

## Oxidation by-products of the *C.I. Direct Blue 106* dye after ozonation

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*The oxidation of the often used oxazine direct dye C.I. Direct Blue 106 (Direct Dye 106) in an aqueous solution (600 mg L<sup>-1</sup>) by ozonation was investigated. VIS spectra showed degradation of the oxazine groups in the initial Direct Dye 106 structure. The oxidation by-products, such as sulphate, nitrate, nitrite, chloride ions and phenolic compounds, were identified by MS-MS and the LC-MS analyses. After ozonation the wastewater containing the Direct Dye 106 showed no toxic characteristics, according to Daphnia magna test (24 h- EC<sub>50</sub> > 75 %).*

**Key words:** ozone, coloured wastewater, C.I. Direct Blue 106, oxazine, oxidation by-products, MS-MS, LC-MS, Daphnia magna toxicity test

### 1. Introduction

Textile wastewater from the dyeing-and-finishing textile industry contains high levels of chemicals, a high biochemical oxygen demand, suspended solids and an intensive colour [1-3]. The decolourization of wastewaters from textile dyeing and dye manufacture is one of the main problems of the textile industry [3]. Conventional wastewater-treatment technologies, such as granular activated carbon absorption, coagulation, flocculation, based on aerobic and anaerobic digestion, produce large amounts of sludge with expensive

handling requirements [4]. Limitations of conventional wastewater-treatment methods can be overcome by the application of Advanced Oxidation Processes. Ozone (O<sub>3</sub>) is considered as one of the potential strong oxidants for the treatment of effluents from the textile dyeing-and-finishing industry [3, 5].

Chemical oxidation using oxidants, such as ozone, hypochloride or hydrogen peroxide, can be used to degrade textile dyes to a colourless solution. After this the breakdown products can be removed by conventional biological treatment processes [3, 4]. Ozone oxidation is known to

be effective for decomposing organic chemicals with their carbon-carbon double bonds, olefinic double bonds, acetylenic triple bonds, aromatic compounds, phenols, polycyclic aromatics and complex structures of different types of dyes [3, 5]. Ozone specifically attacks the conjugated chains that impart colour to the dye molecule [6]. The cleavage of C=C double bonds and other functional groups shifts the absorption spectra of the molecules out of the visible range [3]. The high reactivities of the ozone and OH<sup>·</sup> radicals are the reasons for the less-selective reactions: as a result, a variety of products is

formed in small amounts [7]. Certain by-products formed, e.g., resorcinol and salicylic acid, are considered to be more harmful than the initial compounds [8]. Therefore, the general ecological requirement for the decolourized water before its disposal is for it to be non-toxic or for its oxidation by-products to have a negative impact on the environment [9].

Direct dyes contain chromophoric groups, such as oxazine, tiazol, phtalocyanine, etc. During ozonation they lose colour by the oxidation of the conjugated double-bond system, while at the same time the toxicity of the treated wastewater can be reduced [10].

It is generally known, that azo dyes represent the largest class of organic colorants (60-70 % of all listed in Color Index), and moreover their relative share among direct, acid and reactive dyes is even higher [11]. Azo dyes and by-products are toxic, due to presence of toxic amine in the effluents [12].

By-products derived from direct dyes are less ecologically problematic in comparison to reactive dyes due to the absence of heavy-metal ions in their structure. Some studies confirmed that direct dye's by-products have a less-toxic effect on the environment compared to reactive dyes [13].

Dyes with oxazine chromophore are less prone to formation of toxic amine. During the  $TiO_2$  photocatalytic degradation of 1,4 oxazine dye morpholine the formation of hydroxy and oxo derivatives as degradation intermediates was demonstrated. All organic intermediates were eventually destroyed and organic nitrogen was transformed into ammonium ions [14].

Based on an extensive literature review, we found that no paper has explicitly reported on *Direct Dye 106* decolourization/oxidation and the identification of by-products and intermediates resulting from the ozonation.

Oxidation by-product studies can be carried out using a high-resolution mass analyzer, according to the mass-spectroscopy method (MS-MS).

