)$$

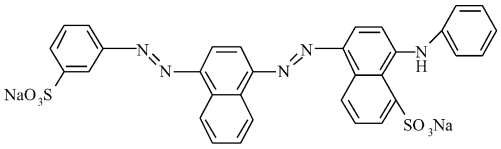
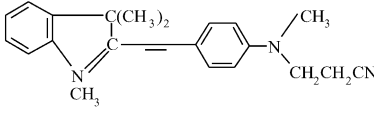
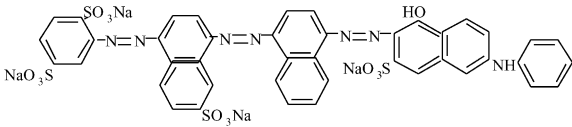
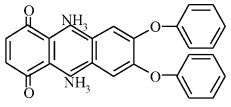
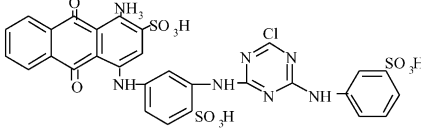
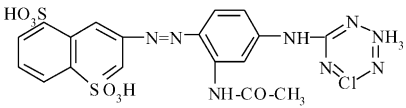
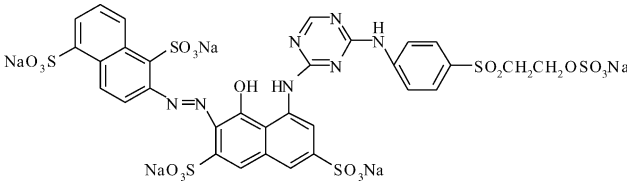
where C_{dye} (mg/L) is the dye concentration, TOC (mg/L) the total organic carbon, C_{O_3} (g/m^3) the ozone concentration and ‘i’ and ‘o’ correspond to inlet and outlet, respectively. Q_G (cm^3/min) is the gas flow rate and Q_L (cm^3/min) is the liquid flow rate.

3.1.1. Effect of inlet dye concentration

The inlet dye concentration plays an important role in determining the economical use of ozone for decolourisation. Several studies [8,13] have demonstrated that the time required for decolourisation of the dye solution is dependent on inlet dye concentration as well as ozone consumption.

From Fig. 2 it can be seen that increasing the inlet dye concentration, colour and TOC removal at steady state decrease and ozone consumption has a tendency to increase. The experimental results show that, with the increase of inlet dye concentration from 50 to 100 mg/L, the colour removal decreases from 93 to 76%, the TOC removal decreases from 10 to 4% and the ozone consumption increases from 21 to 27 $\text{g O}_3/\text{m}^3$. These results can be explained by the increase of the dye oxidation by-products when the concentration of dye increases, which enhances ozone consumption. Ozone was found to be effective to treat highly

Table 1
Selected dyes and main characteristics [19]

Class	Commercial and generic name	Molecular structure	Chemical class	λ_{\max} (nm)
Acid	Erionyl Navy R, C.I. Acid Blue 113		Diazo	566
Basic	Astrazon Brilliant Red 4G, C.I. Basic Red 14		Cianina	513
Direct	Solophenyl Blue 4GL, C.I. Direct Blue 78		Trisazo	604
Disperse	C.I. Disperse Violet 26		Anthraquinone	564
Reactive	Cibacron Blue BR, C.I. Reactive Blue 5		Anthraquinone	597
Reactive	Cibacron Yellow R, C.I. Reactive Yellow 3		Monoazo	411
Reactive	Rifaxil Red 3BN, C.I. Reactive Red 241		Monoazo	540
Sulphur	Sulphur Black B, C.I. Sulphur Black 1	$C_{24}H_{16}N_6O_8S_7$ or $C_{24}H_{16}N_6O_8S_8$	Sulphur	652

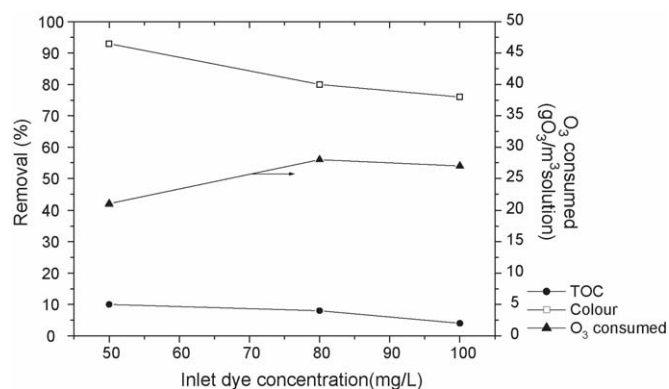


Fig. 2. Effect of inlet dye concentration on steady state colour and TOC removal and ozone consumption in the ozonation of an acid dye ($Q_L = 10 \text{ cm}^3/\text{min}$; $\tau = 7.36 \text{ min}$; $Q_G = 10 \text{ cm}^3/\text{min}$; $C_{O_3,i} = 40 \text{ g}/(\text{N m}^3)$; pH 7).

concentrated dye solutions, but to achieve higher decolourisation efficiencies higher ozone doses would be required.

