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The chemical degradation of C.I. Acid Brown 349 in aqueous solution using hydrogen peroxide and sodium hypochlorite and its implications for biodegradation

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ABSTRACT

The use of hydrogen peroxide and sodium hypochlorite for the oxidation of a 1×10^{-4} M aq solution of C.I. Acid Brown 349 was investigated. The influence of Fe^{2+} concentration ranging from 0 to 50 mg L^{-1} and various doses of oxidant at different pH values and temperatures was investigated. High decolorisation (~100%) was obtained under optimal reaction conditions. A tentative mechanistic pathway for the oxidative degradation of the dye in aqueous solution is postulated; in addition, the thermal degradation of the in air was discussed.

1. Introduction

Owing to the marked stability and resistance to biodegradation of synthetic dyes, their removal from industrial wastewater is a very difficult process. These characteristics can be changed through chemical pre-degradation of the dye molecules, which increases their biodegradability [1]; such chemical pre-degradation of dyes is an unavoidable initial step before subsequent biological wastewater purification [2]. To achieve this goal, advanced oxidation processes (AOP) can be used, whose characteristics include very high reactivity induced by oxidant decomposition together with the production of by-products of higher redox potential [3,4]. The disadvantages of AOP's include the rather low stability of the compounds and the need for experimental examination of their effectiveness. An example of such a process is Fenton's reaction of ferrous ions with either hydrogen peroxide or acidic hypochlorite [5,6]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^-$$

$$Fe^{2+} + HOCl \rightarrow Fe^{3+} + OH^{\bullet} + Cl^-$$

Hydroxyl radicals generated in these reactions react non-selectively with most organic compounds [7]. The reaction with H_2O_2 requires low pH, whereas hypochlorite can react over a wide range of pH values [8]. The additional advantages of Fenton's process are the absence of harmful products of oxidant reduction coupled with the fact that the process can be carried out under homogeneous conditions. Fenton's process has been successfully applied to the treatment of coloured wastewater of high turbidity [9].

This paper focuses on the use of hydrogen peroxide and sodium hypochlorite in the decolourisation of aq. solutions of C.I. Acid Brown 349. The aim of this work was to determine the optimal conditions for Fenton's degradation of the dye, taking into account the pH, reaction temperature and concentration of ferrous ions [9]. In addition, on the basis of GC/MS analysis, a mechanism for the decomposition of the dye in aqueous solution is proposed.

2. Experimental

2.1. Materials

C.I. Acid Brown 349 ($C_{28}H_{18}O_{15}N_8S_2$), which is a representative trisazo (Fig. 1) acid dye and is partially degradable under normal environmental conditions, was used. Dried press cake product (~92% dye content) obtained from the Boruta – Kolor factory in

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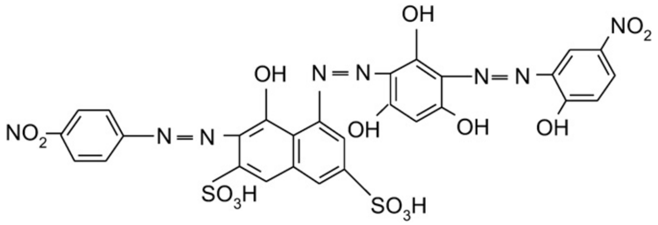

Fig. 1. Structure of Acid Brown 349.

Zgierz, Poland, was used. Aqueous, 1×10^{-4} mol L^{-1} solutions of the dye were prepared in demineralised water.

2.2. Apparatus and procedure

Experiments were carried out in a reactor with a fixed capacity. A concentrated dye solution with a specified volume was introduced to the reactor, the pH was adjusted to a fixed value and an appropriate amount of Fe(II) ions (in the form of $FeSO_4$ solution) was added. The reactor was then topped up with demineralised water to a total volume100 mL. After stirring, the initial absorbance (A_o) of the solution was determined. A specified amount of oxidant was added to the reactor and, after 120 min, the absorbance (A) of the ensuing solution was measured at 409 nm (the λ_{max} of the dye solution). The UV–VIS absorbance was measured using a Hach Odyssey DR 2500 spectrophotometer. The degree of decolorisation was calculated using Eq (1):

$$\alpha = (1 - A/A_0) \cdot 100\% \quad (1)$$

Total organic carbon (TOC) was determined using a TOC 505 Shimadzu analyzer. Chemical oxygen demand (COD) (measured using the dichromate method) were determined after 2 h mineralization using a Hach DRB 100 thermo-reactor, employing a Hach Odyssey DR 2500 spectrophotometer, according to the procedure accepted by USEPA. The experiments were monitored by recording UV–VIS spectra on a Shimadzu UV-2401. The experiments were carried out under thermostated conditions at 20, 40 and 60 °C. The dye molar absorption coefficient was $\varepsilon_{max} = 23\ 000$.

