

# Oxidative decomposition of Acid Brown 159 dye in aqueous solution by $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ and ozone with GC/MS analysis

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Received 11 September 2005; received in revised form 20 December 2005; accepted 13 January 2006

Available online 13 March 2006

## Abstract

The oxidative degradation of metal-complex Co(II) Acid Brown 159 in aqueous solution by  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  and ozone was investigated. Optimal conditions for decolorization and total decomposition processes were found for dye oxidation during  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  and ozone treatments. The full 100% decolorization is attained during first minutes of  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  and ozone oxidation processes. The complete mineralization of aqueous solutions of Acid Brown 159 dye cannot be achieved even under the optimal reaction conditions. Fenton's process appeared to be more effective in comparison with ozonation. A tentative mechanistic pathway for the oxidative degradation of Acid Brown 159 dye in aqueous solution was postulated.

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*Keywords:* Fenton process; Ozonation; Metal-complex azo dye; Oxidation; Decolorization; Decomposition

## 1. Introduction

Metal complexes of monoazo compounds are principally useful as trivalent chromium and cobalt complexes for dyeing of protein and polyamide fibers [1].

Metal-complex dyes are very versatile in terms of applications. Virtually all substrates, apart from a few synthetic fibers, can be dyed and printed with this class of dyes. Countless shades from greenish yellow to deep black can be generated, depending upon the metal, the dye ligands, and the combination of dye ligands in mixed complex dyes [2]. In commercial terms the most important chelated metals are chromium, cobalt, copper, iron, and nickel. The resulting dyeing of chromium and cobalt complex dyes is in general dull but exhibits a high standard of fastness, particularly light fastness. Because of the dullness, these metal complexes are chiefly used for deep colors procedure for which a large amount of dye must be applied. Their use is restricted to nitrogen-containing substrates, such as

wool, nylon, and leather, since they have only a little affinity to cellulosed fibers. However, with the advent of reactive dyes, chromium and cobalt complex dyes containing a fiber-reactive group also find application in cellulose dyeing.

Acid Brown 159 is one of the metal-complex derivatives belonging to the overwhelming majority of synthetic dyes currently used in the industry. The impact and toxicity of dyes that are released in the environment have been very important and extensively studied [3]. Our knowledge concerning dyes behavior in the environment and health hazards involved in their use is still incomplete. Standard wastewater treatments appeared ineffective because of the chemical stability of most dye pollutants that makes them non-biodegradable. A wide range of methods have been developed for the removal of synthetic dyes from waters and wastewaters to decrease their impact on the environment. The applied methods involve adsorption, decolorization by photocatalysis, and/or by oxidation process, biological decomposition, etc. [3]. The efficiency of various methods of dye removal, such as chemical precipitation, chemical oxidation, adsorption and their effects on biological treatment were reported in earlier papers [4,5]. Strongly dependent on oxidant type, chemical oxidation

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pretreatment is a prerequisite condition for the subsequent activated sludge process [6].

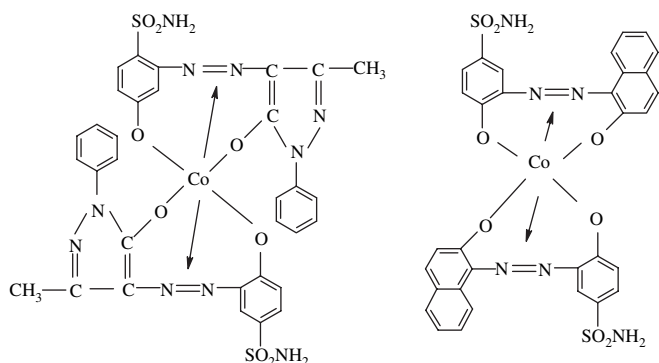
Hydrogen peroxide can effectively decolorize dye from wastewaters in the presence of Fe(II) sulfate [7,8]. Optimal conditions for decolorization were found to be different for each type of dye, indicating that the development of a general oxidation method for a mixture of dyes would be very difficult. Thus, compromise must be made that is suitable for the decomposition of each dye at a reasonable oxidation rate [9]. UV/H<sub>2</sub>O<sub>2</sub> treatment can be successfully used for the decolorization of acid, basic and reactive dyes [10]. The influence of operating parameters on the decolorization of reactive dye by ozone has been studied in detail [11]. The results indicated that the decomposition rate increased with increasing pH and temperature [12].

