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Treatment and degradability of direct dyes in textile wastewater by ozonation: A laboratory investigation

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ABSTRACT

In this study the factors affecting the rate of chemical oxygen demand of a synthetic waste solution containing water soluble direct dyes (Sirius Red F3B and Sirius Blue SBRR) by ozone gas were investigated. The research was conducted using a batch bubble column to take the advantage of the intensive back-mixing that prevails in bubble columns. In result of our experimental study, we have shown that the COD of direct dyestuff wastewater was reduced 58.89% for Sirius Red F3B and 60.95% for Sirius Blue SBRR after ozone bubbling treatment for 2 h. In addition the results indicate that during the ozonation, even though complete Sirius Red F3B and Sirius Blue SBRR degradation occurs in 10 min, ozone consumption goes on for a further 20 min after which time most degradation reactions are completed. Results of kinetic study showed that ozonation of the aqueous direct dyes were a pseudo-first-order reaction with respect to the dye. The apparent rate constant increased with both applied ozone dose and temperature, but declined logarithmically with the initial dye concentration. The main ozonation by-products, identified by HPLC, IC and GC-MS are formaldehyde, acetaldehyde, glyoxal, acetone, acetic acid, formic acid, oxalic acid and carbonic acid, plus nine Sirius Red F3B and twelve Sirius Blue SBRR derivatives are scarcely degradable.

Keywords: Ozonation; Sirius Red F3B; Sirius Blue SBRR; Direct dye; Chemical oxygen demand; Degradability; Wastewater treatment

1. Introduction

The textile industry produces large amounts of wastewater during all phases of textile production and finishing. Major pollutants in textile wastewaters are high suspended solids, chemical oxygen demand, heat, color, acidity, and other soluble substances [1]. Textile washing operations are the most water intensive processes in textile production. Wastewater from textile washing contains high quantities of chemical residues, which originate from previous textile processing steps, including dyes. The raw materials used in the manufacturing of dyes are mainly aromatic hydrocarbons [2]. The removal of color in textile industry and dyestuff manufacturing industry wastewaters represents a major environmental concern [3].

Dyes are classified according to their application and chemical structure. They are composed of a group of atoms responsible for the dye color, called chromophores, as well as an electron withdrawing or donating substituents that cause or intensify the color of the chromophores, called auxochromes [4]. The most important chromophores are azo (—N=N—), carbonyl (—C=O), methine (—CH=), nitro (—NO_2) and quinoid groups. The most important auxochromes are amine (—NH_2), carboxyl (—COOH), sulfonate (—SO_3H) and hydroxyl (—OH). The auxochromes can belong to the classes of reactive, acid, direct, basic, mordant, disperse,

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pigment, vat, anionic and ingrain, sulphur, solvent and disperse dye [5–7].

A rather innovative approach is provided by the so-called "integrated-processes" where the effectiveness of combining biological and physicochemical treatments is specifically designed to be synergetic rather than additive [8]. A typical example of such processes is the combination of a chemical oxidation with an activated sludge treatment where the chemical oxidation is specifically aimed to partially degrade the recalcitrant contaminants to more easily biodegradable intermediates avoiding the high costs of a total mineralization [9].

The most commonly used oxidants for such a purpose are: Fenton's reagent, permanganate, and ozone. Hydrogen peroxide, combined with a ferrous ion catalyst is known as Fenton's reagent. It has been shown to be effective in treating a variety of recalcitrant organic compounds. Its effectiveness strongly depends on solutions pH that must be acid [10]. Permanganate is another strong oxidant. Permanganate is long known to be effective in removing tastes and odors caused by the decomposition of organic matter; it has also been proved effective in oxidizing a variety of organic as well as inorganic compounds. Like Fenton's reagent, the reactivity of permanganate depends to a great extent on the pH [11]. As for ozone, it is known to be a very powerful oxidizing agent appropriate to treat water and wastewater. It is widely used also as disinfectant. The main factors governing its efficiency are: specific selectivity for target compounds, pH, temperature, and mass transfer dispersion [12]. The reactions of ozone with organic compounds in aqueous media have been under investigation by different authors. These reactions are complex with many intermediates. Chemical oxidation is frequently another tool in wastewater treatment; the chemical oxidants that are in wide use today are chloride, ozone and hydrogen peroxide. However, the use of chloride for such applications have come under intense scrutiny because, ozone, on the other hand, with only a short half life is found to be effective in many applications for color removal, and in oxidation of many complex inorganic materials [13–18].