Table 1
The effect of the concentration of Fe(II) ions on the decolorisation at room temperature by hydrogen peroxide, 0.5 mg H_2O_2 per mg of Acid Brown 349 dye at pH = 2.5.

Fe(II) ions concentration [mg L^{-1}]	0	2.5	5	10	20	30	40	50
Decolorisation degree α [%]	3	44	56	57	71	66	63	53

2.3. GC/MS analysis

Both the methanol and water used for liquid chromatography were HPLC-grade (Fluka). GC–MS analyses were performed using an Agilent 6890N GC system interfaced with an Agilent 5973 mass-selective detector. The gas chromatograph was equipped with an HP-5MS (cross-linked 5% phenyl-methylsilicone) fused-silica capillary column, 30 m × 0.25 mm × 0.25 μm.

The intermediates were collected, extracted and concentrated by solid phase extraction (SPE). Each sample of dye (1 mL) was passed through the SPE and washed with 1 mL water and eluted with 1 mL methanol. The eluted solutions were collected and analyzed using the GC/MS system; GC conditions were: initial oven temperature 40 °C for 0.7 min, increased to 80 °C at 10 °C/min and then to 280 °C at 4 °C/min. Helium was used as the carrier gas at a flow of 0.9 mL min^{-1}. The temperature of the MS transfer line was 280 °C, the MS source temperature being 230 °C. The MS quadrupole temperature was 150 °C and ionization was performed by electron ionization at 70 eV. The products were identified by comparing the mass spectra with those stored in the NIST98 Library.

2.4. The inhibition test

The test for the inhibition of oxygen consumption by activated sludge was performed by measuring the rate of oxygen consumption at a constant temperature of 20 °C. The oxygen consumption rate was measured using an OxiTop OC 100 instrument. Oxygen consumption by the dye solution was measured as function of the concentration of dye, using EN ISO 8192 and Eq (2):

$$I = (R_B - R_T)/R_B \quad (2)$$

where R_B and R_T are the rates of oxygen consumption of the blank and control samples, respectively. From the value of I obtained, the

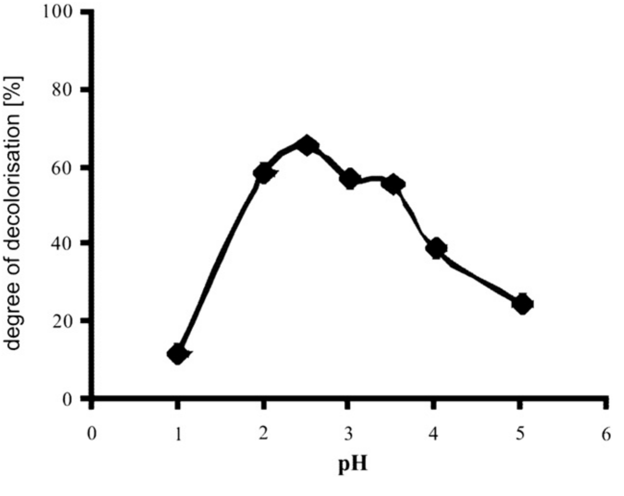

Fig. 2. Dependence of the degree of decolorisation on pH at room temperature, for 5.0 mg Fe(II) L^{-1} and 0.5 mg H_2O_2 per mg of Acid Brown 349.

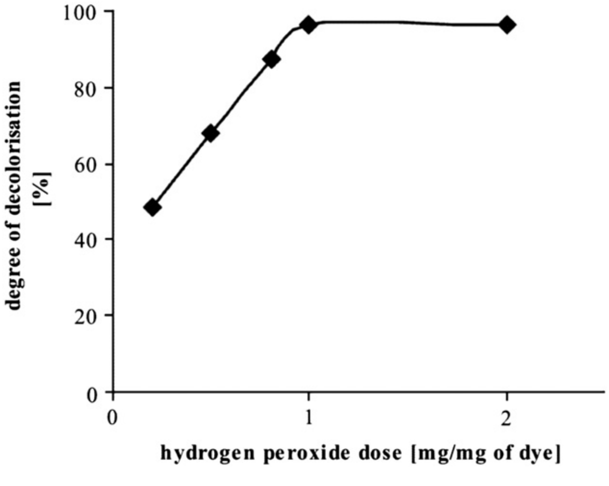

Fig. 3. Dependence of the degree of decolorisation on the hydrogen peroxide dose at pH = 2.5 and 60 °C and 20 mg Fe(II) L^{-1} for Acid Brown 349.