3.1.2. Effect of applied ozone dose

Determination of the required ozone dose in the treatment of effluents is essential for the economical evaluation of the process. It is evident that the treatment cost increases with the applied ozone dose, which can be adjusted by three processes: ozone gas concentration, gas flow rate and liquid flow rate. To evaluate the effect of this parameter, the effects of liquid and gas flow rate and inlet ozone concentration were investigated, and the results are compiled in Fig. 3.

3.1.2.1. Effect of liquid flow rate. When the liquid flow rate decreases, contact time and applied ozone dose per volume of solution increase. Decolourisation efficiencies of 100, 93 and 76% and TOC removal efficiencies of 27, 10 and 3% were observed in steady state, for liquid flow rates of 5, 10 and

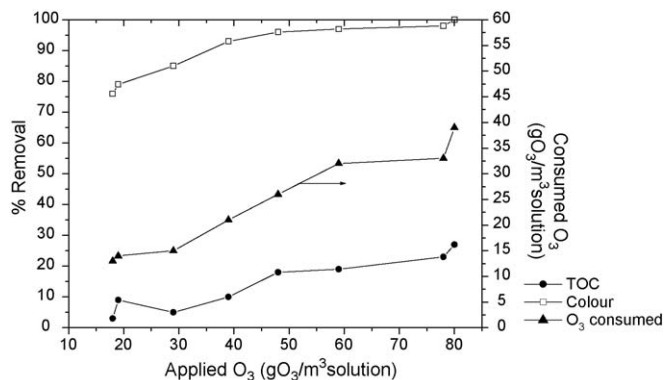


Fig. 3. Effect of applied ozone dose on steady state colour and TOC removal and ozone consumption in the ozonation of an acid dye ($C_{\text{dye},i} = 50 \text{ mg/L}$; pH 7).

$20 \text{ cm}^3/\text{min}$, respectively. It was observed that ozone consumption per volume of dye solution is higher for the lower liquid flow rate.

3.1.2.2. Effect of inlet ozone concentration. It was observed that increasing the inlet ozone concentration, both the decolourisation and TOC removal of solution in steady state increase, because the applied ozone dose per volume of dye solution also increases. Decolourisation efficiencies vary from 85 to 97% and TOC removal efficiencies from 5 to 19% for the ozone concentrations studied (30–60 $\text{g}/(\text{N m}^3)$). It was observed that the ozone consumption per volume of dye solution increases with the applied ozone dose; however, ozone utilization ratio is similar for all the concentrations studied (0.45–0.48), indicating that ozone is always in excess.

3.1.2.3. Effect of gas flow rate. The higher values of colour and TOC removal in steady state were observed for the highest gas flow rate studied. Although the decolourisation is between 79 and 98%, mineralization is relatively low, varying from 9 to 23%. It was also observed that ozone consumption per volume of dye solution is higher for the highest flow.

It was observed in Fig. 3 that mineralization by ozonation is very low compared to colour removal, which is in agreement with previous publications [6,8]. This may be explained by the fast destruction of the chromophore groups, responsible for the colour, and by the fact that the resulting sub-products are very difficult to mineralize. Removal efficiency increases with the increasing of the applied ozone dose; however, it was observed that increasing the applied dose above $50 \text{ g O}_3/\text{m}^3$ solution (that corresponds to an ozone consumption of about $25 \text{ g O}_3/\text{m}^3$ solution) only a marginal effect in the removal efficiency is obtained. It was also observed that ozone consumption per volume of solution increases with the increase of the applied ozone dose. In the experimental conditions used in this work, the efficiency of ozone utilization was not very high, the fraction of ozone unused ($C_{\text{O}_3,o}/C_{\text{O}_3,i}$) being close to 0.5 for the majority of the experiments. This fraction slightly increases when the ozone dose increases. The results clearly show that the highest efficiency in terms of ozone consumption is obtained for the lowest

applied ozone dose. Similar results can be found in literature [13,21].

3.1.3. Effect of solution pH

Several researchers observed that ozone decomposition is directly affected by the solution pH [5,22]. Hydroxyl radicals are formed from ozone decomposition at high pH values, while the molecular ozone remains as the main oxidant at low pH values. The extent of decolourisation is favoured by the direct ozone attack, at low pH values, since molecular ozone is selective for the destruction of chromophore groups. The hydroxyl radicals have a higher oxidizing potential and are less selective than molecular ozone, leading to a decolourisation decrease and a mineralization increase for high pH values [5,8,22].