This paper is devoted to Acid Brown 159 in aqueous solution neutralized by advanced oxidation process (AOP) involving ozonation (O<sub>3</sub>) and Fenton (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>) processes. The operating parameters such as oxidant dosages, initial dye concentration, pH of solution and reaction time were determined to find optimum conditions for complete decolorization and total oxidation of dye solution. The toxicity of initial and final solutions was determined using Texoallert tests. Also, on the basis of GC/MS analysis a tentative mechanistic approach of Acid Brown 159 dye decomposition in aqueous solution is postulated.

## 2. Experimental

### 2.1. Materials

Acid Brown 159 is a synthetic mixture of two Co-complex dyes with a molar ratio equal to 1:2; complex A about 70%, molecule of 2-aminophenyl-4-sulphonoamid coupling with 1-phenyl-3-methylpirazol-5 and complex B about 30%, molecule of 2-aminophenyl-4-sulphonoamid coupling with 2-naphthol. This dye was obtained from Dyestuff Industry Works "Polfa-Pabianice" in Poland and it is applied in tanning and textile industries. Molecular formulas of these two complexes of Acid Brown 159 dye are as follows:



### 2.2. Apparatus and procedure

The H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> Fenton oxidation experiments were carried out in a reactor with constant volume. Concentration of dye in

demineralized water, 100 mg/dm<sup>3</sup>, was applied. Varied doses of FeSO<sub>4</sub> compound were added to the reactor, which contained dye solution and then pH was adjusted by means of H<sub>2</sub>SO<sub>4</sub> and NaOH solutions. After stirring the reactor content, the initial UV absorbance (A<sub>0</sub>) of the solution was determined at the specified wavelength 458 nm. Then the specified amount of oxidant H<sub>2</sub>O<sub>2</sub> was added to the reactor and the influence of reaction time on decolorization (UV absorbance A) and chemical oxygen demand (COD) were measured. From the measured absorbance values percentage of decolorization was calculated according to the formula:  $\alpha = (1 - A/A_0)100\%$ . Experiments of Acid Brown 159 oxidation by hydrogen peroxide were carried out at 40 °C.

The ozonation experiments were carried out in a reactor containing aqueous solution of dye, 100 mg/dm<sup>3</sup>, saturated in oxygen containing about 17 ppm of ozone with volume velocity 15 dm<sup>3</sup>/h. In the course of the experimental run the following parameters were measured: concentration of ozone, redox potential, pH, temperature, time and UV absorbance.

Total organic content (TOC) was determined in TOC 505 Shimadzu analyzer. The FT-IR spectra of Acid Brown 159 dye compound were recorded on a Shimadzu 8150 spectrophotometer over the range 4000–400 cm<sup>-1</sup> using pellets of solid dye and KBr mixture. The concentrations of Co and Fe were analysed by ICP method.

### 2.3. GC/MS analysis

Samples were prepared by the extraction of dye decomposition products with hexane and tetrachloromethane solvents and finally solutions were concentrated in SPE (NEXUS, Varian) apparatus with octadecyl columns. An Agilent 6890N gas chromatograph (GC) with 5973 mass-selective (MS) detector and Chem Station data system was employed to identify the intermediates of dye Acid Brown 159 solution degradation. The capillary column HP-5MS (cross-linked 5% phenyl-methylsilicone) was 30 m × 0.25 mm × 0.25 μm. The temperature ramp was programmed from 40 °C to 80 °C with linear rate 10 °C/min, then to 280 °C at 4 °C/min. Helium was used as the carrier gas with a volume flow 0.9 cm<sup>3</sup>/min. The MS quadrupole of mass analyser, ion source temperature was 150 °C, ionization at 70 eV. Comparison of the experimental mass spectra with those stored in NIST 98 Library identified GC of fragmentation products of dye degradation.

