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Discoloration and detoxicification of a Congo red dye solution by means of ozone treatment for a possible water reuse

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ABSTRACT

The objective of this study was to investigate the degradation and mineralization of an azo-dye, the Congo red, in aqueous solutions using ozone. Phytotoxicity and the inhibitory effects on the microbial activity of the raw and the ozonated solutions were also carried out with the aim of water reuse and environment protection. Decolorization of the aqueous solutions, disappearance of the parent compound, chemical oxygen demand (COD) and total organic carbon (TOC) removal were the main parameters monitored in this study. To control the mineralization of the Congo red, pH of the ozonated solution and heteroatoms released from the mother molecule such NH_4^+, NO_3^- and SO_4^{2-} were determined. It was concluded that ozone by itself is strong enough to decolorize these aqueous solutions in the early stage of the oxidation process. Nonetheless, efficient mineralization had not been achieved. Significant drops in COD (54%) were registered. The extent of TOC removal was about 32%. Sulfur heteroatom was totally oxidized to SO_4^{2-} ions while the central –N=N– azo ring was partially converted to NH_4^+ and NO_3^-. Results of the kinetic studies showed that ozonation of the selected molecule was a pseudo-first-order reaction with respect to dye concentration. The obtained results also demonstrate that ozone process reduced the phytotoxicity of the raw solution and enhanced the biodegradability of the treated azo-dyes-wastewater. Hence, this show that ozone remains one of the effective technologies for the discoloration and the detoxification of organic dyes in wastewater.

1. Introduction

It is broadcasted that more than 60% of the dyes world production is consumed by textiles industries and more than half of this quantity is discharged into receiving water bodies more or less without treatment hampering thus the function of the ecological process. Moreover, different papers report that in most cases, biochemical oxygen demand/chemical oxygen demand ratio of the composite textile wastewater is around 0.25 implying the non-biodegradability of the organic matter therein [1–4]. Among the used dyes, azo-dyes are the most commonly utilized reagents owing to the presence of the azo-group which confers to these chemicals a certain resistance to light, acids, bases and oxygen, the desired proprieties for clothes' makers [5,6]. More than 53% of these commonly used azo-dyes are identified as non-biodegradable compounds [7]. As a consequence, wastewaters bearing such type of dyes are known to be highly resistant to the mostly widespread used conventional wastewater treatment method: the biological process [8–10]. Other technologies evaluated for dyes removal included: adsorption [11], coagulation, flocculation [12] and reverse osmosis processes [13,14]. Although these methods resulted in a significant color removal, they were either costly to apply in the actual field or enable to meet the discharge criteria of wastewater in term of chemical oxygen demand. Adsorbent regeneration, excess sludge production and the rapid fouling of the used membranes are some of other handicaps of these processes. It appears that applying a post-oxidation treatment able to degrade the so likely refractory molecules into smaller ones, which can be further oxidized by biological methods, remains the alternative way while dealing with colored wastewater. Within this regard, different oxidation processes such as NaOCl, H_2O_2 and O_3 as a single process or combined have been tested [15]. One aspect which is relevant to hypochlorite based decolorization process is that for environmental reason, the future use of chemicals containing chlorine should be restricted. The use of H_2O_2 is usually limited due to its relatively low oxidation power (1.78 V). As to ozone, which is considered one of the powerful oxidizing agents (2.07 V) [16], its application as a pretreatment for the improvement of wastewater biodegradability is thoroughly investigated [17–19]. It has been shown that ozone cleaves the conjugated bonds of azo-dyes chromophores,

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leading to color removal and enhancing the biodegradability of the treated wastewater [17,20]. In contrast, other studies [21] claim that short-term ozonation of a model aqueous azo-dye solution and dye-bath effluents from a textile dyeing and finishing industry formed toxic compounds. These results were proved by testing the biodegradability of the effluent and bioluminescence tests [21,22]. Likewise Martins et al. [23] have shown that in order to obtain high toxicity removal, longer ozonation periods with high ozone dozes have to be applied. Zhang et al. [24] reported that the major disadvantage of using ozone is the possible formation of toxic byproducts even from biodegradable substances. Hence, this makes it necessary to test the toxicity and the phytotoxicity of the compounds generated by ozonation to determining whether the treated wastewaters present a risk once discharged to the environment or planned to be reused. In the present work, a short-term ozonation of a widely used commercial azo-dye, the Congo red, was carried out. The dye was selected due to its complex chemical structure, high molecular weight, high solubility in water and its persistence one it is discharged into natural environment. The effect of some auxiliary dyeing additives on the ozonation process as well as the formation of potential toxic by-products and their inhibitory effects on the microbial activity and on a model plant were investigated.