The measurement of the molar masses with a deviation of less than 5 mg  $L^{-1}$  allows a determination of the empirical formulae, which is especially efficient when chemical structure of the original dye is known and it enables to define the oxidation products' structures [9]. Ibanez with co-workers studied the oxidation of triazine derivatives with UV radiation and identified the by-product structures on the basis of accurate masses [15]. Another example of an LC-MS application with accurate masses was reported by Calbiani, who were investigated Sudan dyes in hot chilli products [16]. Similarly, in the presented research, we determined some ionized structures as the possible oxidation products of *Direct Dye 106* using the MS-MS method.

The aim of the presented research was to identify the oxidation products of the direct dye *Direct Dye 106* with oxazine chromophore after ozonation, since there is a lack of in-

formation in the literature regarding the oxidation products and their toxicity after ozonation of the chosen dye. Relevant data about the formed dye by-products and their toxicological impact represent helpful information for the selection of the wastewater-treatment method in the case that the wastewater contains a dye of a similar structure.

## 2. Experimental part

In the experimental work the commercially available *Direct Dye 106*, *C.I. Direct blue 106*, *C.I. 51300*, known as Tubantin dye (598 nm) of unknown purity, was used. The molecular structure of *Direct Dye 10* is presented in Fig.1.

Preliminary decolourization experiments were performed at different pH values (4; 7 and 12) to learn about the optimal conditions to achieve the highest decolourization rate in shortest time. The optimal pH ~12 corresponds with findings from literature [3].

The ozonation was performed using model wastewater with an initial dye concentration ( $C_0$ ) of 600 mg  $L^{-1}$

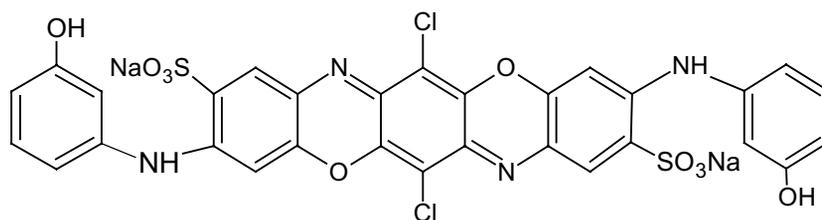


Fig.1 Molecular structure of *Direct Dye 106*

Tab.1 Characteristics of the model wastewater before and after the ozonation

Parameters	Units	MAC*	Method/standard	before/after ozonation	
pH	-	6.5-9.5	SIST ISO 10523	12.0	11.4
Conductivity	mS $cm^{-1}$	-	SIST EN 2788	2.1	1.5
Colour at 525 nm (SAC)	$m^{-1}$	5	SIST ISO 11083	453	3.4
Toxicity ( <i>Daphnia magna</i> )	$S_D$	4	SIST EN ISO 6341	1.5	1.3
COD	mg $O_2 L^{-1}$	200	SIST EN ISO 6060	3084**	164

\*MAC – maximum allowed concentration for direct disposal into water – (OG, RS, no. 7/2007)

\*\* pH adjusted ~ 12

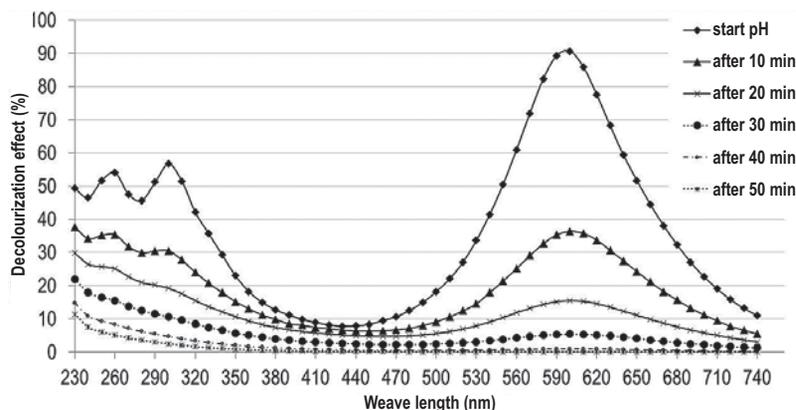


Fig.2 Changes in the absorption spectra of Direct Dye 106 ( $C_0 = 600 \text{ mgL}^{-1}$ ; pH  $\sim 12$ ) during 60 min of ozonation ( $2 \text{ gL}^{-1}\text{h}^{-1} \text{ O}_3$ )