### 2.4. The test for the inhibition of oxygen consumption by activated sludge

The test for the inhibition of oxygen consumption by activated sludge was performed on the basis of oxygen consumption rate changes at the constant temperature 20 °C. The oxygen consumption rate was measured in an OxiTop OC 100 device. Total volume of the solution was equal to 432 cm<sup>3</sup> in all the experiments. The oxygen consumption in dye solution was measured as a function of dye amount. The special program (EN ISO 8192) was used according to the formula:  $I = (R_B - R_T)/R_B$ , where R<sub>B</sub> and R<sub>T</sub> are the rates of

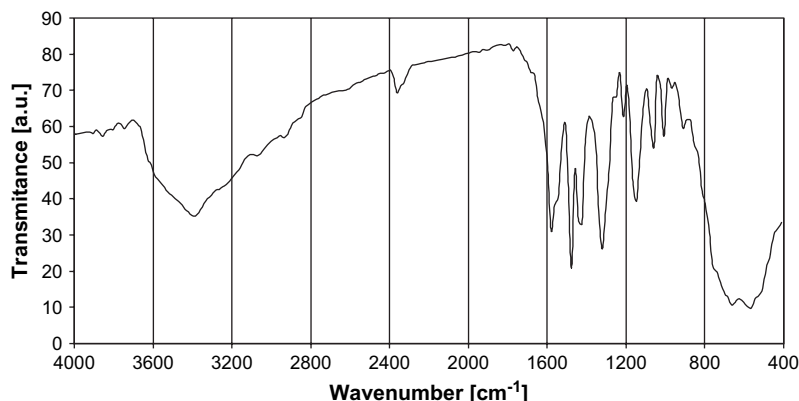


Fig. 1. FT-IR spectra of Co-complex dye Acid Brown 159 compound.

oxygen consumption of blank and controlled samples, respectively. On base of the obtained value  $I$  an influence of the examined dye solution on the oxygen consumption was estimated as inhibition when  $I \gg 0.1$  or stimulation when  $I \ll 0.1$ .

### 3. Results and discussion

#### 3.1. IR spectra of dye Acid Brown 159 identification

The metal-complex dye Acid Brown 159 compound can be identified by its characteristic IR spectrum, presented in Fig. 1. The assignment of registered IR bands is as follows. In the range of 2800–3620  $\text{cm}^{-1}$  the broad band and small features can be assigned to hydrogen bonded OH and NH stretching vibrations. The most characteristic bands are ring stretching C=C and C=N vibrations appearing in the range of 1600–1520  $\text{cm}^{-1}$ , doublet of C=C skeletal vibrations of the aromatic ring in the range 1500–1400  $\text{cm}^{-1}$ , singlet of C–CH<sub>3</sub>

vibrations at 1380  $\text{cm}^{-1}$ . In the range of 1360–1260  $\text{cm}^{-1}$  stretching “out of the plane” vibrations C–C, and in 1160–1120  $\text{cm}^{-1}$  C–H stretching vibrations appear. In the range of 1080–1040  $\text{cm}^{-1}$  coupling conjugation between S, O and N is observed. The characteristic “out of the plane” hydrogen deformation modes in naphthalene ring located in the range of 720–480  $\text{cm}^{-1}$  are overlapped with those characteristic of Co–O interactions in 550–400  $\text{cm}^{-1}$ , and also “out of the aromatic ring plane” vibrations are overlapped with C–S and C–N vibrations.

#### 3.2. Oxidation

The influence of the experimental parameters such as hydrogen peroxide concentration (mg of H<sub>2</sub>O<sub>2</sub> per 1 mg of a dye), Fe<sup>2+</sup> ion concentration and pH on the effectiveness of solution decolorization is presented in Fig. 2. The degree of decolorization higher than 80% can be easily achieved after 2 h of dye solution oxidation. The effect of pH of the reaction habitat ranging from 1 to 5 was investigated. The degree of dye decolorization higher than 70% (curve a) was achieved in pH range 2–3. The effect of ferrous ions was investigated in the concentration range from 0 to 50  $\text{mg}/\text{dm}^3$  (curve b).