2. Materials and methods

2.1. Oxidation process

Congo red was purchased from Merk as a commercially available dye with 98% purity. The dye's chemical structure and its main characteristics are shown in Fig. 1. All aqueous ozonated solutions of Congo red were prepared with ultra pure water and had a concentration of 0.30 g/l to simulate a medium loaded textile wastewater. Ozonation was conducted in a 100 ml cylindrical glass reactor using a glass bubble diffuser as shown in Fig. 2. All connections from the ozone generator to the reaction vessel were Teflon made tubing. Due to small reactor volume, a fresh dye sample of 50 ml was used for each run. A Triligaz ozone generator was used to produce ozone from the oxygen feed gas with a flow rate of 2.7 g of O_3/h corresponding to its minimum producing capacity enabling us following the kinetics studies. The ozone leaving the reactor was trapped by tow-sequential bubblers containing a potassium iodine (KI) aqueous solution (2%). The influence of some salts that may coexist with the dye on the ozone decolorization efficiency was investigated. Experiments were also conducted using the advanced oxidation process (O_3/H_2O_2). Therefore, hydrogen peroxide (31%, w/w) was added to the Congo red aqueous solution to achieve a final concentration of 7.5 mM just before the ozone containing gas entered the reactor.

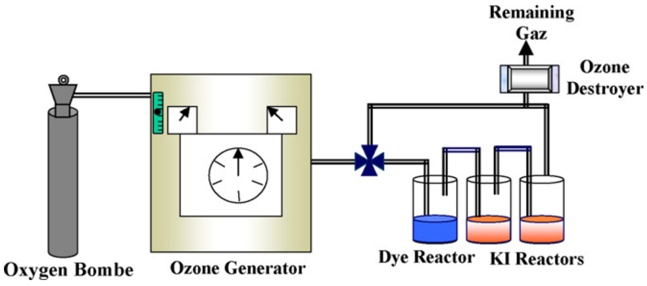

Fig. 2. Sketch of the experimental apparatus used for the ozonation.

2.2. Monitored parameters

Oxidation advancement was followed by monitoring the fading of color, chemical oxygen demand (COD), total organic carbon (TOC) and pH. These parameters were analyzed according to the standard methods described in the Japanese International Standard (JIS) handbook [25]. Absorbance was determined using a Hitachi U-2000 UV/vis spectrophotometer. Total organic carbon was measured using a Shimadzu-TOC-5000A analyzer (catalytic oxidation on Pt at 680 °C) via calibration using standards of potassium phthalate.

2.3. Inorganic ions evolution during the ozonation

To control the mineralization of the Congo red, heteroatoms, released from the mother molecule, such NH_4^+, NO_3^- and SO_4^{2-} were quantified using an ionic chromatography (HIC-6A Shimadzu type) equipped with a conductivity detector and a Shim-pack column. The separation was achieved using an isocratic elution at a flow rate of 1.0 ml/min. A mobile phase of 1 mM of tris(hydroxymethyl)aminomethane and 1 mM of phthalic acid was used for nitrite, nitrate and sulfate ions and a 25 mM of metasulfonic acid in the case of ammonia.

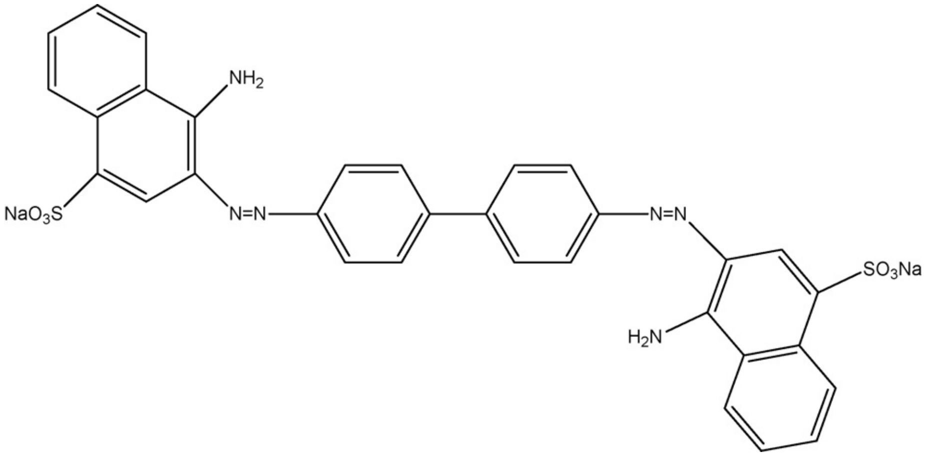

Fig. 1. Chemical structure of the studied molecule (molecular formula, $C_{32}H_{22}N_6Na_2O_6S_2$, molecular weight = 696.68 g, solubility in water at 25 °C = 25 g/l; λ_{max} at pH 7 = 550 nm; color index = 22120).