To evaluate the effect of solution pH, different experiments were carried out with the same inlet dye concentration at various pH values. It was observed that the pH value decreases with the ozonation time until a steady state was reached, which was indicative of the generation of by-products of acid nature as a result of the oxidation by ozone. To guarantee that solution pH did not change with time, additional experiments with buffer solutions were performed.

Fig. 4 shows the results of colour and TOC removal and ozone consumption during the ozonation of an acid dye solution with the same inlet dye concentration at different pH values. It can be observed that pH has an effect on decolourisation efficiency. When buffered solutions were used in the preparation of dye solution the decolourisation is lower than the observed in unbuffered solutions. Unbuffered solutions with initial pH between 5 and 9 did not show any significant difference in the decolourisation efficiency. This is explained by the fact that in buffered solutions the final pH is close to the initial pH and in unbuffered solutions with initial pH of 5, 7 and 9 the final pH is practically the same for all experiments (4–5). Under these conditions, the direct ozone molecular reactions (fast in acid medium) prevail, leading to higher rates of decolourisation. Decolourisation efficiencies were 92, 93 and 93% in unbuffered solutions and 90, 88 and 82% in buffered solutions with initial pH of 5, 7 and 9, respectively. It was also observed that TOC removal increases with pH and it was slightly higher for buffered solutions when compared to unbuffered solutions. The

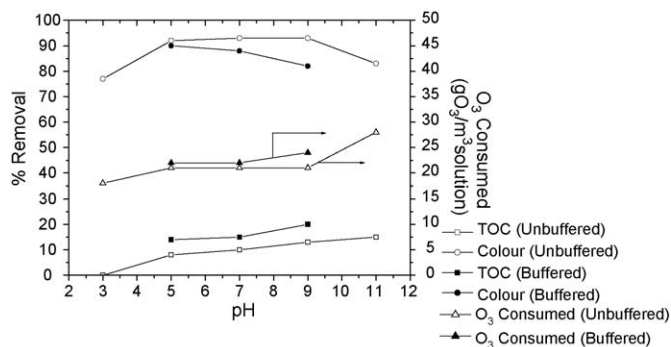


Fig. 4. Effect of pH on steady state colour and TOC removal and ozone consumption in the ozonation of an acid dye ($Q_L = 10 \text{ cm}^3/\text{min}$; $\tau = 7.36 \text{ min}$; $C_{\text{dye},i} = 50 \text{ mg/L}$; $Q_G = 10 \text{ cm}^3/\text{min}$; $C_{\text{O}_3,i} = 40 \text{ g}/(\text{N m}^3)$).

differences in removal efficiencies at high pH values can be attributed to higher fractions of ozone that are decomposed to generate hydroxyl radicals. Hydroxyl radicals have higher oxidation potential than ozone molecule and attack dye molecules and intermediates more vigorously than ozone molecule, resulting in a faster mineralization of the solution.

The lowest decolourisation efficiencies were observed for the initial pH values of 3 and 11 (77 and 83%, respectively). This fact may be associated with the ozone consumption, which has the lowest value for pH 3. For pH 11, the mineralization observed is the highest and the decolourisation decreases as a result of ozone decomposition into hydroxyl radicals, which are less selective but have a higher oxidation potential than ozone. At pH 3 there is no TOC removal, which confirms that, at this pH, hydroxyl radicals are practically not formed.

The ozone consumption was practically the same in all experiments. However, buffered solution with pH 9 and unbuffered solution with pH 11 presents the highest ozone consumption, probably because the ozone decomposition is higher in basic conditions.

Several researchers [5,7,8,13,23] observed that decolourisation is dependent on the solutions pH; however, others have shown that the decolourisation of dye solutions was independent of pH in the range 4–9. The reason for these contradictory results may be explained by the fact that some researchers used buffer solutions to control the pH and others only adjusted the initial pH with a solution of acid or alkali. In the present work, it was shown that pH has an effect on the decolourisation efficiency in the ozonation of dye solutions if the solution is buffered to maintain the initial pH.

3.1.4. Effect of conductivity of dye solution

Textile effluents have high concentrations of organic and inorganic compounds which could confer high values of conductivity. The study of the effect of conductivity was carried out among the typical values of these effluents. To evaluate the effect of the conductivity, different dye solutions with conductivity values between 0.0493 mS/cm (original sample) and 10.4 mS/cm were prepared by addition of different amounts of sodium chloride, at neutral pH. During the experiments, it was observed that the value of conductivity did not change with time.