[17]. The dye, as purchased from the manufacturer, was dissolved in hot distilled water ( $90 \pm 3 \text{ }^\circ\text{C}$ ). Before the ozonation the pH of the model solution was adjusted to  $\sim 12$  ( $0.1 \text{ M NaOH}$ ).

The wastewater samples were collected prior to, and during, the oxidation process after 10; 20; 30; 40 and 60 min and analysed according to standardized methods. Characteristics of the model wastewater before and after the ozonation are presented in Tab.1.

### 2.1. Apparatus and methods

A lab-scale ozonator Ozomatic LAB 802 generator (Wedeco GmbH, GER) was used to perform the ozonation. Initially, the model wastewater with a volume of 1000 mL was put into the reactor with a volume of 1.5 L. Pure oxygen was pumped into the ozone generator to produce ozone. The diffusion rates of the ozone, introduced at the bottom of the reactor, were 2 and  $2.5 \text{ g L}^{-1} \text{ h}^{-1}$ . The excess ozone was passed into a gas-absorption bottle containing 2 % KI solution [13].

The pH value and the conductivity were determined using an electronic T/pH/conductivity meter (Mettler Toledo Ltd., UK) [18,19]. The total organic carbon (TOC) was determined spectrophotometrically using the cuvette test LCK 386 (Dr. Lange GmbH, GER). The absorbance was measured using a Cary 50 spectrophotometer (Varian, Inc., USA) [20].

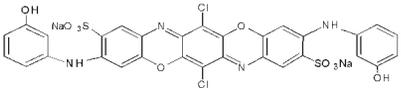
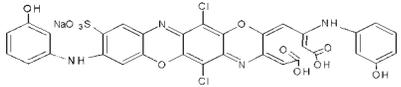
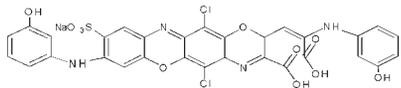
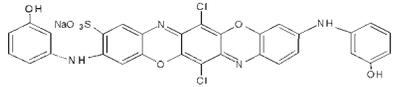
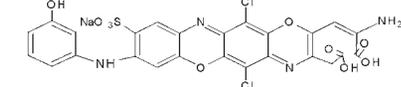
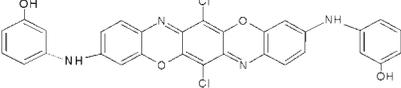
The decolorization effect was determined at three wavelengths in the visible range according to the Slovenian environmental regulation [21]:  $\lambda = 436, 525$  and  $620 \text{ nm}$ . The wavelength  $\lambda = 525 \text{ nm}$  matches the absorption maximum of the *Direct Dye 106* ( $\lambda_{\text{max}} = 598 \text{ nm}$ ); the maximum allowed spectral absorbance coefficient (SAC) after the decolorization

process is  $5 \text{ m}^{-1}$ . The decolorization efficiency was evaluated at  $\lambda_{\text{max}} = 598 \text{ nm}$ .

The toxicity tests of the prior and ozone-treated samples were performed according to the standard method [22]. Similar toxicity tests were performed for measurements on 24 h newborn *Daphnia magna* at different dilution rates (5; 15, 30; 60 and 90 %) [23]. Five daphnids in 10 mL of effective volume were exposed for 24 h. All the tests were run as triplicates. The results were evaluated on the basis of the immobilization percentage obtained by dividing the number of immobilized daphnids by the total number of exposed daphnids.