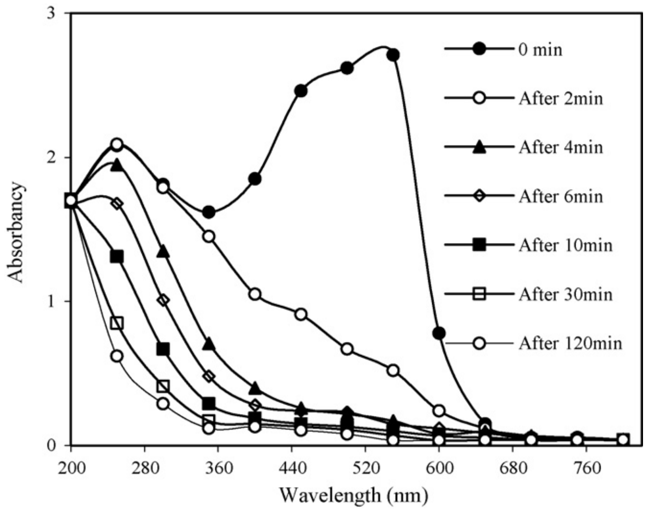

Fig. 3. UV–vis spectra of the Congo red solution at different contact time (contact time = 5 min, initial solution pH 8.7).

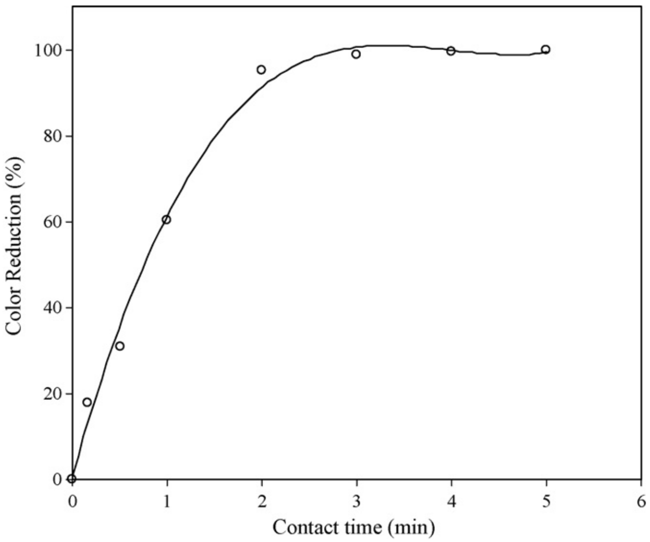

Fig. 4. Color reduction of the Congo red solution versus contact time ([Dye] = 0.30 g/l, $[O_3]$ = 2.7 g/h, treated volume = 50 ml, initial solution pH 8.7).

2.4. Phytotoxicity test

Phytotoxicity tests were conducted to assess the impact of the treated colored water on vegetation once it is thrown to the ecosystem as well as to explore the possible reuse of the treated solution in irrigation fields such as parks, golf-courses, etc. Series of pots containing broad bean seeds, one of the most sensitive and fast growing plants were irrigated with the raw and the 5-min-ozonated discolored solutions. For a comparison, control tests by irrigating the seeds with distilled water were also conducted. Phytotoxicity was assessed by studying the modification morphology of the grown plant such as measuring the plant high, the number of the leaves and the root lengths of the seedlings.

2.5. Microtoxicity test

For the purpose of assessing the impact of the studied dye on the fauna and flora in case it is discharged into the environment or prior to a biological treatment plant, microtoxicity tests were performed on the raw and the 5-min ozonated solutions as described elsewhere [22]. The microtoxicity assessment was evaluated based on the inhibition of the natural luminescence of the marine photobacterium *Vibrio fischeri* via mixing 0.5 ml of the sample to 0.5 ml of the bacterial suspension and incubation at 15 °C during different exposure time. All samples were adjusted to pH 7 prior to each measurement. The decrease of light emission was performed using a DR LANGE LUMIStox 300 photometer. The microtoxicity was expressed at the percent of the inhibition of bioluminescence with relation to a control sample of 0.5 ml solution containing 7.5% NaCl.

3. Results and discussions

3.1. Discoloration

Fig. 3 shows the UV–vis spectra of the raw and the ozonated Congo red solutions at different contact times. The UV–vis absorption of the raw Congo red solution (0 min) is characterized by one band in the visible range, with its maxima located at nearly 550 nm and a second band in the ultraviolet region located at around 240 nm. These two peaks are attributed to benzene and naphthalene rings in the mother molecule. The subsequent illumination of the Congo red by ozonation causes continuous decreases of the intensities of the UV band and an abrupt disappearance of the visible band without the appearance of new absorption bands in the UV–vis region. Disappearance of the visible band suggests the sensitivity of the oxidized model molecule towards ozone. It has to be noted that ozone reacts with conjugated systems such as dye molecules through either direct or indirect oxidation. In direct oxidation, the reactive species is the molecular ozone, which is highly selective for electron rich structures such as the double bonds and are very suitable for opening aromatic rings by means of ozone cycloaddition [26]. In indirect oxidation, the ozone decomposes in aqueous solution to form radical species that have a very strong oxidation potential [27]. Hence both ozone and/or the free radicals break the double bonds (–N═N–; –C═C–) in the conjugated chains of the dye molecule and discoloration is achieved via electrophilic cleavage of their chromophoric groups [16]. As shown in Fig. 4, a complete discoloration reaching nearly 98% was achieved after only 4 min of ozonation confirming thus our visual observation.