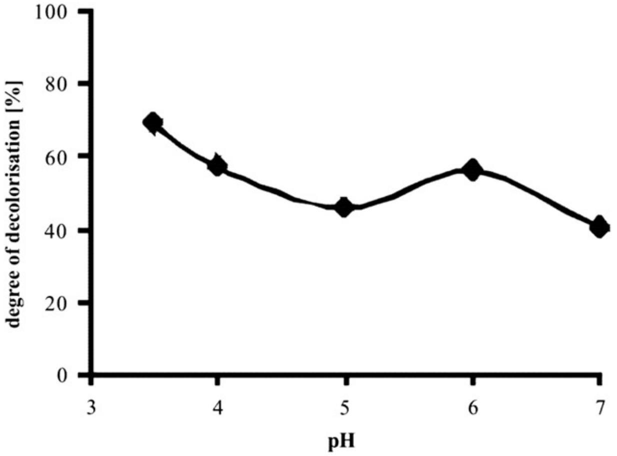

Fig. 4. Dependence of the degree of decolorisation on pH at 60 °C for Acid Brown 349: Fe(II) = 20 mg L^{-1}, D_{NaClO} = 0.5 mg per mg of the dye.

Table 2
The influence of the concentration of Fe(II) ions on the decolorisation by sodium-hypochlorite at 60 °C, pH = 3.5 and 0.5 mg NaClO per mg of Acid Brown 349.

Fe(II) ions concentration [mg L^{-1}]	0	5	10	15	20	25	30
Decolorisation degree α [%]	62	47	62	52	57	56	54

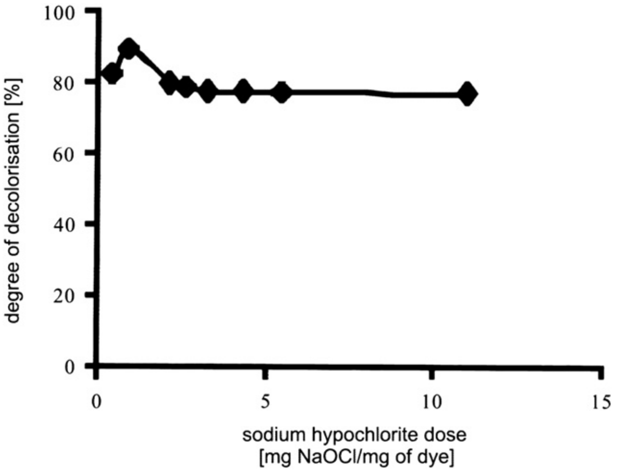

Fig. 5. Dependence of the degree of decolorisation on the dose of sodium hypochlorite at 60 °C and pH = 3.5 for Acid Brown 349.

Table 3
The optimal conditions for degradation of Acid Brown 349 dye, η – degree of reduction, parameters of process: a) after decolorisation by H_2O_2: α = 96%, pH = 2.5, 20 mg Fe(II) L^{-1}, 1 mg H_2O_2 per mg of dye, t = 60 °C, b) after decolorisation by NaOCl: α = 90%, pH = 3.5, 0 mg Fe(II) L^{-1}, 1 mg H_2O_2 per mg of dye, t = 60 °C.

Azo-dye	Parameter	Before decolorisation	After decolorisation by H_2O_2	After decolorisation by NaOCl
Acid Brown 349	COD [mg O_2 L^{-1}]	72	20	10
	TOC [ppm]	318	188	277
	η_{COD} [%]	–	72	86
	η_{TOC} [%]	–	41	13

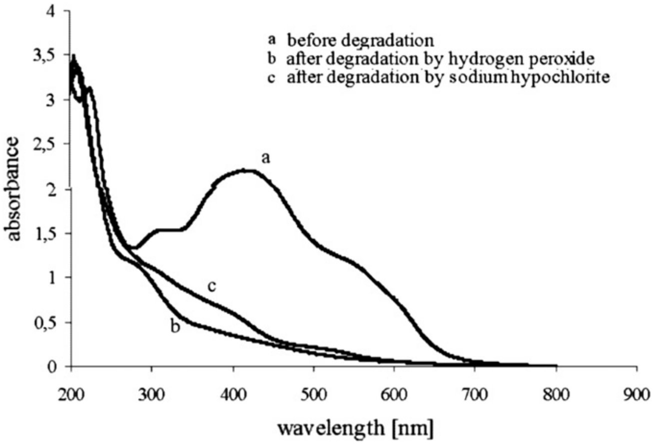

Fig. 6. UV–VIS spectra of Acid Brown 349 solutions (a) before and after decolorisation by: (b) H_2O_2 and (c) NaOCl.

influence of the dye solution on the oxygen consumption was designated as inhibition when $I >> 0.1$ or stimulation when $I << 0.1$, according to EN ISO 8192.