The toxicity results are interpreted as the 24 h- $\text{EC}_{50}$ , from the data interpolation on the graph representing immobilized daphnids in % vs. tested solution diluted at different dilution rates. From the determined 24 h- $\text{EC}_{50}$  the dilution factor ( $S_D$ -values) were

Tab.2 Ionized structures of the *Direct Dye 106* with exact molecular masses identified by the MS method

Ionized structures Direct Dye 106	Empirical formula	Molecular weight [g mol <sup>-1</sup> ]
<b>O</b> 	$C_{30}Cl_2H_{16}N_4Na_2O_8S_2$	<b>773</b>
<b>A</b> 	$C_{32}Cl_2H_{19}N_4NaO_{11}S$	<b>761</b>
<b>B</b> 	$C_{30}Cl_2H_{19}N_4NaO_{11}S$	<b>737</b>
<b>C</b> 	$C_{30}Cl_2H_{17}N_4NaO_7S$	<b>671</b>
<b>D</b> 	$C_{25}Cl_2H_{13}N_4NaO_{10}S$	<b>655</b>
<b>E</b> 	$C_{30}Cl_2H_{18}N_4O_4$	<b>569</b>

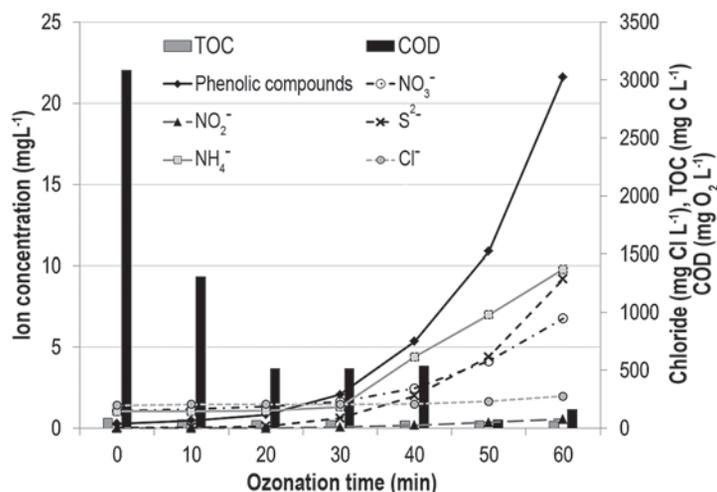


Fig.3 TOC and COD removal of *Direct Dye 106* and the measure of the ion concentration, pH ~12;  $C_0 = 600 \text{ mg L}^{-1}$ ;  $O_3$  dose  $2 \text{ g L}^{-1} \text{ h}^{-1}$ ; room temperature

acetonitrile (1:1, v/v) mixture. The MS and MS-MS analyses in the positive- and negative-ions mode by direct flow injection were performed using an MDS Sciex API-3000 triple quadrupole MS instrument (Applied Biosystems). The data were acquired in the range of  $m/z$  40 to 400 with 2 s per scan in the negative-ion mode. The interface temperature was set at  $100 \text{ }^\circ\text{C}$ . The sample flow rate was  $0.5 \text{ mL min}^{-1}$ .

Anions were determined by ionic chromatography (IC) using an IonPac AS12A column (Dionex,  $250 \times 4 \text{ mm}$ ) and a conductivity detector (Dionex CD20). The IC was performed

calculated according to the equation Eq. (1):

$$S_D = 24 h - EC_{50} / 100 \% (v/v); \quad (1)$$

where:  $24 h - EC_{50}$  is effective concentration after 24 h (%) and  $S_D$  is dilution factor according to the Slovenian legislation [21]. The textile wastewater is allowed to be disposed of directly into surface water up to  $S_D = 4$ , where it is understood that the higher the  $S_D$  value is, the more toxic is the sample.

The mass-spectroscopy (MS) analyses were performed using an API 3000 mass spectrometer system. The detector mass range was  $m/z$  50–800 at 1 s per scan for the initial dye solution and varied according to the analyzed sample. The MS was operated with a heated capillary at a temperature of  $400 \text{ }^\circ\text{C}$ . The source voltage was 4.5 kV. The analytical column was a C18. The analytical column was a C18, as mobile phase 10 mM ammonium acetate was used. The flow rate was  $5 \mu\text{L min}^{-1}$  with acetonitrile 20 mM ammonium acetate ratio 5:95 and increased to 30:70 within 20 min.