It can be observed in Fig. 5 that the presence of salt in dye solution has a negative effect in decolourisation, but this effect is not proportional to the salt concentration. Decolourisation efficiencies decreased from 93 to 84%, the lowest result being obtained for the higher concentration of salt tested. However, the presence of salt has a slightly positive effect in TOC removal, which is also not proportional to the increase of salt concentration. This may be explained by the presence of salt which may improve ozone decomposition into hydroxyl radicals [24], decreasing the decolourisation efficiencies and increasing the mineralization. Muthukumar and Selvakumar [24] reported that the presence of salt in solution affects the time necessary for complete decolourisation. The higher the salt content, the longer the time required for complete decolourisation. This result is in agreement with our conclusions.

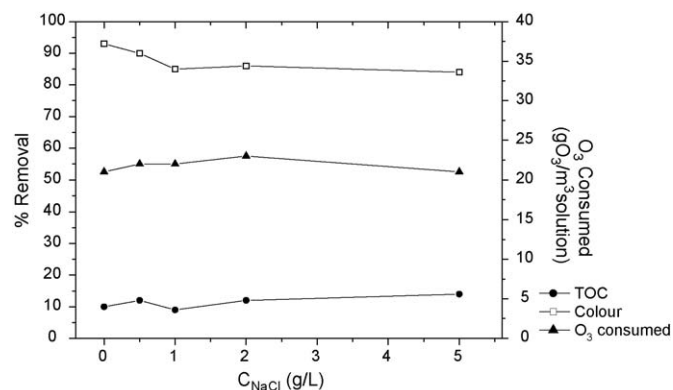


Fig. 5. Effect of conductivity on steady state colour and TOC removal and ozone consumption in the ozonation of an acid dye ($Q_L = 10 \text{ cm}^3/\text{min}$; $\tau = 7.36 \text{ min}$; $C_{dye,i} = 50 \text{ mg/L}$; $Q_G = 10 \text{ cm}^3/\text{min}$; $C_{O_3,i} = 40 \text{ g}/(\text{N m}^3)$; pH 7).

3.2. Chemical oxidation of different dyes

In this work, dyes with different chemical structures were used, belonging to the most representative classes in terms of application in the Portuguese textile industry. All selected dyes are currently used in dyeing processes of textile fibers.

Fig. 6 summarizes the results obtained. It can be observed that ozonation is effective for decolourisation of almost all dyes, with colour removal efficiencies higher than 86%, with the exceptions of Disperse Violet 26 and Sulphur Black 1 dyes that present decolourisation efficiencies of 32 and 50%, respectively.

Disperse Violet 26 presents very low decolourisation efficiency. For this reason, new experiments were carried out increasing the applied ozone dose. It was observed that increasing the ozone concentration to 80 and 110 g/(N m³) the decolourisation efficiency increased to 50 and 71%, respectively, but TOC removal remained in 8% in all cases. These results clearly show that it was necessary to apply a higher ozone dose to increase the decolourisation efficiency. For all dyes studied, mineralization is very low when compared to decolourisation. Reactive and direct dyes present the higher mineralization values.

Comparing the results obtained for Reactive Red 241, it is evident that the hydrolysed dye exhibits a higher mineralization and a lower decolourisation. This fact may be associated with the presence of salt and with the solution pH. As already mentioned, the presence of salt has a positive effect in TOC removal and a negative effect in colour removal. On the other hand, the final pH after ozonation when dye is hydrolysed is close to 7 and is 3.9 when it is not hydrolysed, and, as previously explained, the increase of pH increases the mineralization and decreases the colour removal.

Comparing the reactive dyes, it was observed that Reactive Blue 5 presents the highest decolourisation (97%) and Reactive Yellow 3 the lowest (86%). Reactive Red 241 presents the highest mineralization.

3.3. Chemical oxidation of industrial textile effluents

In order to evaluate the practical application of this process, the ozonation of an industrial textile effluent was studied, as a