2.5. Thermal stability in air – TG–DTA–MS

The TG–DTA–MS method was used for the temperature-programmed degradation of 20 mg of dye in an air stream (40 mL/min) using a constant 10 °C per minute increase of temperature over the range 25–1000 °C. The measurements were carried out in equipment incorporating both thermo-gravimetric TG and differential thermal analysis DTA devices SETSYS-16/18 (Setaram) and combined on line with a mass spectrometer MS (Balzers).

3. Results and discussion

The experiments with aqueous solutions of dye were carried out in two phases. In the first step, hydrogen peroxide was applied at room temperature to determine the preliminary conditions of oxidation with Fe(II) ions. Then, the temperature was increased to 40 and 60 °C for the two oxidative agents H_2O_2 and NaOCl and the optimal conditions for the degradation of the dye were determined.

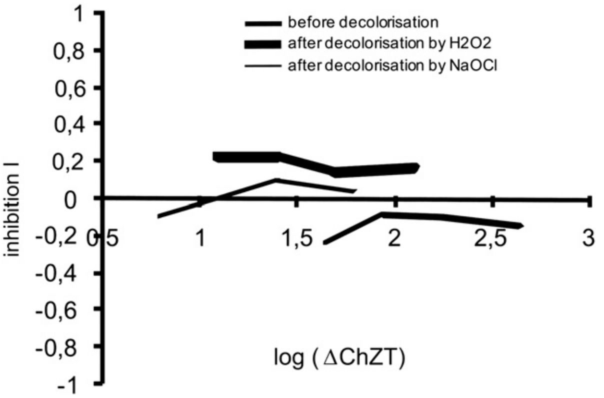

Fig. 7. The influence of Acid Brown 349 dye chemical treatment on the oxygen consumption index for biological microorganisms in activated sludge.