3.2. Evolution of pH during the ozonation

Congo red oxidation has been monitored by pH measurements as a function of contact time. As observed in Fig. 5, the pH of the

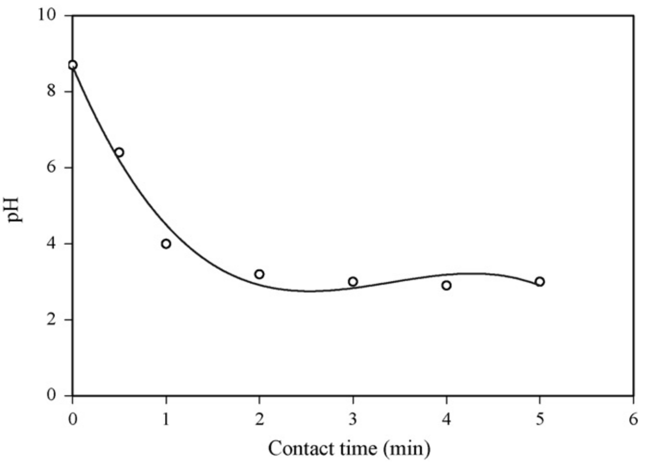

Fig. 5. pH evolution during ozonation ([Dye] = 0.30 g/l, $[O_3]$ = 2.7 g/h, treated volume = 50 ml, initial solution pH 8.7).

solution decreases rapidly at the early stage of the experiment, dropping from the initial solution (pH 8.7 at $t = 0$ min) to about 3.8 after nearly 2 min of ozonation when almost complete discoloration occurred. Afterwards, the decrease of pH continued more slowly until a steady state was reached. The drop of the pH indicated the formation of acidic by-products, such as H_2SO_4 originating from the sulfonate groups and a lesser extent, from the formation of aliphatic acids and NH_4^+. Correlation between, the release of SO_4^{2-} and NH_4^+ with pH (data not shown) gave somehow a good relationship with a correlation coefficients of 0.86 and 0.96, respectively. It has to be noted that the formation of aliphatic acid compounds is usually encountered while dealing with ozonation of benzene derivatives [26,28].

3.3. COD and TOC removal

Chemical oxygen demand and total organic carbon reductions are given in Fig. 6. After 4 min of ozonation (at nearly complete discoloration) more than 50% of the initial COD was removed. Similarly with what was reported by Zhao et al. [26] and as mentioned earlier, the ozonation of dyes usually leads to small organic molecular fragments, such as acetic acids, epoxides, aldehydes, ketones, etc. leading to a residual COD. This COD resulting from these small new formed molecules can be further reduced by a biological process as described by Lin and Lin Chi [29]. Under the same ozonation operating conditions the corresponding TOC removal efficiency was about 25%. The drop in TOC values suggests that CO_2 molecules are formed simultaneously with other volatile organic compounds such as formaldehyde and acetaldehyde during the ozonation process as mentioned by Koch et al. [30]. Similar results were found by Boye et al. [31] and also reported by Gandini et al. [32] who succeeded to destroy carboxylic acids to CO_2 and H_2O stages.

3.4. Inorganic ions evolution during the ozonation

Besides TOC elimination, mineralization usually implies the appearance of inorganic products, since heteroatoms are generally converted into mainly anions in which they generally are at their highest oxidation degree during an oxidation process [33]. Fig. 7 shows the evolution of SO_4^{2-}, NO_3^- and NH_4^+ in solution during ozonation. The appearance of SO_4^{2-} can be accounted for an initial attack of the generated radical $OH^\bullet$ on the sulfonyl group in the Congo red molecule according to Eqs. (1) and (2).

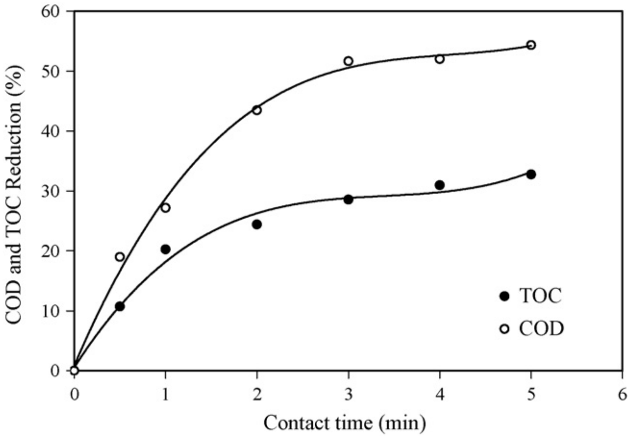

Fig. 6. COD and TOC removal ([Dye] = 0.30 g/l, [O_3] = 2.7 g/h, treated volume = 50 ml, initial solution pH 8.7).