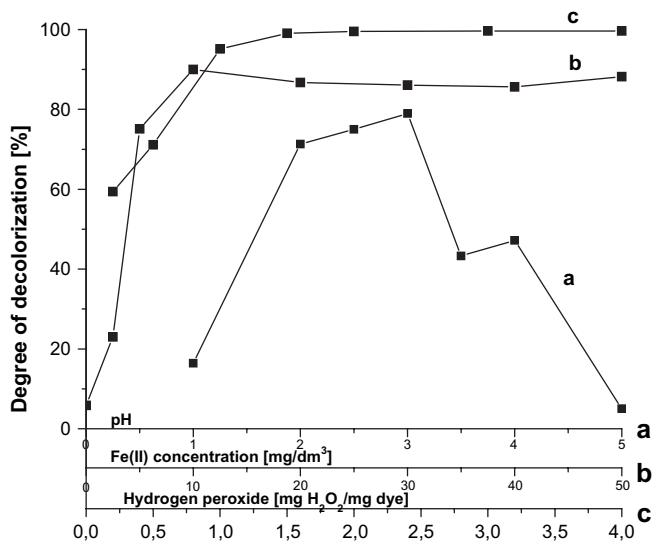


Fig. 2. Dependence of the degree of Acid Brown 159 dye solution decolorization on H<sub>2</sub>O<sub>2</sub> dose, Fe<sup>2+</sup> concentration and pH value of aqueous solution after 2 h of oxidation.

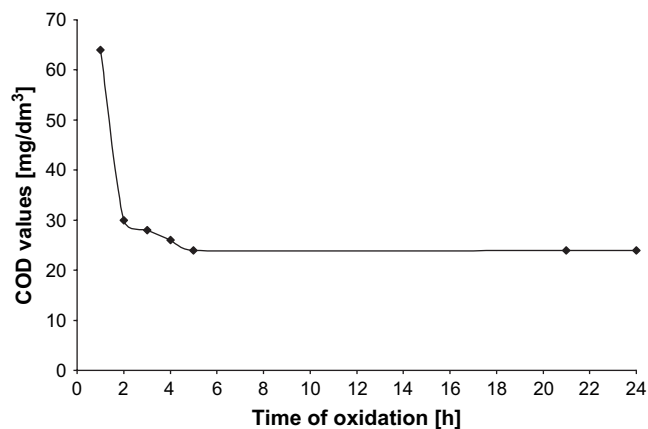


Fig. 3. COD values as a function of oxidation time of Acid Brown 159 dye solution by H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>.

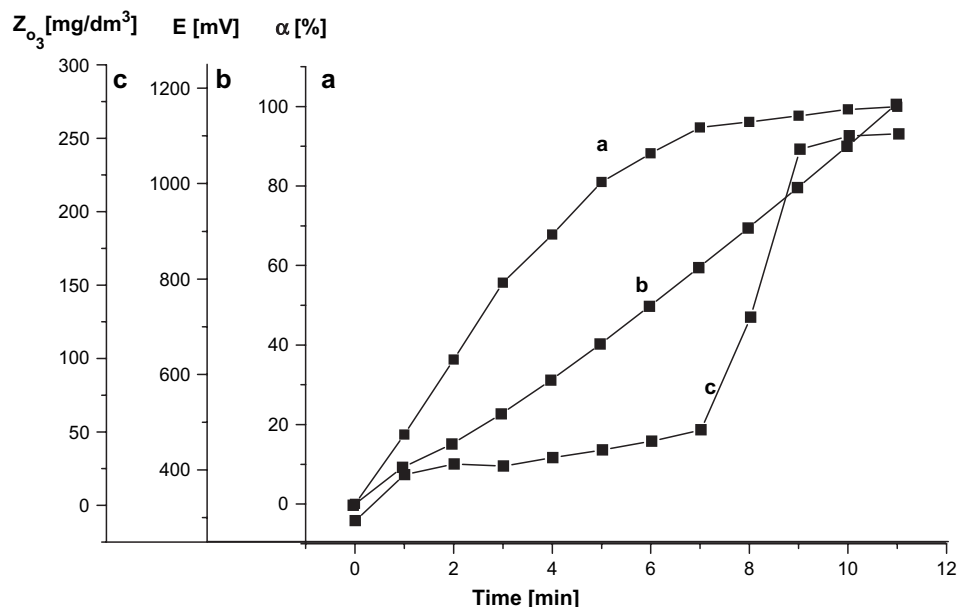


Fig. 4. Dependence of the ozonation parameters of dye solutions on ozonation time. (a)  $\alpha$  – Degree of decolorization (%), (b)  $E$  – redox potential (mV), and (c)  $Z_{O_3}$  – ozone consumption (mg/dm<sup>3</sup>).

The process of decolorization does not take place in the absence of  $Fe^{2+}$  ions. The efficiency was the highest when the concentration of  $Fe^{2+}$  ions was in the range 5–50 mg/dm<sup>3</sup>. The increase in  $H_2O_2$  concentration up to 2 mg per 1 mg of dye leads to 100% complete decolorization (curve c) at 40 °C. Thus, the following parameters were chosen as optimal conditions for further experiments of Acid Brown 159 oxidation: hydrogen peroxide concentration with the ratio of 2 mg of  $H_2O_2$  per 1 mg of a dye,  $Fe^{2+}$  ion concentration 10 mg/dm<sup>3</sup> and pH = 2.5.