Ozone can react with substrates directly, as molecular-ozone, or indirectly, by radical-intermediates which from when ozone decomposes in water. Depending on which mechanism takes place, ozone selectivity can be high (direct reaction) or nil (indirect reaction). In the first case ozone is considered to be much more selective than Fenton's reagent and permanganate particularly towards molecules containing multiple and/or conjugated bonds and aromatics having activating ortho-substituents such as $-OH$, $-NH_2$, $-OCH_3$, etc. [19–21]. Many ozone processes based on such a high selectivity have been used and proved successfully since many years. On the contrary, if radical type reactions occur, ozone behaves as an unselective oxidant and its oxidative performances have not been investigated so extensively as in the case of direct reactions.

Previous researchers documented that COD and TOC removals using ozonations were dependent on pH. Lidia et al. (2001) reported low COD removal of disperse dyes (10%) at pH 8 using 0.5 g L^{-1} of ozone concentration, while, Arslan et al. (2002) documented high TOC removal for simulated reactive dye bath effluent at pH 7 when using ozone concentration of 2970 mg L^{-1}. At pH 7, the radical type reaction becomes effective and simultaneously the inhibiting effect of carbonate ions is not yet very pronounced. Thus higher TOC and COD removals could be expected [22,23]. Furthermore, Rajeswari (2000) showed that TOC and COD removals efficiency was dependent on temperature. He recorded that TOC and COD removals increased with increasing temperature from 25°C to 50°C [24]. Koch et al. (2002) documented TOC removal of hydrolyzed reaction dye was less than COD throughout the ozonation process and it was 30% and 25% after 60 and 90 min with an ozone concentration of 18.5 and 9.1 mg/L, respectively [26–28].

Sheng and Chi (1993) documented COD removal depended on strength of dye waste, where COD reduction was slight from the medium and high dye waste. The low COD reduction is attributable to the fact that the structured polymer dye molecules are oxidized by ozonation to small molecules, such as acetic acid, aldehyde, ketones, etc., instead of CO_2 and water. Thus, considerable amount of COD is attributed to these small organic molecules [29]. According to Gianluca and Nicola (2001), COD removal of biotreated textile wastewater was depended on initial COD of textile wastewater. About 67% and 39% of COD removal was achieved when COD initial was 160 and 203 mg L^{-1}, respectively [30]. According to Koch et al. (2002), COD removal throughout ozonation process was 50% and 40% after 60 and 90 min with an ozone concentration of 18.5 and 9.1 mg L^{-1}, respectively [25].

The effectiveness of ozone treatment for improving the biodegradability of recalcitrant pollutants has been proved by investigating the ozonation reaction of Fast Violet B (FVB) a bioresistant chemical intermediate of azo dyes by Lopez et al. Laboratory scale experiments have been carried out, at room temperature, by bubbling, for 90 min, ozonated air (9 mg O_3 L^{-1} min) into 0.35 L of an alkaline (pH = 11), aqueous solution (50 mg L^{-1}) of FVB. At the end of the ozonation, i.e. after 30 min, the initial values of TOC (35 mg C L^{-1}) and COD (103 mgO_2 L^{-1}) are respectively 27 and 25 and correspond to a relative removal of about 23% and 76% [21].

Wastewater obtained from acid dye and reactive dye manufacturing was treated by ozone bubbling in a batch reactor for the purpose of reducing COD to

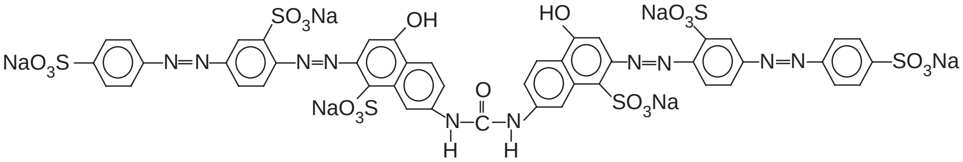

Fig. 1. Structure of Sirius Red F3B (Direct Red 80).