Model wastewater samples (10 mL) for MS-MS analyses were collected during the ozonation in 10 min intervals. Before analyses the samples were evaporated to a constant mass at room temperature and then re-dissolved in a 1 mL solution of water-

Tab.3 Ionized structures of possible degradation by-products of the *Direct Dye 106* with exact molecular mass identified by the MS method

Structures of empirical formula degradation products	Empirical formula	Molecular weight [g mol <sup>-1</sup> ]
<b>F</b> 	$C_{20}Cl_2H_{20}N_4O_8$	515
<b>G</b> 	$C_{14}Cl_2H_6N_2O_{10}$	433
<b>H</b> 	$C_{18}Cl_2H_{18}N_4O_3$	409
<b>I</b> 	$C_{30}Cl_2H_{18}N_4O_4$	351
<b>J</b> 	$C_{18}Cl_2H_4N_2O_2$	301
<b>K</b> 	$C_{11}Cl_2H_6N_2O_3$	285
<b>L</b> 	$C_{10}Cl_2H_4N_2O_2$	255

med in suppressed conductivity-detection mode, with an ASRS UII/4 suppressor (Dionex). The mobile phase was prepared each day by mixing 2.7 mM Na<sub>2</sub>CO<sub>3</sub> and 0.3 mM NaHCO<sub>3</sub> in mili Q water. A 20 µL sample loop injection volume was used at a 1.5 mL min<sup>-1</sup> flow rate of the mobile phase.

### 3. Results and discussion

#### 3.1. Oxidation of the oxazine group

The effect of decolourization achieved during ozonation of the model wastewater containing *Direct Dye 106* was analyzed by VIS spectroscopy. The samples, taken every 10 min and additionally every 2 min between 20 to 40 min, during the 60 min long treatment were analysed by measuring the absorbance. The decolourization rates during ozonation are presented in Fig.2.

The absorption maximum of the treated solution was determined at  $\lambda_{\max} = 598$  nm. This corresponds to the blue colour that originates from the conjugated  $\pi$  – bonds present in the investigated dye structure. The spectra shows that the colour intensity at the absorption maximum decreases most rapidly between 10 and 24 min of treatment, where decomposing of the oxazine chromophore group is assumed. The band in the visible range disappears after 50 min of ozonation and the absorption value is below 0.02, indicating the ultimate breakdown of the oxazine chromophoric group.

COD and TOC were monitored during the oxidation in order to evaluate the toxicity and mineralization rate of the organic substances in water. The COD reduction corresponds well with decolourization rates and was reduced by 60 %, from initial 1310 mg L<sup>-1</sup> O<sub>2</sub> to 520 mg L<sup>-1</sup> O<sub>2</sub>, after 20 min of ozonation at pH ~12 with 2 g L<sup>-1</sup> h<sup>-1</sup> O<sub>3</sub>, while the final COD value after 60 min was reduced to less than 85 % (164 mg L<sup>-1</sup> O<sub>2</sub>) of initial value

and corresponds good with the MAC for waste water disposal (200 mg L<sup>-1</sup> O<sub>2</sub>). After 60 min of ozonation at pH ~12 with 2 g L<sup>-1</sup> h<sup>-1</sup> O<sub>3</sub> the initial TOC value (Fig. 3) was reduced by 30 %, from 84.4 mg C L<sup>-1</sup> to 59.9 mg C L<sup>-1</sup>. This result indicates that the *Direct Dye 106* molecule was split into smaller organic molecular fragments, probably acetic acids, aldehydes, ketones [5,9] although the initial chloride concentration was around 200 mg/L due to the salt content in the dye (-SO<sub>3</sub>Na). The residual TOC consisted of other unidentified oxidation by-products derived from the partial mineralization. It is considered [24] that the reaction does not result in a complete mineralization to carbon dioxide, even in the presence of excess ozone.