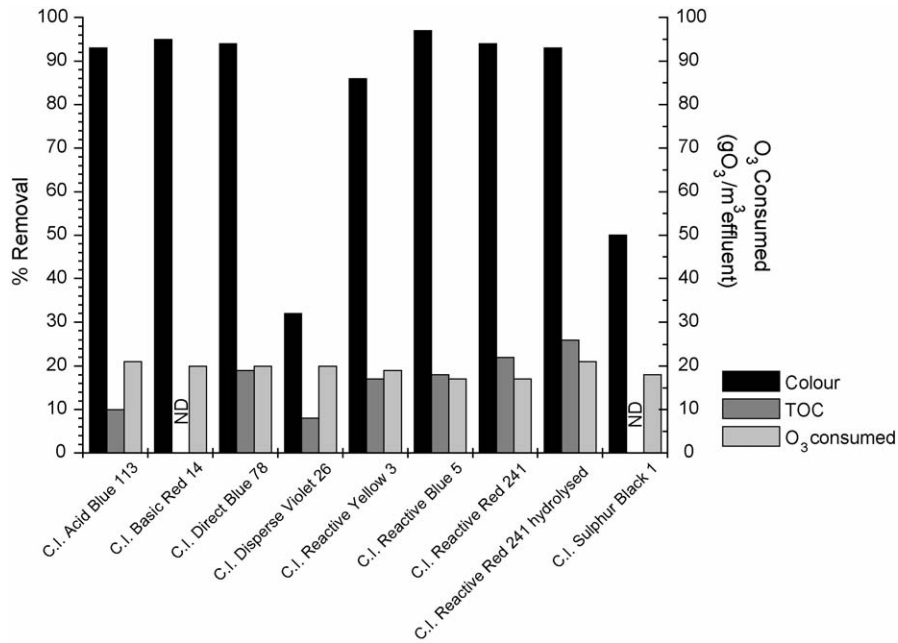


Fig. 6. Steady state colour and TOC removal and ozone consumption in the oxidation with ozone for the dyes studied ($Q_L = 10 \text{ cm}^3/\text{min}$; $\tau = 7.36 \text{ min}$; $C_{\text{dye},i} = 50 \text{ mg/L}$; $Q_G = 10 \text{ cm}^3/\text{min}$; $C_{O_3,i} = 40 \text{ g}/(\text{N m}^3)$; pH 7) (ND—not determined).

tertiary treatment. The effluent to be treated by ozonation was previously submitted to two distinct types of biological treatments in order to remove most of the organic matter: TE1—raw textile effluent treated in an airlift pilot plant system; TE2—a blend of 50% of a raw textile effluent with 50% of a raw textile effluent previously treated in an anaerobic pilot digester, treated together in an airlift pilot plant system. The biological treatments substantially decreased the organic matter content, but the resultant effluent was still fairly coloured.

The parameters of the samples collected after the biological treatments are shown in Table 2.

3.3.1. Effect of applied ozone dose

Fig. 7 shows the effect of the applied ozone dose on the decolourisation efficiency of effluent TE1. Increasing the

Table 2

Parameters of the industrial textile effluents after the biological treatments

	TE1	TE2
pH	7.6	8.4
Conductivity (mS/cm)	2.8	3.5
COD (mg/L)	258	162
TOC (mg/L)	88	56
$\alpha(254) \text{ (m}^{-1}\text{)}$	1835	1505
$\alpha(436) \text{ (m}^{-1}\text{)}$	235	142
$\alpha(525) \text{ (m}^{-1}\text{)}$	183	115
$\alpha(620) \text{ (m}^{-1}\text{)}$	129	65

COD is the chemical oxygen demand; $\alpha(\lambda)$ is the spectral absorption coefficient (absorption per unit path length) defined by ISO7887:1994.

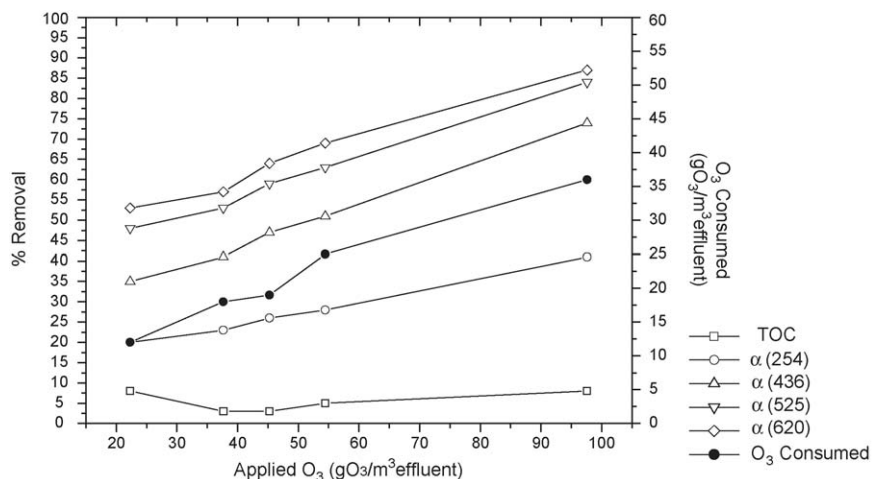


Fig. 7. Effect of applied ozone dose on steady state and TOC removal and ozone consumption in the ozonation of the effluent TE1 ($Q_G = 10 \text{ cm}^3/\text{min}$; pH 7.6).