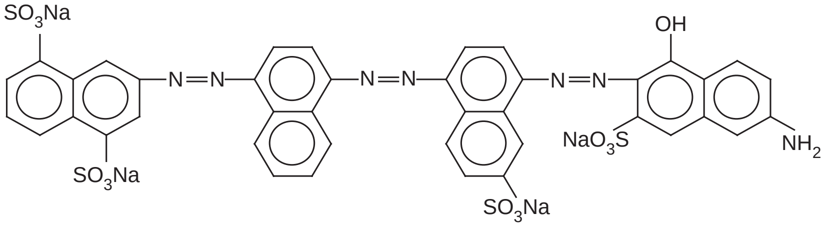

Fig. 2. Structure of Sirius Blue SBRR (Direct Blue 71).

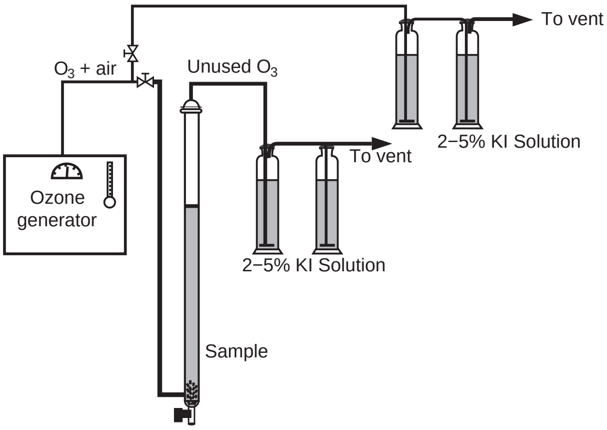

Fig. 3. Schematic diagram of the bench-scale reactor system.

below 150 mg L^{-1} by Na et al. At pH of 11, the COD of acid dyestuff wastewater was reduced to 95 mg L^{-1} after 90 min, and the COD of reactive dyestuff wastewater was reduced to 120 mg L^{-1} after 120 min [31].

The aim of the present work is to study the factors affecting the rate of COD of a synthetic waste solution containing water-soluble direct dyes (Sirius Red F3B and Sirius Blue SBRR) by applying ozone gas in a batch bubble column.

2. Materials and methods

2.1. Reagent and chemicals

The dye named commercially Sirius Red F3B (Direct Red 80) ($C_{44}H_{26}N_{10}Na_6O_{21}S_6$) was purchased from Dystar. The dye used in the present work was water soluble (Mw: 1378.54 g mol^{-1}) structure is given in Fig. 1.

The dye named commercially Sirius Blue SBRR (Direct Blue 71) ($C_{40}H_{23}N_7Na_4O_{13}S_4$) was purchased from Dystar. The dye used in the present work was water soluble (Mw: 965.94 g mol^{-1}) of which structure is shown in Fig. 2.

HPLC solvents were from Aldrich Chemicals Co. used water was Milli-Q quality. All other reagents were from Merck and were used without any further purification.

2.2. Experimental set-up

The experimental set-up that was shown in Fig. 3 consists of oxygen gas, ozone generator, a glass bubble column reactor and two washing bottles. Fischer 502 Model ozone generator was used for the production of ozone from dry oxygen (99.9% purity). The reactor had a glass column of 5 cm diameter and 110 cm height with sintered glass at the bottom through which ozone was introduced to the solution. The reactor was followed by two washing bottles, each of them containing 500 mL of acidified 2–5% KI solution for determining unused ozone. Before each run the bubble column reactor was filled with 2000 mL of dye solution. Oxygen gas was allowed to pass through the ozonizer where ozone formation takes place. The outlet stream from the ozonizer containing O_3 and O_2 mixture was allowed to pass through tygon tubing connected to the bottom of the bubble column. The gas flow rate was controlled by a needle valve and was measured by air flow meters. The temperature was fixed at $20 \pm 1^{\circ}C$ during all the experiments. The pH of wastewater was adjusted to the desired level with Merck quality analytical grade 0.1 N NaOH and H_2SO_4.