#### 3.2. Identification of lower structures

To obtain detailed information about the reaction pathway and the oxidation by-products during the ozonation, the ozonated solutions were analysed for specific ions contents spectrophotometrically. Sulphate, nitrate, nitrite, chloride, ammonium ions and phenolic compounds were identified as the main oxidation fragments of the *Direct Dye 106* after 60 min of ozonation. Most abundant ions' concentrations during ozonation are presented in Fig. 3. According to literature findings [3] a possible explanation for the pH decrease during ozonation from pH 12 to pH 11.4, besides the formation of certain inorganic acids, is that some of the nitrogen was degassed from the solution by the formation of NH<sub>3</sub>, N<sub>2</sub>, NO or NO<sub>2</sub>. The nitrate originates from the oxidation of the amino group [3], as a result of chromophore group oxidation. The oxidation of the sulphonic groups from the original dye structure leads to an increase in the sulphate content during ozonation treatment.

Similar results were obtained [2] during the 150 min of oxidation for the purified, hydrolyzed azo dye, C.I.

Reactive Red 120, with 12.8 mg L<sup>-1</sup> of ozone. Increased concentrations of chloride and sulphate ions determined by IC confirmed the formation of oxidation by-products with lower structures and molecular masses.

The MS-MS analysis results show that when a single-dye solution is ozonated, the formed products probably originate only from the weakest part of the structure of the decomposed direct dye. Considering this fact and the measured accurate molar masses, it is possible to determine the correct empirical formulae and often the structures of formed by-products [9]. The chemical structures, originating from the initial model solution containing *Direct Dye 106* before the ozone treatment, are compared to those detected after ozonation using the MS detector.

The masses of fragments, deriving from the initial dye structure, formed before the ozonation and mineralization were detected and identified by MS-MS (Fig.4a, Tab.2). The major peaks, resulting from ionized initial structures of *Direct Dye 106*, appear at  $m/z$  values of 655 (structure D), 569 (E) and 671 (C) as shown in Fig.4a. After 10 min of ozonation these structures were split into fragments with lower molecular masses and  $m/z$  values of 351 (structure I), 301 (J), 255 (L), 285 (K), 409 (H), 515 (F) and 433 (G), as shown in Table 3 and in Fig.4b. The ionized structures of the presumed oxidation by-products are presented in Table 3 without functional groups. The ozone attacked the amino groups that bind the phenol with the rest of the *Direct Dye 106* molecule. It is anticipated that during ozonation the ozone decomposes the benzene rings on each side of the oxazine chromophore and after 40 min of ozonation; the chromophore is also degraded, as shown by VIS absorption spectra.

Based on the presented results, it can be stated that the peaks at  $m/z$  351, 368, 255, 385 and 431 (in Tab.3) are the prevalent oxidation products of

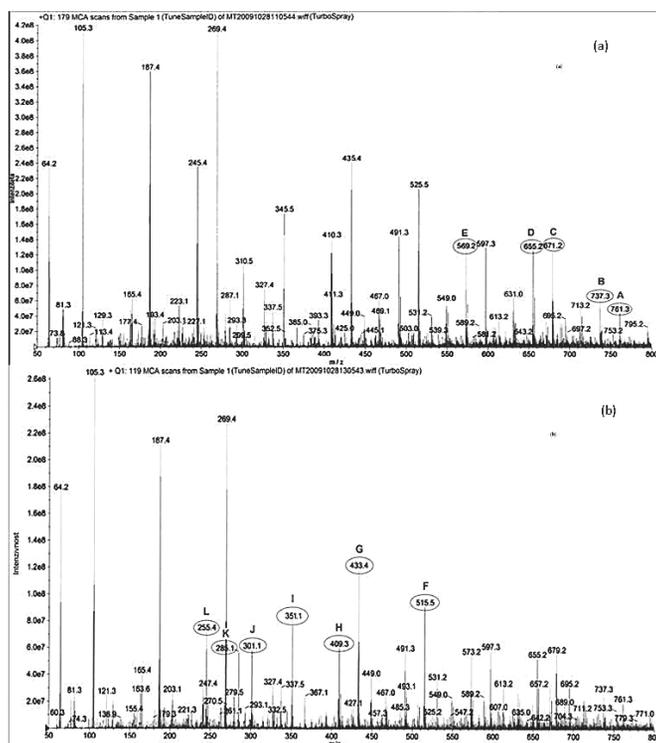


Fig.4 The MS mass spectra of Direct Dye 106 ( $C_0 = 600 \text{ mgL}^{-1}$ ): a) before ozonation and b) after 10 min of ozonation