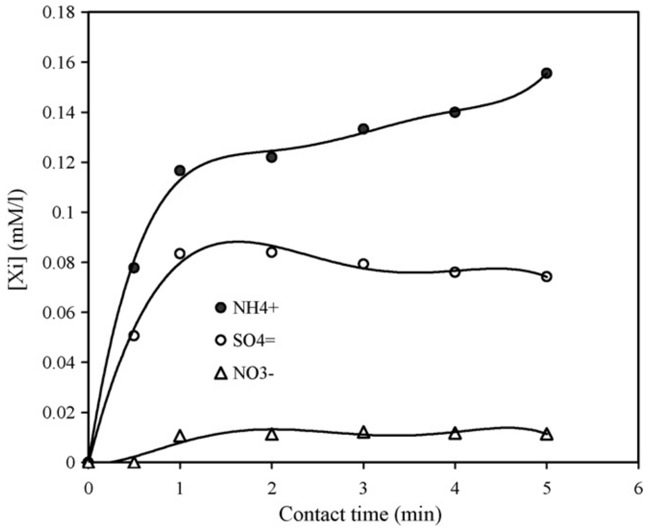

Fig. 7. Inorganic ions evolution during the ozonation ([Dye] = 0.30 g/l, [O_3] = 2.7 g/h, treated volume = 50 ml, initial solution pH 8.7).

First, and above pH 6, ozone is decomposed generating free radicals such as $OH^\bullet$ [34–36],

$$O_3 + 2OH^- \rightarrow OH^\bullet + O_2^- + HO_2^\bullet \tag{1}$$

then the formed radical attacks the dye molecule to release sulfate ions according to the following equation:

$$Na^+, SO_3^-{-}R{-}SO_3^-, Na^+ + 2OH^\bullet \rightarrow R^\bullet + 2HSO_4^-, 2Na^+ \Leftrightarrow (2H^+, 2SO_4^{2-})4 \tag{2}$$

The $R^\bullet$ itself can further react with ozone species through different pathways.

Based on Eq. (3), the theoretical expected sulfate stoichiometric value is equal to 0.086 mM/l suggesting a total mineralization of the ozonated molecule. It can be deduced from Fig. 7 that the maximum amount of sulfate found in the ozonated solution was about 0.084 mM/l and was reached after 2 min of ozonation. This established sulfate mass balance emphasizes the attacks of ozone or the generated radicals on the sulfonate groups and therefore their release into the bulk phase.

$$C_{32}H_{22}N_6O_6S_2Na_2 + 30O_3 + (1/2)O_2 \rightarrow 32CO_2 + 6NO_3^- + 2Na^+ + 2SO_4^{2-} + 8H^+ + 7H_2O \tag{3}$$

Regarding nitrogen, based also on Eq. (3), the theoretical stoichiometric quantity of nitrogen should be equal to 2.58 mM/l. However, the obtained results indicate that only 6.5% of the theoretical value was found. The absence of nitrogen mass balance suggests the formation of either other non-detected nitrogen-species or a partial release of nitrogen from the mother molecule. It is also likely that ammonium was formed first without changing in the oxidation degree of nitrogen, and then converted into nitrate enabling the nitrogen to be at a higher oxidation state. Similar deductions were found by Lachheb et al. [37]. With regard to the nitrogen species, Lopez et al. [38] found that one of the oxidation products of azo-dyes might be nitro-aromatics as a result of the oxidative breakage of the molecules by ozone. Karkmaz et al. [28] demonstrated that N_2 was formed during the photocatalytic degradation of the alimentary azo-dye amaranth. Nitrite ion was not detected due to its rapid conversion to nitrate.

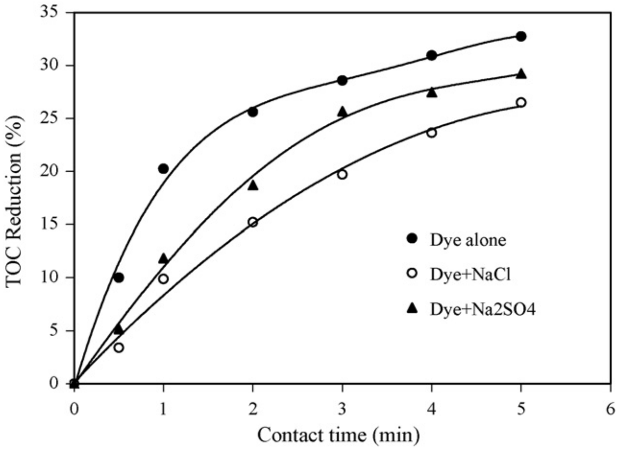

Fig. 8. Effect of NaCl and Na_2SO_4 on TOC removal ([Dye] = 0.30 g/l, $[O_3]$ = 2.7 g/h, treated volume = 50 ml, initial solution pH 8.7, $[Na_2SO_4]$ = [NaCl] = 5 g/l).