The unused ozone was taken out of the bubble column reactor through the Tygon tubing, and bubbled into 2% KI solution in the washing bottles, where the potassium iodide solution reacted with the excess ozone according to the following equation:

$$O_3 + KI + H_2O \rightarrow I_2 + 2KOH + O_2.$$

The resulting iodine was titrated using standard sodium thiosulfate, in the presence of starch as indicator. The values of unused ozone were determined, accordingly [28,32].

2.3. Equipments

HPLC, GC-MS and IC Analyses. Sirius Red F3B and Sirius Blue SBRR analyses were performed by HPLC using a Varian 9012 gradient pump, a C-18 reversed-phase column (Varian, Palo Alto, CA, USA) and water–methanol eluant gradient (methanol concentration was increased from 40% to 70% in 20 min).

According to its UV spectrum, Sirius Red F3B and Sirius Blue SBRR decays were monitored in UV mode Agilent 8453 model spectrophotometer at 528 nm and 594 nm, respectively. COD measurement was carried out according to the Standard Methods [9].

Analysis of Organic Residues, Aldehyde analyses were also carried out by HPLC-UV according to EPA method 8315 (Environmental Protection Agency, 1992). GC-MS analyses were performed by a 5971 mass spectrometer interfaced to a 5890 gas-chromatograph (Hewlett-Packard, Palo Alto, CA, USA). The used column was SPB-5 (30 m length, 0.25 mm i.d. and 25 μm film thickness) from Supelco (Bellofonte, PA, USA); its end part was introduced directly into the ion source through a transfer line heated at 280°C. 1 μL sample was injected into a splitless injector warmed at 200°C. The operative conditions were: carrier gas (helium) flow rate: 1 mL min^{-1}, initial temperature: 40°C (1 min), increasing temperature rate: 15°C min^{-1} up to 280°C, then isothermal for 5 min. Electron impact mass spectra, at an electron energy of 70 eV, were recorded by scanning the quadruple from mass 35 to 550 Dalton at 1.4 scan s^{-1}. The background-subtracted mass spectra were matched against those of the NIST mass spectra library and interpreted on the basis of the observed fragmentation. Samples were concentrated according to following solid–liquid extraction procedure: after having conditioned a 500 mg Bondelut C-18 solid phase cartridge (Varian, Harbor City, CA, USA) by loading sequentially (methylene chloride)/(methanol) 1/1 (v/v) solution, methanol, and water, 50 mL of quenched sample were let to flow through the cartridge; after a 5 min drying step, the cartridge was eluted by methanol whose volume was reduced to 1 mL by a gentle stream of purified air. Organic acid analyses were carried out by a Dionex mod. 4000i ion chromatograph (Dionex, Sunnyvale, CA, USA) equipped with an IonPac HPICE-AS1 column (Dionex) and operating in suppressed conductivity detection mode. Samples, injected by a 50 μL loop, were eluted by a 1 mM octanesulfonic acid solution at a flow rate of 0.8 mL min^{-1}.

3. Results and discussion

According to previous experiments, high pH, high ozone-air flow rate and high ozone concentration were required for the effective treatment of the dyestuff wastewater by ozone. Experiments were performed with an ozone-air flow rate 120 L h^{-1}. The resulted reaction time was 120 min. The samples volume 2000 mL, output ampere of 2.5 A and pH of 12 were fixed.

The results with the direct dyestuff wastewater showed that COD reduction was remarkable under the basic condition of pH 12. A large amount of bubble was formed at high inlet gas flow rate. High ozone concentration was effective for the reduction of COD.

Result are given as follows,

Sirius Red F3B: The pH of raw direct dyestuff wastewater was measured to be 5.8. The COD of direct dyestuff wastewater was reduced from 2870 mg L^{-1} to 1180 mg L^{-1} after ozone bubbling treatment for 2 h. When the pH was changed to 8.0, the COD of direct dyestuff wastewater was reduced to 844 mg L^{-1}.