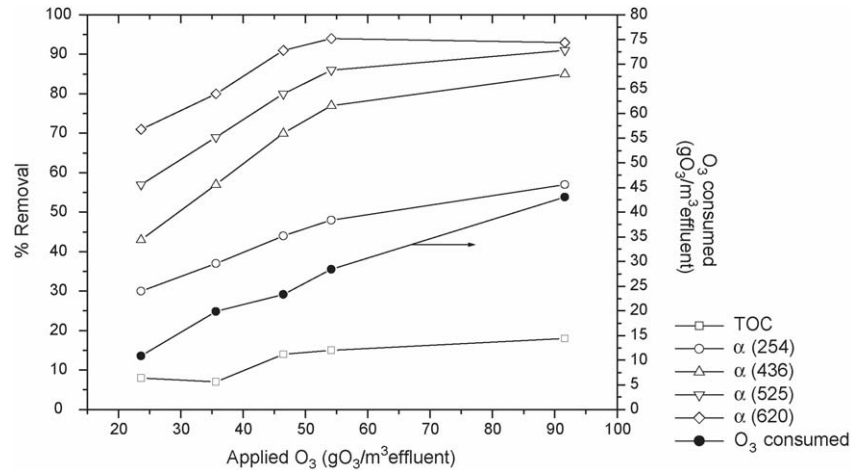


Fig. 8. Effect of applied ozone dose on steady state colour and TOC removal and ozone consumption in the ozonation of the effluent TE2 ($Q_G = 10 \text{ cm}^3/\text{min}$; pH 8.4).

applied ozone dose, the colour removal increases continuously but TOC removal is low and practically does not change. On the other hand, the removal of aromatic organic matter, measured by the absorbance at 254 nm, increased and is higher than TOC removal. This result confirms that ozone provokes the decrease of the aromaticity, leading to side products harder to mineralize. Ozonation can be effective to treat this type of effluent but it would be necessary to apply a higher ozone dose or increase the contact time to improve the decolourisation efficiency. However, ozonation has only a slight effect on TOC removal for this type of effluent.

Fig. 8 shows the effect of applied ozone dose on decolourisation efficiency of effluent TE2. It can be observed that ozonation is more effective to treat this effluent than TE1. As was already observed for TE1, the mineralization is low but, in this case, the TOC removal slightly increases with the applied ozone and the removal of aromatic organic matter, measured by the absorbance at 254 nm, is higher than TOC removal. Colour removal efficiency and ozone consumption increase with the increase of applied ozone dose. However, increasing the applied amount

above $55 \text{ g O}_3/\text{m}^3$ effluent, which corresponds to a consumption of about $25 \text{ g O}_3/\text{m}^3$ effluent, does not have a very significant improvement in the colour and TOC removal efficiency. Therefore, the increase of applied ozone dose above this value is not justified because it will greatly increase the operation costs without the corresponding increase in the removal efficiency. A similar situation was observed for the acid dye solution (cf. Fig. 3).

3.3.2. Effect of effluent pH

The influence of pH was evaluated by adjusting the solution pH to the selected value by adding an acid or an alkaline solution. It was observed that pH practically does not change during these experiments. This may be associated with the industrial dyeing process, where some of the used chemical compounds have a buffer effect, which is confirmed by the high alkalinity values of these effluents.

Figs. 9 and 10 show the results of colour and TOC removal and ozone consumption, at different pH values, during the ozonation of the effluents TE1 and TE2, respectively. From these

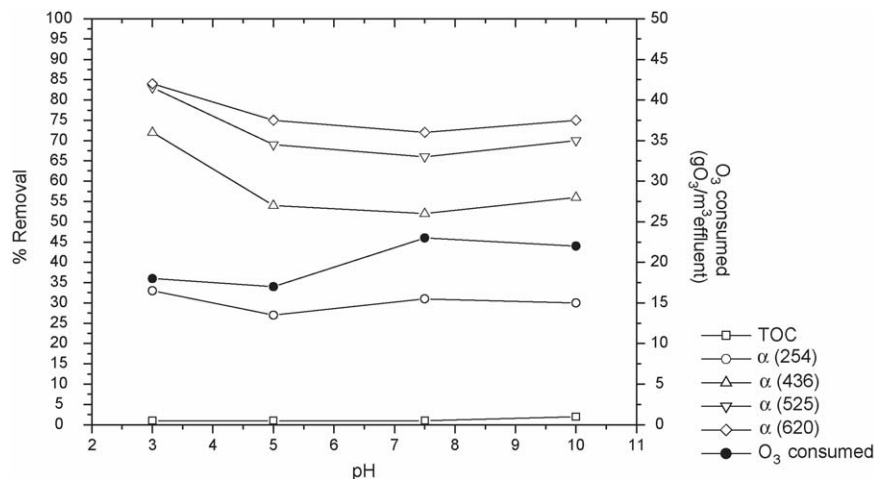


Fig. 9. Effect of pH solution on steady state colour and TOC removal and ozone consumption in the ozonation of the effluent TE1 ($Q_L = 10 \text{ cm}^3/\text{min}$; $\tau = 7.36 \text{ min}$; $Q_G = 10 \text{ cm}^3/\text{min}$; $C_{O_3,i} = 50 \text{ g}/(\text{N m}^3)$).