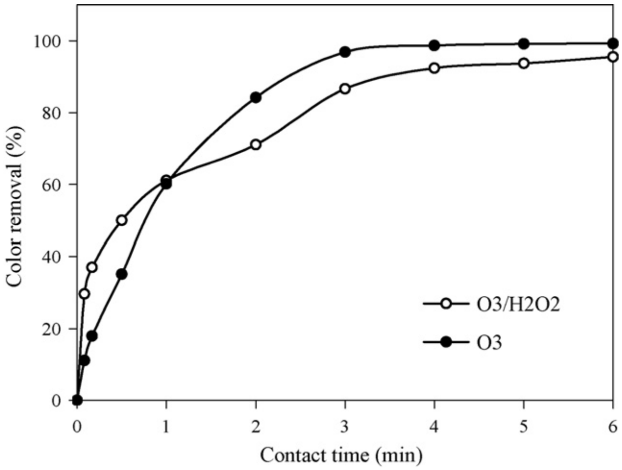

Fig. 9. Effect of H_2O_2 addition on the ozonation of the Congo red solution ([Dye] = 0.30 g/l, $[O_3]$ = 2.7 g/h, treated volume = 50 ml, initial solution pH 8.7, $[H_2O_2]$ = 7.5 mM/l).

3.5. *Effect of coexistence ions on the ozonation*

It is known that ozone stability is affected by the presence of salts, pH and temperature. Mallevialle [39] reported that if alkaline salts are present, the solubility of ozone is reduced, while neutral salts may increase its solubility. Moreover, Ergas et al. [40] reported that those auxiliary chemicals were shown to have negative impact on ozone oxidation performance. Keeping this in mind, the effect of the addition of some salts on the ozonation of the Congo red solution was studied to assess the favorable conditions of ozone utilization. The obtained result is shown in Fig. 8. It can be observed that the ozonation was slightly affected by the presence of Na_2SO_4 at a dose of 5 g/l and more pronounced by a similar dose of NaCl. This fact can be explained by the attitude of Cl^- to consume $OH^\bullet$ and O_3 via serial groups of chemical reactions as mentioned by Muthukumar and Selvakumar [41]. We recall that these kinds of salts are commonly present in dye house effluents since they are used to help dye attachment to the fiber during the dyeing process [42]. It is also worth mentioning that Muthukumar and Selvakumar [41] reported that the presence of salt in solution affects the time necessary for complete decolorization. The higher the salt content, the longer the time required for complete discoloration. This result is in agreement with our conclusions.

3.6. *Effect of H_2O_2 addition*

Usually H_2O_2 addition is known to increase the rate of ozone oxidation by allowing an enhancement in the quantum yield of formation of hydroxyl radical $OH^\bullet$ [28]. It was shown that the conjugate base of hydrogen peroxide at mill-molar concentrations could initiate the decomposition of ozone into more reactive hydroxyl radicals as shown in the following reactions [43]:

$$H_2O_2 + H_2O \rightarrow HO_2^- + H_3O^+ \quad (4)$$

$$HO_2^- + O_3 \rightarrow OH^\bullet + O_2^- + O_2 \quad (5)$$

As depicted in Fig. 9, it can be seen that the addition of H_2O_2 had an adverse effect on color removal just a few second after the start of ozone/hydrogen peroxide application. The presented results revealed that at the start up, discoloration using O_3/H_2O_2 process was faster and more efficient compared to ozone alone. However, after 1 min of ozonation, O_3 combined with H_2O_2 was less efficient than O_3 alone. This phenomenon can be explained by considering the scavenging effect of hydrogen peroxide on hydroxyl radicals. It is worth noting that hydrogen peroxide can react with $OH^\bullet$ decreasing thus the concentration of the free hydroxyl radicals leading to less reactive species as shown below [44]:

$$H_2O_2 + OH^\bullet \rightarrow OOH^\bullet + H_2O \quad (6)$$

Another possible explanation could be an early different reaction pathway depending on H_2O_2 concentration that leads to more resistant intermediate products to further oxidation using O_3/H_2O_2 process. Swaminathan et al. [45] reported that the addition of 1.132 mg/l H_2O_2 did not enhance COD and color removal compared to the oxidation using only ozone. Oguz and Keskinler [46] mentioned that O_3/H_2O_2 process negatively affected the COD removal efficiency for the removal of Bomaplex Red CR-L dye as compared to the ozonation process alone.

3.7. *Kinetics of Congo red ozonation*

The kinetics of aqueous ozonation process plays an important role in assessing the efficiency and feasibility of treating dye contaminated wastewater. In ozone applications where semi-batch reactions with ozone bubbling from the bottom of reactor are used, the reaction takes place at the gas–liquid interface [47]. The direct reaction of ozone is assumed to be first order with respect to dye and ozone, respectively. When the amount of ozone is in excess or when the ozone concentration is assumed to reach a stationary stage at the interface, the oxidation rate follows a pseudo-first-order kinetics with respect to the concentration of the organic substances. In this study, the kinetics of Congo red ozonation was evaluated by plotting $\mathrm{Ln}(C_t/C_0)$ values versus reaction time following the below equation:

$$\mathrm{Ln}(C_t/C_0) = -k_d t$$

where C_t and C_0 are dye concentration at any reaction times (t) during the ozonation and the dye initial concentration, respectively. k_d stands for the pseudo-first-order reaction rate constant.