Sirius Blue SBRR: The pH of raw direct dyestuff wastewater was measured to be 5.9. The COD of direct dyestuff wastewater was reduced from 2420 mg L^{-1} to 985 mg L^{-1} after ozone bubbling treatment for 2 h. When the pH was changed to 8.0, the COD of direct dyestuff wastewater was reduced to 778 mg L^{-1}. Ozone treatment experiments were performed with various pH of samples since the differences in the results stem out these variations.

The COD values measured after the pH ozonization process at the pH values between 2 and 12 are shown in Fig. 4, the variation of COD during the ozonization period are given in Fig. 5 for the studied two dyes.

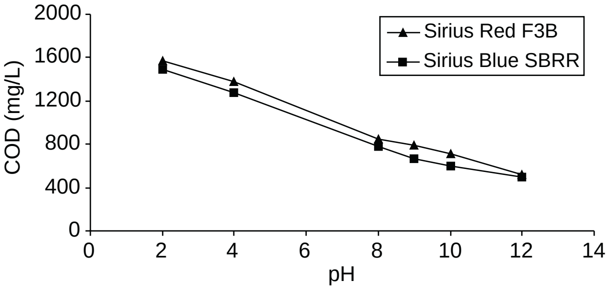

Fig. 4. Effect of initial solution pH on COD (COD raw direct dyestuff: 2870 mg L^{-1} for Sirius Red F3B; COD raw direct dyestuff: 2420 mg L^{-1} for Sirius Blue SBRR; COD environmental standard: 150 mg L^{-1}).

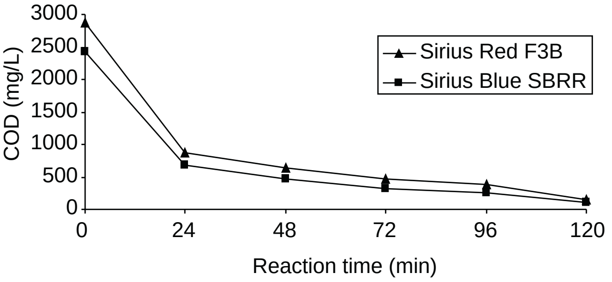

Fig. 5. COD reduction during ozonization for Sirius Red F3B and Sirius Blue SBRR.

3.1. Decolorization kinetics

Pseudo-first-order trends typical for the ozone-dye reaction [33] were observed in all the experimental runs (Figs. 6 and 7). The rate constant k was defined by the graph slope using the kinetic equation for first order reaction (ln C = –k.t + const) transformed into equation (1) [34–38]:

$$k.t = \ln(C_0 - C) \quad (1)$$

where,

k : rate constant, min^{-1}
C_0 : the initial dye concentration, mg L^{-1}
C : dye concentration at the specific time, mg L^{-1}.