The application of the above optimal conditions of dye solution oxidation leads to the results of the influence of reaction time on chemical oxygen demand (COD) values which are presented in Fig. 3. After 5 h of oxidation reaction the reduction of initial COD value was about 50% and after 24 h more than a 70% decrease in COD value was observed.

The results of ozonation for Acid Brown 159 in aqueous solutions with concentration of 100 mg/dm<sup>3</sup> are presented in Fig. 4. The time necessary to achieve nearly full decolorization  $\alpha = 100\%$  was 7 min. Also, the ozone consumption and redox potential are included in Fig. 4.

The comparative effects of the oxidation by hydrogen peroxide and ozone on the changes of chemical oxygen demand

(COD) and the total organic carbon (TOC) in aqueous Acid Brown 159 dye solution are presented in Table 1. Results of TOC analysis indicate that organic compounds are not completely oxidized to final products of oxidation,  $H_2O$  and  $CO_2$ . The decreases in TOC values were 90.4% and 54.1% after 2 h of oxidation by  $H_2O_2$  and ozone, respectively. The reduction of COD values was about 73.7% for hydrogen peroxide and 56.1% for ozone treatment.

### 3.3. UV–vis spectra

The comparison of UV–vis spectra of Acid Brown 159 in aqueous solutions before and after 2 h of oxidation by hydrogen peroxide and ozone is presented in Fig. 5. Both processes were performed in optimal conditions, which were chosen after preliminary measurements. The spectra of dye initial solution represent UV bands characteristic of  $-N=N-$  groups (514 cm<sup>-1</sup>) and related it to the benzene and naphthalene rings bonded to the  $-N=N-$  groups (220 and 322 cm<sup>-1</sup>) [13–15]. Absorption bands in visible region (458, 557 nm) are relevant to the whole conjugated structure. Thus, the  $\pi-\pi^*$  transition of electrons in the azo group connecting phenyl and naphthyl rings is responsible for the band. Within near ultraviolet region

Table 1  
An effect of the oxidation by hydrogen peroxide and ozone on changes of chemical oxygen demand (COD) and the total organic carbon (TOC) in aqueous Acid Brown 159 dye solution

Dye (Acid Brown 159)	Before oxidation		After oxidation by $H_2O_2$		After oxidation by $O_3$		$H_2O_2$		$O_3$	
	COD (mg of $O_2$ /dm <sup>3</sup> )	TOC (ppm)	COD (mg of $O_2$ /dm <sup>3</sup> )	TOC (ppm)	COD (mg of $O_2$ /dm <sup>3</sup> )	TOC (ppm)	$\eta_{COD}$ (%)	$\eta_{TOC}$ (%)	$\eta_{COD}$ (%)	$\eta_{TOC}$ (%)
	114	36	30	3.5	50	16.6	73.7	90.4	56.1	54.1

$\eta$  – Denotes the decrease of TOC and COD values (%).

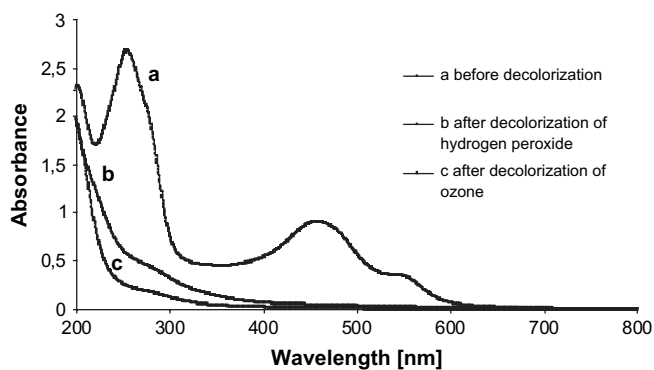


Fig. 5. UV-vis spectral changes of Acid Brown 159 solutions before and after 2 h of oxidation by  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ .

(260 nm), the absorption band results from the un-saturated character of benzene and naphthalene rings. The dramatic changes of UV spectra represent a disappearance of both azo and aromatic groups in the course of Acid Brown 159 dye degradation. Ozone treatment appears much more efficient than Fenton's process but this statement refers to the decolorization rather than to the process of the entire oxidation (compare COD and TOC values in Table 1).