Fig. 10 illustrates the disappearance of the concentration of the dye against time which was quite fast in the first 3 min of ozonation, afterward; the disappearance speed of the dye was slower. Using data obtained from the above mentioned equation, Fig. 11 shows that the curve was well fitted to the pseudo-first-order kinetics, and the square of the relative correlative coefficient (R^2) of the experimental results was higher than 0.985. The slope of the linear curve represents the pseudo-first-order rate constant and

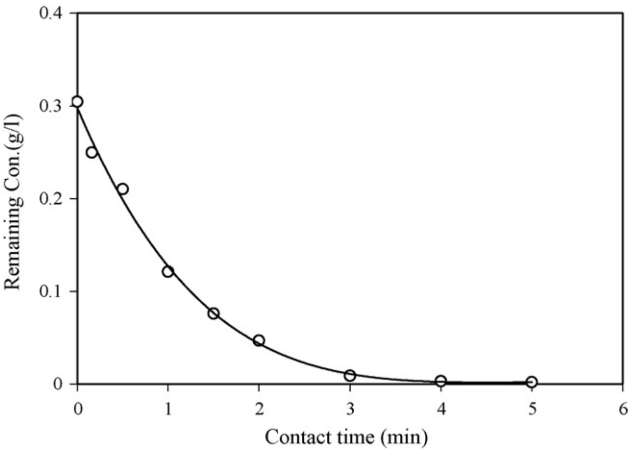

Fig. 10. Remaining concentration as function of contact time ($[O_3] = 2.7$ g/h, treated volume = 50 ml, initial solution pH 8.7).

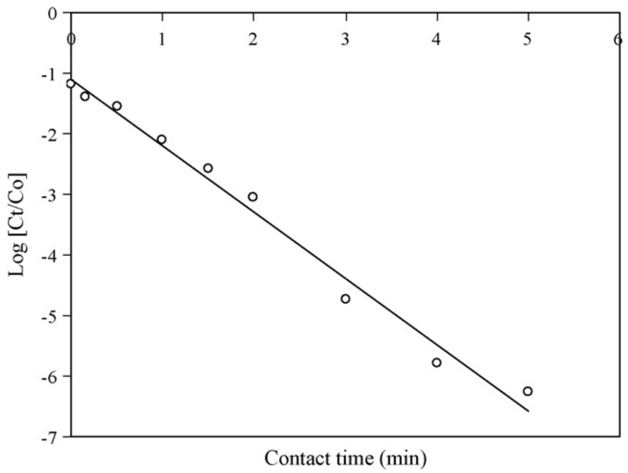

Fig. 11. Kinetics of the Congo red ozonation ($[O_3] = 2.7$ g/h, treated volume = 50 ml, initial solution pH 8.7).

was about 1.09 min^{-1}. We denote that pseudo-first-order behaviors were also observed during ozonation of azo-dyes [47].

3.8. Phytotoxicity

As stated earlier, phytotoxicity tests were conducted to assess the impact of the release of the ozonated solution to the environment as well as to evaluate the possible use of the pretreated aqueous solution in the irrigation field. Indeed, this practice can alleviate the burden on underground water overexploitation and promote the practice of using treated water to irrigate golf courses, parks and gardens. Phytotoxicity tests were carried out via irrigating broad beans by the raw and the 5-min ozonated solutions. Obtained results are presented in Fig. 12. The main withdrawn conclusions can be summarized as following: plants irrigated with the ozonated solution grow in a similar manner as the plant irrigated with the distilled water. The only exception is that the later exhibited smaller leaves length. However plants irrigated with the raw solution remain fade and presented a reddish colored leaves. Seeds germination in case of raw solution was retarded and the root length of all seedlings was smaller than that of the seeds incubated in the ozonated solution (data not shown). These results suggest that ozonation is able to illuminate the phytotoxicity of azo-dyes aqueous solutions. Anyhow, the germination of seeds and the growth of the plant treated with the ozonated water could help promoting the reuse of the treated water in the irrigating field under certain circumstances.

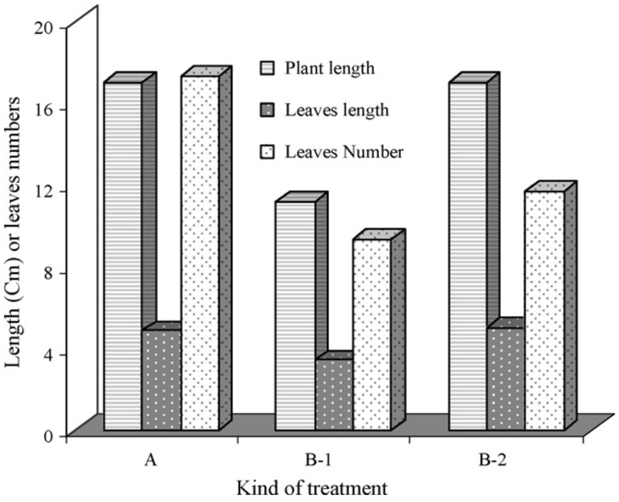

Fig. 12. Effect of toxicity; morphology of plants irrigated with the raw and the ozonated solutions (A: control; B1: plant irrigated with the raw solution; B2: plant irrigated with the ozonated solution 0.3 g/l).