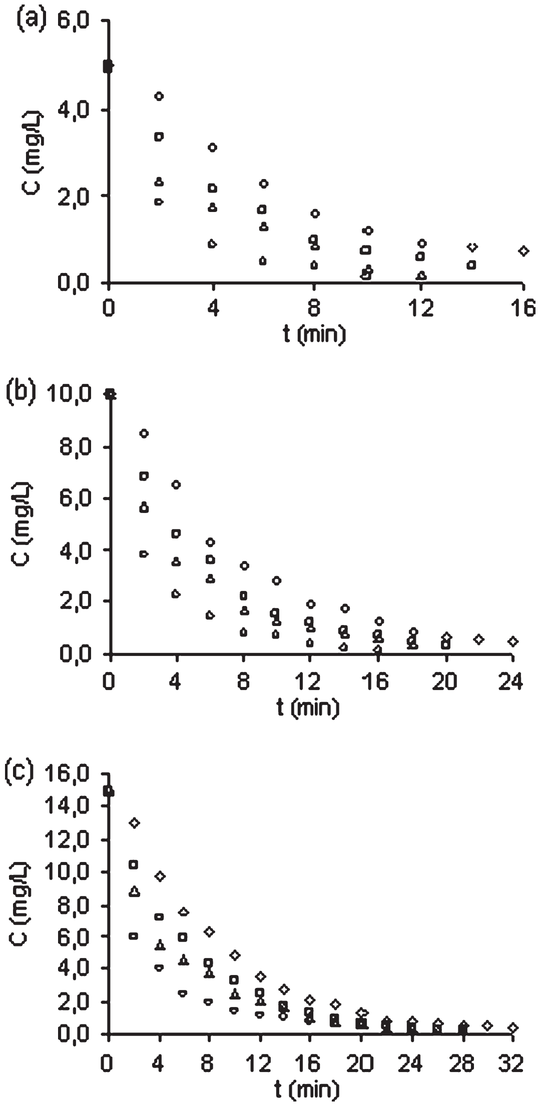

Fig. 6. Ozonation of Sirius Red F3B at T = 20°C and initial pH: (◊) 6,0, (□) 8,0, (△) 10,0, (○) 12,0; C_0= (a) 5, (b) 10, (c) 15 mg L^{-1}.

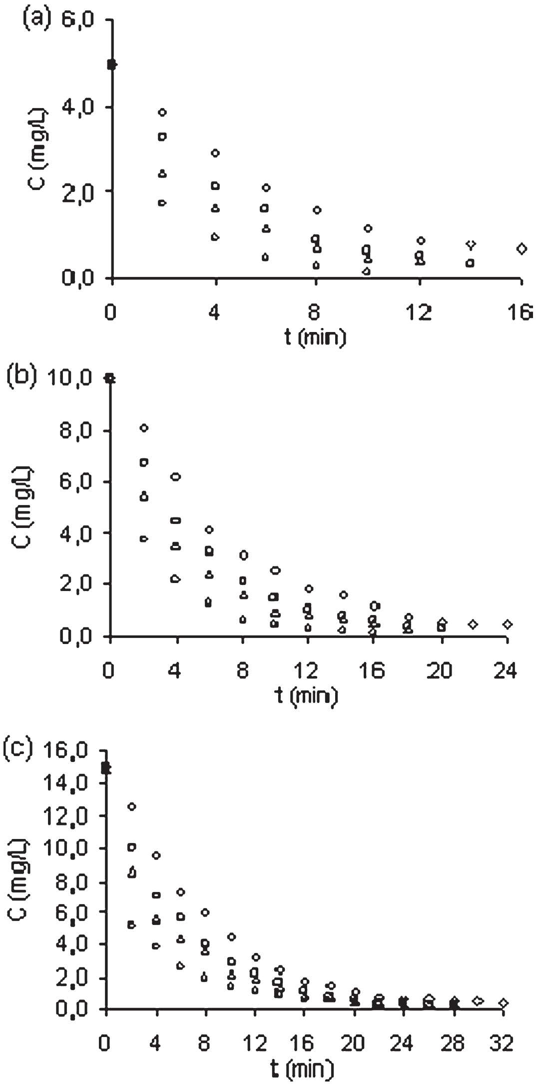

Fig. 7. Ozonation of Sirius Blue SBRR at T = 20°C and initial pH: (◊) 6,0, (□) 8,0, (△) 10,0, (○) 12,0; C_0= (a) 5, (b) 10, (c) 15 mg L^{-1}.

Table 1
Line-fitted values of rate constant k, min^{-1}.

Azo dye	pH	k (min^{-1})		
		$C_0 = 5$ mg L^{-1}	$C_0 = 10$ mg L^{-1}	$C_0 = 15$ mg L^{-1}
Sirius Red F3B	6.0	0.139	0.124	0.115
	8.0	0.201	0.172	0.155
	10.0	0.297	0.235	0.182
	12.0	0.471	0.305	0.222
Sirius Blue SBRR	6.0	0.148	0.133	0.121
	8.0	0.226	0.193	0.166
	10.0	0.305	0.265	0.198
	12.0	0.495	0.343	0.254

The line-fitted values of k for the pH and the corresponding dye studied are given in Table 1.

Previously published data by Chu and Ma (2000), Demirev and Nenov (2005) and Turhan and Turgut (2007) indicate that at the condition of constant ozone concentration, which is the case in our study, the ozonation becomes pseudo-first order with respect to the dye [28,38,39].