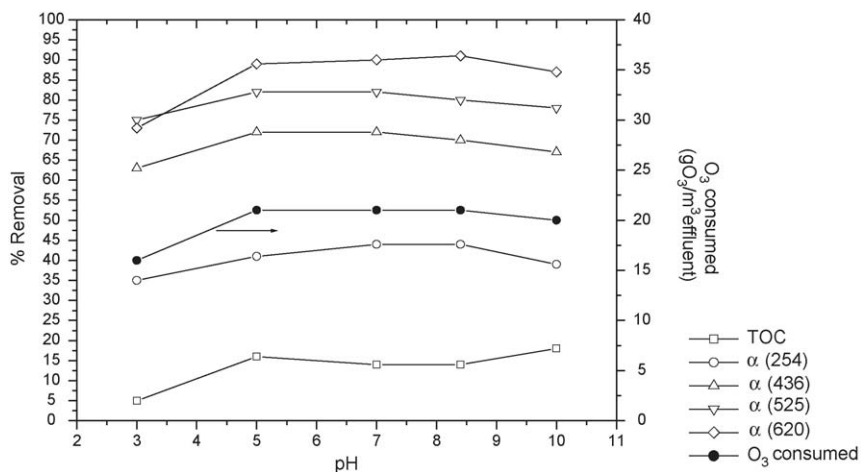


Fig. 10. Effect of pH solution on steady state colour and TOC removal and ozone consumption in the ozonation of the effluent TE2 ($Q_L = 10 \text{ cm}^3/\text{min}$; $\tau = 7.36 \text{ min}$; $Q_G = 10 \text{ cm}^3/\text{min}$; $C_{O_3,i} = 50 \text{ g}/(\text{N m}^3)$).

figures it can be observed that pH has an effect on decolourisation efficiency.

For effluent TE1, the higher decolourisation efficiency is obtained at pH 3 and there are no significant differences among the other pH values, although the ozone consumption slightly increases with the increase of pH. TOC removal is marginal for all the pH values studied.

On the contrary, for effluent TE2, the lowest removal efficiency occurs at pH 3 and, as in the case of the effluent TE1, there is no significant difference among the other pH values. This fact may be due to the ozone consumption, since pH 3 has the lowest value and for the other pH values it practically does not change. TOC removal increases with pH.

The results for effluent TE2 are similar to those obtained when the ozonation was applied to the acid dye solution. The difference observed between the two industrial effluents may be explained by the high initial values of organic matter of effluent TE1 and by the positive effect of the previous anaerobic treatment of part of the TE2 effluent.

4. Conclusions

The continuous ozonation of coloured effluents in a bubble column was investigated. According to the experimental results, the following conclusions can be drawn:

1. Ozonation is highly efficient in the decolourisation of the solutions, but considerably less efficient in terms of TOC removal.
2. For the acid dye solution selected and for all the operation conditions tested, decolourisation efficiency increases with the increase of the applied ozone dose. For typical dyes concentration, a consumption of about $25 \text{ g O}_3/\text{m}^3$ effluent was shown to be the optimal value, if the balance between colour removal and operation costs is taken into consideration.
3. The increase of inlet dye concentration implies an increase of the applied ozone dose or contact time in order to maintain high decolourisation efficiencies.

4. pH has an effect on decolourisation efficiency and its evidence depends on whether the solution is buffered or not. The pH of the treated unbuffered solutions usually decreases indicating the generation of weak organic acids during ozonation. Buffered solutions have higher TOC removal but lower decolourisation. Colour removal is favoured at low pH and TOC removal increases at high pH values.
5. The presence of salts in the acid dye solution decreases the decolourisation efficiency but slightly increases TOC removal.
6. Ozonation was found to be effective for the decolourisation of almost all types of dyes studied, with a colour removal higher than 86%. The exceptions were the disperse and sulphur dyes corresponding to values lower than 50%.
7. The conclusions obtained for the acid dye solution were confirmed when ozonation was used as tertiary treatment of textile effluents previously submitted to biological treatments. High colour removal but low TOC efficiencies were obtained. In order to overcome this limitation, catalytic ozonation in the presence of activated carbon is being tested in the same reactor, with promising preliminary results. This will be the subject of a future communication.

Acknowledgements

This work was carried out with the support of Fundação para a Ciência e a Tecnologia (FCT) under programme POCTI/FEDER (POCTI/1181) and Agência de Inovação (ADI) under programme POCTI/FEDER (project ANOXITRATA).