3.9. Microtoxicity

The microtoxicity measurements were conducted to find out whether the ozonation of the red Congo produces any toxic by-products for any further biological treatment or to the receptor medium. The results expressed as bioluminescence inhibition rate (%) at three incubation periods are presented in Fig. 13. It can be seen that as the incubation period increases, the inhibitory effect of the raw and the ozonated solutions decreases and this can be explained by the acclimatization effect of the *V. fischeri* to the medium as times goes on. Similar results were also reported by Zhang et al. [48]. On the other hand, the raw solution showed toxic potential toward the used bacteria and varied from 87 to 27% for 0 and 30 min exposure time, respectively. In contrast, the 5-min ozonated solutions demonstrated no toxic effect for all tested incubation periods. As shown in Fig. 14, the inhibitory effect on the bioluminescence of the bacteria is decreasing as a function of ozonation time suggesting that no toxic intermediates stronger than the parent molecule were formed. These results contrast with the ones reported by

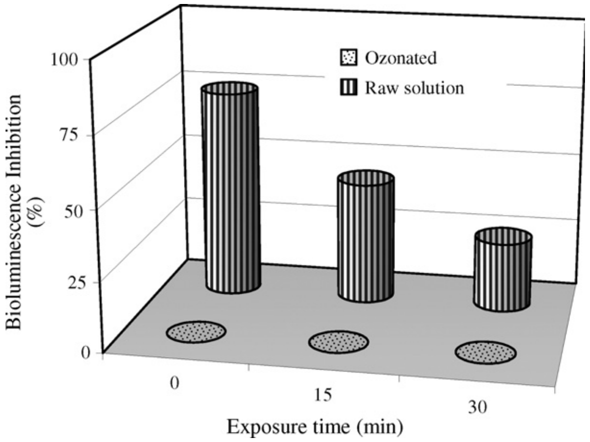

Fig. 13. Toxicity of the raw and ozonated solutions at different exposure time ($[\text{Dye}] = 0.30$ g/l, $[O_3] = 2.7$ g/h, treated volume = 50 ml, ozonation time = 5 min).

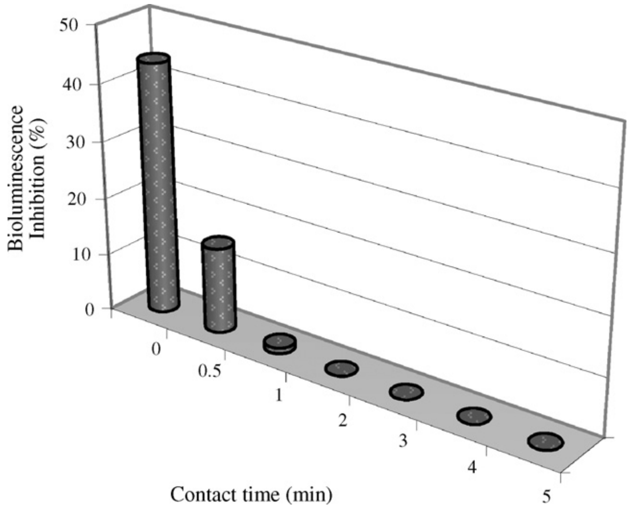

Fig. 14. Toxicity of the raw and ozonated solutions versus ozonation time ([Dye] = 0.30 g/l, [O_3] = 2.7 g/h, treated volume = 50 ml, incubation period = 15 min).

Chunxia et al. [49] who found that the toxicity of some azo-dyes showed an increase upon the start up of the ozonation and seems to be destroyed by further ozonation. The increase of the toxicity in former study might be due to the formation of toxic intermediates resulting from the high initial used concentration of dye (2 g/l) which was much higher than the amount used in our case. The bioluminescence test demonstrated clearly that the ozonation had a positive effect on microtoxicity of the raw Congo red solution. Therefore, a combined treatment of ozonation and biological degradation might be a choice for an advanced treatment of dye bath effluent containing typical dyes.

4. Conclusion

This study aimed to evaluate the effectiveness of using ozone to decolorize and detoxify an aqueous colored solution. According to the results obtained, the following conclusions can be drawn:

1. Ozone treatment proves to be very effective for complete removal of color but provides only partial reduction of COD and TOC.
2. Heteroatoms such as SO_4^{2-}, NH_4^+ and NO_3^- were released confirming the destruction of the mother molecule.
3. The oxidation of the Congo red followed a pseudo-first-order kinetics with respect to dye.
4. Color removal efficiency was lower in case of H_2O_2 and O_3 combination as compared to ozone alone and was related to the scavenging effect of high H_2O_2 used dose.
5. The presence of salts in the dye solution decreases the discoloration efficiency.
6. Sodium chloride reduces the discoloration efficiency of ozone more than that of sodium sulfate.
7. Phytotoxicity test via treating broad bean plants with the ozonated water revealed no significant change in the shape and the morphology of the grown plant compared to that irrigated with the distilled water.
8. Ozonated solutions showed no toxic effect toward the tested bacteria.

Complementary tests are under investigation to identify the ozonation by-products as well as to assess the biodegrability of the treated aqueous solution prior to a further biological treatment.

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