Using equation [1] in the form of $C = C_0.e^{-kt}$, was calculated for the different C_0 based on the k graph values.

The above results clearly show that the rate of ozonation increases with the dye concentration. The effects of the initial dye concentration on the apparent rate constant were studied using the dependence log k = f (log C), as illustrated in Fig. 8.

Similarly, the results obtained previously with wastewater containing azo dye [34], the apparent rate constant (k_{app}) declines logarithmically with the initial dye concentration as follows:

Azo dye	K_{app} (min^{-1})
Sirius Red F3B	$0.0778 \times C_{dye}^{-0.6120}$
Sirius Blue SBRR	$0.1196 \times C_{dye}^{-0.5996}$

where C_{dye}, [mg L^{-1}].

3.2. Products of degradation

Practically, a portion of the reaction mixtures (Sirius Red F3B+ozone and Sirius Blue SBRR+ozone) were quenched after 30 min and analyzed by GC-MS trying to identify the more evident peaks. The results of such an identification step are reported in Figs. 9 and 10 where the chemical structures of nine identified by-products for Sirius Red F3B and the chemical structures of twelve identified by-products for Sirius Blue SBRR are shown, respectively.

From the chemical point of view, such structures, particularly those containing the hydroxy-group confirm the radical type mechanism ozone in oxidizing the Sirius Red F3B aromatic ring as well as in achieving its oxidative breakage.

4. Conclusion

An experimental investigation has been carried out to evaluate the effectiveness of indirect ozonation occurring by radical type reactions for enhancing the degradability of aqueous solutions of a model recalcitrant pollutant namely Sirius Red F3B and Sirius Blue SBRR at laboratory scale. A detailed examination of the results allows us to draw the following conclusions:

- It has been shown that the COD of direct dyestuff wastewater was reduced 58.89% for Sirius Red F3B and 60.95% for Sirius Blue SBRR after ozone bubbling treatment for 2 h.
- The results with the direct dyes showed that COD reduction and decolorization were remarkable under basic conditions of pH 12. A large amount of bubbles was formed at high inlet gas flow rates. High ozone concentration was effective for the reduction of COD.
- The results also indicate that during the ozonation, even though complete Sirius Red F3B and Sirius Blue SBRR degradation occurs in 10 min, ozone consumption goes further on for another 20 min after the time when most degradation reactions are completed.
- Decolorization kinetics Pseudo-first-order trends for the ozone dye reaction were observed in all of the

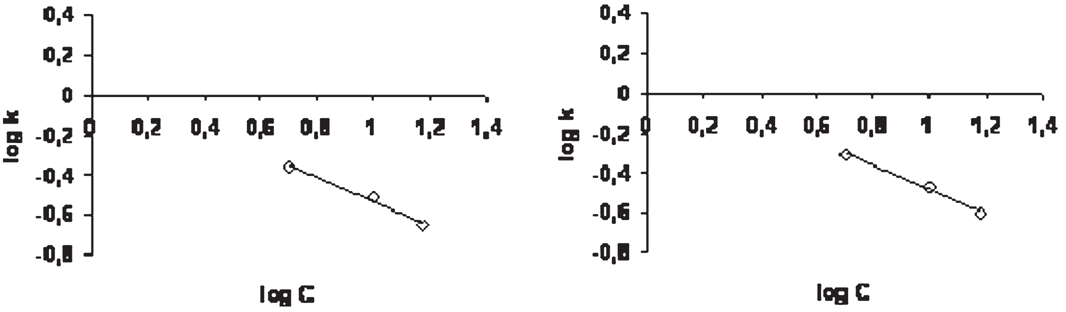

Fig. 8. log k = f (log C) plots, (a) Sirius Red F3B, (b) Sirius Blue SBRR.