#### 3.4. The inhibition test

The relationship  $I$  versus  $\log(\Delta_{\text{COD}})$  for the Acid Brown 159 dye in solutions before and after hydrogen peroxide or ozone oxidation is illustrated in Fig. 6. It is rather obvious that in the case of hydrogen peroxide oxidation the measured values  $I$  were about 0.1. After ozone oxidation a different range of value  $I$  from 0.1 to 0.5 is observed. Acid Brown 159 solution before oxidation gave value  $I \ll 0.1$ . On the basis of the above behavior one can estimate a dye concentration which is toxic for microorganisms of activated sludge and an adequate value  $I \gg 0.1$  is observed.

#### 3.5. GC/MS of dye Acid Brown 159

The main intermediate compounds of dye Acid Brown 159 degradation were identified by GC/MS method and they are

presented as GC chromatogram in Fig. 7. The major peaks were assigned to the most important compounds and they are listed in Table 2 and also their most significant ions are included according to the decreasing order of ion intensities in Fig. 7a. The long chains of carbons and alcohols obtained after hydrogen peroxide oxidation are shown in Fig. 7b, whereas aldehyde and conjugated acid compounds are presented in Fig. 7c after ozone oxidation.

One can anticipate that at the very beginning of dye molecule degradation process the rupture of azo ( $-\text{N}=\text{N}-$ ) and metal oxygen ( $\text{Co}-\text{O}$ ) groups takes place. Further, oxidation probably occurs via a variety of amine and/or nitro type of aromatic compounds formation, which are gradually transformed into long linear compounds as a result of aromatic ring opening by hydroxyl radical, originating from initial oxidation agents,  $\text{H}_2\text{O}_2$  or  $\text{O}_3$ . The results of GC/MS analysis show linear acids and aldehydes after Fenton's oxidation and alcohols and hydrocarbons in the case of ozonation process. The advanced oxidation can lead to deep mineralization of dye solution. The removal of cobalt and/or iron ions from dye solutions can be effectively accomplished in the form of precipitated metal hydroxides during alkalization process. A general oxidative decomposition of Acid Brown 159 dye pathway mechanism is schematically presented in Fig. 8.

## 4. Conclusion

Optimal conditions for decolorization and total decomposition processes were found for dye oxidation during  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  and ozone treatments. An entire decolorization of Acid Brown 159 dye in aqueous solution during the first minutes of oxidation process was obtained.

The complete mineralization of Acid Brown 159 dye solution cannot be achieved even under the optimal reaction conditions. Fenton's process appeared more effective than ozonation in deep oxidation of dye solution. A tentative mechanistic pathway for the oxidative degradation of Acid Brown 159 dye in aqueous solution was postulated.

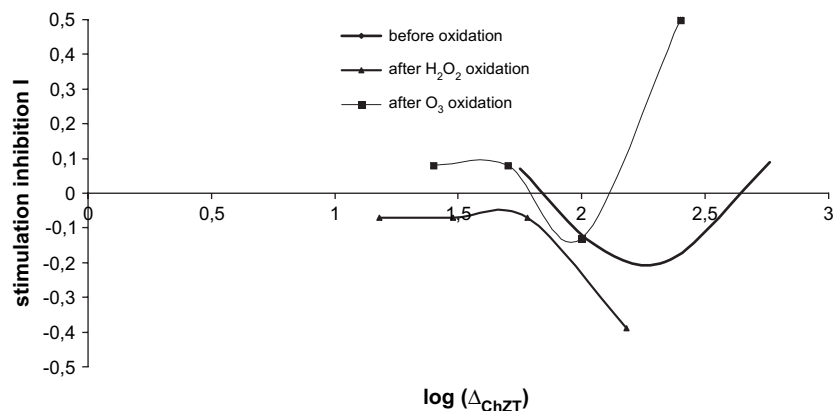


Fig. 6. The inhibition  $I$  of  $\log(\Delta_{\text{COD}})$  for Acid Brown 159 dye solutions before and after hydrogen peroxide and ozone oxidation.