Tab.4 Toxicity test results of samples taken during the ozonation treatment

Sample	24 h- $EC_{50}$ (%)			$S_D$ value		
	I	II	III	I	II	III
I	69.9	68.9	65.7	1.43	1.45	1.52
after 10 min	90.0	87.3	95.2	1.11	1.14	1.05
after 20 min	98.2	92.4	96.8	1.01	1.08	1.03
after 40 min	83.4	72.6	69.8	1.19	1.37	1.43
after 60 min	78.7	75.1	73.2	1.27	1.33	1.36

*Direct Dye 106*. They were further decomposed to hydrogenated organic by-products, resulting in substituted benzene, different ions and phenolic compounds. These substituted products can, under optimal conditions, be further oxidized and finally mineralized into carbon dioxide and water [3]. The breaking of the benzene rings into organic acids was confirmed by a decrease of the pH value and by a substantial increase in the conductivity during the ozonation, as also reported elsewhere [2]. Due to the limitation of the IC separation and the sensitivity of MS-MS detector, some oxidation products could not be identified. More detailed analyses of the complete oxida-

tion pathway could be performed by a combination of the GC-MS and CZE-MS techniques, as suggested in literature [9].

### 3.3. Toxicity test

The environmental impact of the treated model wastewater before and after the ozonation process was determined using the *Daphnia magna* toxicity test. The toxicity test results, presented in Tab.4, showed that the percentage inhibition (24 h- $EC_{50}$ ) of the tested solutions increased on average from 68.1 % to 75.6 %. The average calculated dilution factor ( $S_D$ ) varied from 1.46, for the initial sample, to 1.32 after 60 min of ozonation. According to the Slovenian

legislation [18] the result indicates no toxic potential for the treated wastewater's direct disposal into the environment as the MAC value is  $S_D = 4$ , while for disposal into the sewage system the MAC is not defined.

## 4. Conclusions

Strongly coloured wastewater and process effluents from the textile dyeing-and-finishing industry require well considered and optimized treatment processes, within which the evaluation of the eco-toxicological properties is strongly recommended, before disposing of it directly to the environment or surface water or into the sewage system.

The presented research was focused on an identification of the oxidation by-products of the commercially available oxazine dye *C.I. Direct Blue 106*, which is often used in the textile industry. The aim of the experiments was to evaluate the efficiency of the ozonation treatment for decolorizing the model wastewater containing a chosen dye and to further determine its oxidation structures/by-products and to predict the oxidation pathway.

The identification of the oxidation structures and intermediates is of crucial importance for proposing some general idea about the oxidation pathway [3,9]. The results show that after 20 min of oxidation the colour at a maximum absorption value of 598 nm is reduced to less than 50 % of the initial value (Fig.2), while larger molecules of intermediates are formed already after 10 min of treatment (Fig.4) and further decomposed to lower structures, identified in Tab.3. All after strong oxidation identified by-products, among them sulphate, nitrate, nitrite, chloride, ammonium ions and phenolic compounds in majority do not exhibit toxic properties.

As a result, ozonation has been proved to be a powerful tool for the fast and efficient decolourization of wastewater containing the direct oxazi-

ne *Direct Dye 106* without the formation of any hazardous residues. A detailed determination of the oxidation pathways as well as the corresponding by-products requires further research using a complex analytical approach, employing a combination of the techniques GC-MS and CZE-MS. Nevertheless, the present results show the intermediates and the subsequent lower structures by *Direct Dye 106* oxidation during ozonation. The performed oxidation process proved to be an efficient treatment for the decolourization of textile wastewater containing the chosen oxazine dye without the formation of any harmful residues for the environment.

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