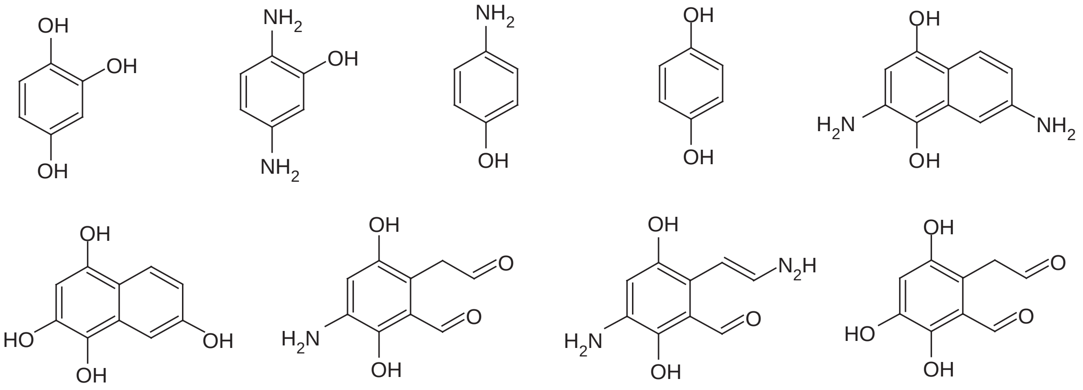

Fig. 9. GC-MS identified Sirius Red F3B ozonation by-products.

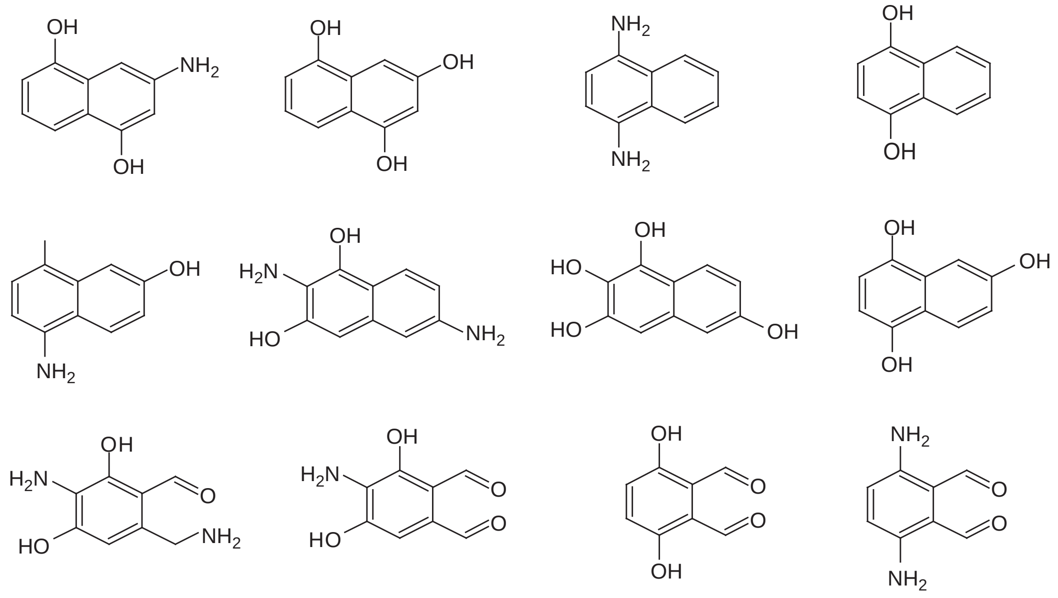

Fig. 10. GC-MS identified Sirius Blue SBRR ozonation by-products.

experimental runs. Aiming to explain the difference in dye kinetics the absolute electronegativity was utilized successfully as a descriptor in dyes reactivity. The explanations for the increase of *k* with the applied ozone dose and temperature observed in Figure 1, are that higher applied ozone dose increased the dissolved ozone concentration, C_{ozone}, which makes the decolorization faster; while higher temperature resulted in larger rate constant according to the Arrhenius equation.

- Among the ozonation by-products; acetone, formaldehyde, acetaldehyde, glyoxal, carbonic acid, formic acid, oxalic acid and acetic acids have been identified by HPLC and IC respectively. In addition, nine structural complex Sirius Red F3B and twelve structural complex Sirius Blue SBRR derivatives, proved to be poorly degradable, have been identified by GC-MS.

Further investigations are currently in progress for better elucidate the whole oxidation pathway as well as for evaluate the effect of ozonation on real samples of industrial wastewaters.

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