References

- [1] P. Cooper, Colour in Dyehouse Effluent, Society of Dyers and Colourists, Bradford, 1995.
- [2] H.M. Freeman (Ed.), Standard Handbook of Hazardous Waste Treatment and Disposal, McGraw-Hill, 1989.
- [3] R. Y. Peng, H.J. Fan, Ozonolytic kinetic order of dye decoloration in aqueous solution, Dyes Pigments 67 (2005) 153–159.
- [4] N.K.V.L.B. Legube, Catalytic ozonation: a promising advanced oxidation technology for water treatment, Catal. Today 53 (1999) 61–72.

- [5] W. Chu, C.W. Ma, Quantitative prediction of direct and indirect dye ozonation kinetics, *Water Res.* 34 (2000) 3153–3160.
- [6] A. Baban, A. Yediler, D. Lienert, N. Kemerdere, A. Kettrup, Ozonation of high strength segregated effluents from a woollen textile dyeing and finishing plant, *Dyes Pigments* 58 (2003) 93–98.
- [7] M.M. Hassan, C.J. Hawkyard, Ozonation of aqueous dyes and dyehouse effluent in a bubble-column reactor, *J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng.* 37 (2002) 1563–1579.
- [8] 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 (2001) 169–176.
- [9] A.H. Konsowa, Decolorization of wastewater containing direct dye by ozonation in a batch bubble column reactor, *Desalination* 158 (2003) 233–240.
- [10] S. Ledakowicz, M. Solecka, R. Zylla, Biodegradation, decolourisation and detoxification of textile wastewater enhanced by advanced oxidation processes, *J. Biotechnol.* 89 (2001) 175–184.
- [11] M. Muthukumar, D. Sargunamani, M. Senthilkumar, N. Selvakumar, Studies on decolouration, toxicity and the possibility for recycling of acid dye effluents using ozone treatment, *Dyes Pigments* 64 (2005) 39–44.
- [12] J.N. Wu, T.W. Wang, Effects of some water-quality and operating parameters on the decolorization of reactive dye solutions by ozone, *J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng.* 36 (2001) 1335–1347.
- [13] M.F. Sevimli, H.Z. Sarikaya, Ozone treatment of textile effluents and dyes: effect of applied ozone dose, pH and dye concentration, *J. Chem. Technol. Biotechnol.* 77 (2002) 842–850.
- [14] F.F. Zhang, A. Yediler, X.M. Liang, A. Kettrup, Effects of dye additives on the ozonation process and oxidation by-products: a comparative study using hydrolyzed CI Reactive Red 120, *Dyes Pigments* 60 (2004) 1–7.
- [15] C.D. Adams, S. Gorg, Effect of pH and gas-phase ozone concentration on the decolorization of common textile dyes, *J. Environ. Eng.-ASCE* 128 (2002) 293–298.
- [16] Y.C. Hsu, Y.F. Chen, J.H. Chen, Decolorization of dye RB-19 solution in a continuous ozone process, *J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng.* 39 (2004) 127–144.
- [17] M. Muthukumar, D. Sargunamani, N. Selvakumar, J.V. Rao, Optimisation of ozone treatment for colour and COD removal of acid dye effluent using central composite design experiment, *Dyes Pigments* 63 (2004) 127–134.
- [18] M.F. Sevimli, H.Z. Sarikaya, Effect of some operational parameters on the decolorization of textile effluents and dye solutions by ozonation, *Environ. Technol.* 26 (2005) 135–143.
- [19] *Colour Index*, vol. 1–9, third revision ed., Society of Dyers and Colourists, Bradford, 1998.
- [20] M.F.P. Pereira, S.F. Soares, J.J.M. Órfão, J.L. Figueiredo, Adsorption of dyes on activated carbons: influence of surface chemical groups, *Carbon* 41 (2003) 811–821.
- [21] M.F. Sevimli, H.Z. Sarikaya, M.S. Yazgan, A new approach to determine the practical ozone dose for color removal from textile wastewater, *Ozone Sci. Eng.* 25 (2003) 137–143.
- [22] J.L. Sotelo, F.J. Beltran, F.J. Benitez, J. Beltranheredia, Ozone decomposition in water—kinetic-study, *Ind. Eng. Chem. Res.* 26 (1987) 39–43.
- [23] M. Muthukumar, N. Selvakumar, Decoloration of acid dye effluent with ozone: effect of pH, salt concentration and treatment time, *Coloration Technol.* 121 (2005) 7–12.
- [24] M. Muthukumar, N. Selvakumar, Studies on the effect of inorganic salts on decolouration of acid dye effluents by ozonation, *Dyes Pigments* 62 (2004) 221–228.