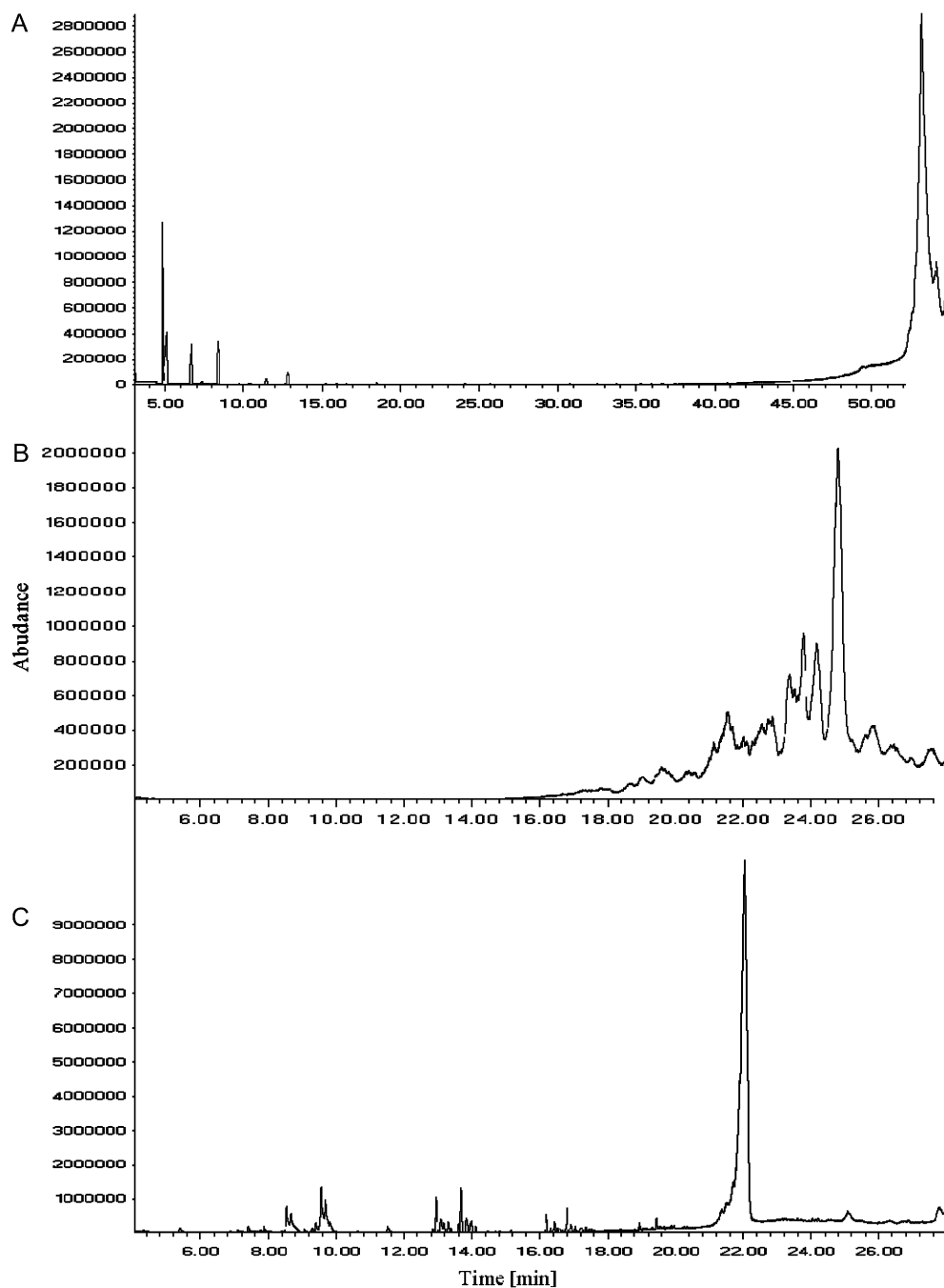


Fig. 7. Total ion GC/MS chromatogram of Acid Brown 159 oxidative decomposition products. (a) Before oxidation, (b) after  $\text{H}_2\text{O}_2$  oxidation, and (c) after  $\text{O}_3$  oxidation. The major peaks are identified in Table 2.

Table 2  
GC/MS analysis of fragmentation products

No.	Retention time on GC	Compound identified by MS	Formula	$M_w$	The major ions ( $m/z$ )
1	4.87	Acetophenone	$\text{C}_8\text{H}_8\text{O}$	105	105, 77, 120, 51, 50
2	5.01	1-methyl-1H-benzimidazol-2-amine	$\text{C}_8\text{H}_9\text{N}_3$	147	147, 119, 105, 90, 77
3	6.66	methyl N-hydroxybenzene carboximidoate	$\text{C}_8\text{H}_9\text{NO}_2$	133	133, 151, 73, 55, 68
4	8.37	N-(3,4-dimethyl-2,6-dinitrobenzyl) pentan-3-amine	$\text{C}_{13}\text{H}_{19}\text{N}_3\text{O}_4$	252	252, 281, 162, 192, 208
5	53.16	N-methylaniline	$\text{C}_7\text{H}_9\text{N}$	106	106, 77, 79, 51, 65

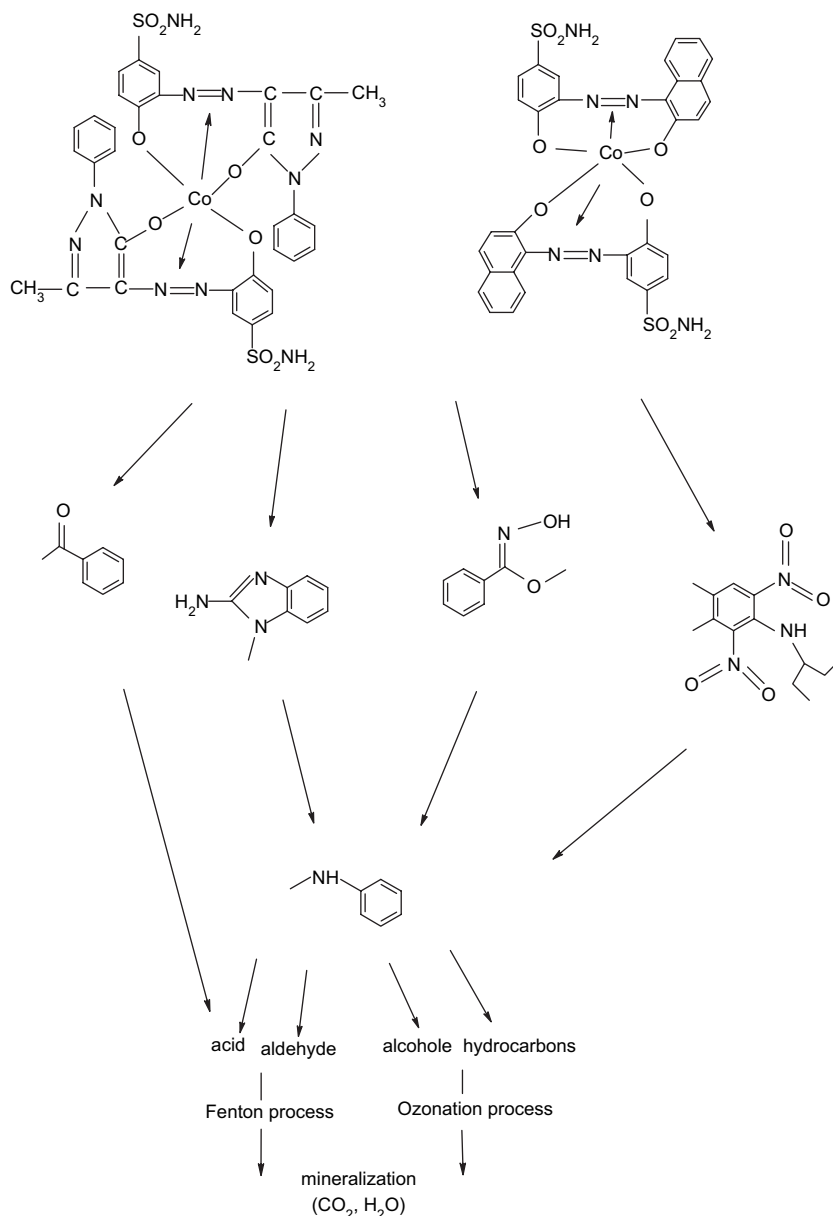


Fig. 8. Tentative pathway of Acid Brown 159 oxidative degradation.

The oxidation by hydrogen peroxide had no serious impact on changes of toxicity features of activated sludge. More toxic compounds were formed in ozone oxidation process.

### Acknowledgements

This study was supported by the Polish State Committee for Scientific Research under Grant No. 3 T09 B 126 27.

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