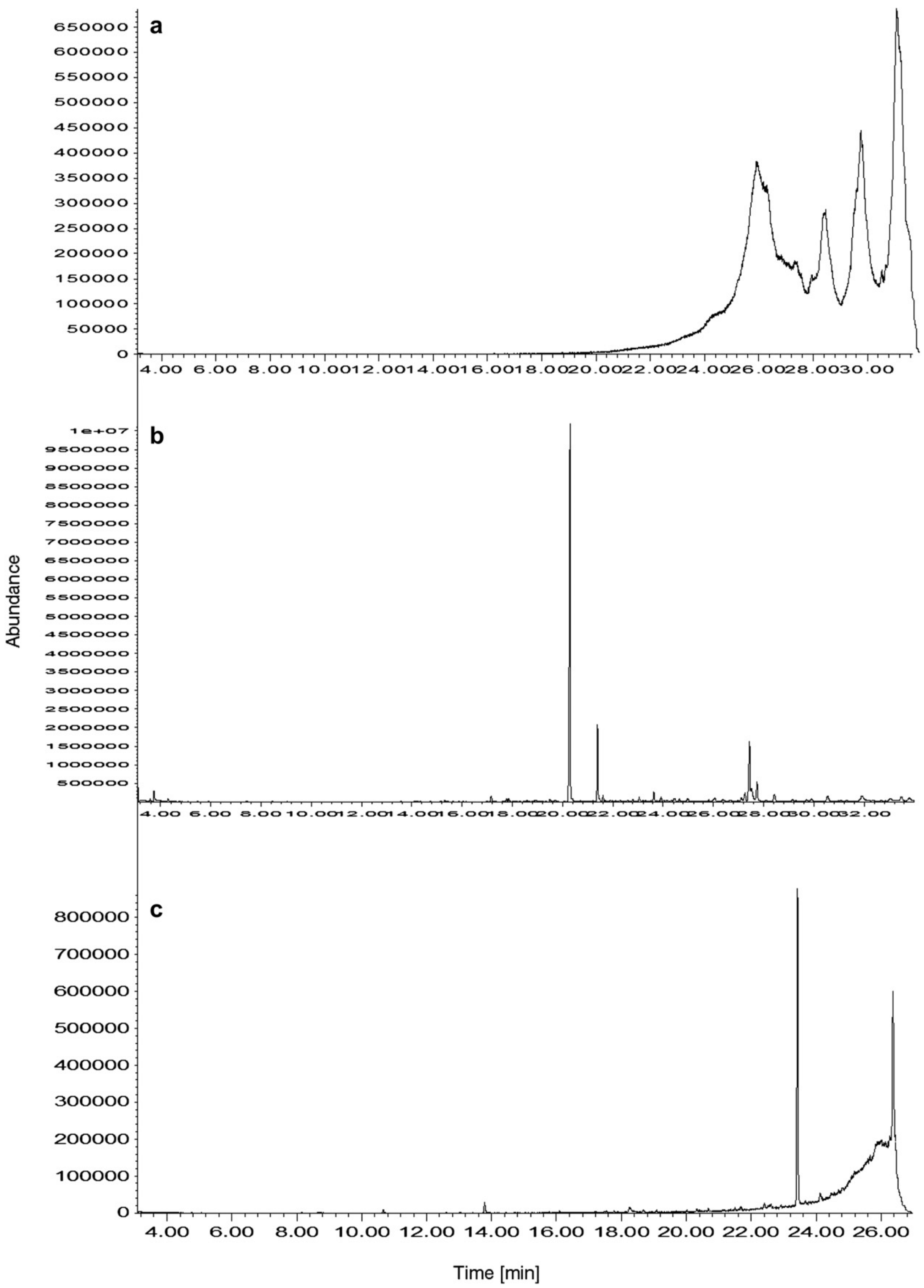

Fig. 8. Total ion GC–MS chromatogram of Acid Brown 349 decomposition products, (a) before oxidation; (b) after oxidation by H_2O_2; (c) after oxidation by O_3. The major peaks are identified in Table 4.

3.1. Decolorisation by hydrogen peroxide

The influence of pH was tested at room temperature using values within the range 1–5 for 0.5 mg H_2O_2 per mg of the dye and concentrations of Fe(II) ions in the range 0–50 mg L^{-1}. The results are presented in Fig. 2 and Table 1. The highest degree of decolorisation was obtained at pH = 2.5 in the presence of Fe(II) ions at a concentration of 20 mg L^{-1}. Under these conditions, the degree of decolorisation amounted to 70%. Therefore, in the next experiments the temperature was increased to 40 and 60 °C. The results of different doses of hydrogen peroxide are presented in Fig. 3, and one can observe that beginning from value of 1 mg H_2O_2 per mg of dye, very high degrees of decolorisation for Acid Brown 349 solutions were obtained.

3.2. Decolorisation by sodium hypochlorite

The influence of pH on the efficiency of decolorisation of the dye by sodium hypochlorite is presented in Fig. 4. First, the pH of the reaction medium ranged from 3.5 to 9.5 for the given oxidant doses and concentrations of ferrous ions. The degree of decolorisation of Acid Brown 349 was highest at pH = 3.5 and further increase of pH value caused it to decrease. Under the same conditions, the influence of the concentration of ferrous ions within the range 0–30 mg L^{-1} on the degree of decolorisation was examined and the results are presented in Table 2. Almost no change of this value with increase of Fe (II) ions over the concentration range 15–30 mg L^{-1} could be observed. Therefore, further experiments were carried out without the presence of ferrous ions. The results with the applied doses of NaOCl from 0.3 to about 11 mg per mg of the dye for pH = 3.5, are presented in Fig. 5. One can see that the best result for the decolorisation process was achieved at 1 mg NaOCl L^{-1} for Acid Brown 349. The degree of decolorisation obtained amounted to 90% at pH = 3.5 for Acid Brown 349 oxidation at 60 °C.

3.3. Assessment of the effectiveness of the dye degradation

To evaluate the efficiency of the degradation of the dye, an analysis of the total organic carbon TOC, chemical oxygen demand COD and UV–VIS spectra was made for Acid Brown 349 aqueous solutions using the optimal applied conditions for the decolorisation process. The results are presented in Table 3. These data show that the decolorisation by hydrogen peroxide results in a greater decrease of total organic carbon compared with the use of sodium hypochlorite. The decolorisation results amounted to 41% with the use of hydrogen peroxide and 13% during oxidation with sodium hypochlorite. These results confirm the partial degradation of the dye, which means that molecular oxidation does not result in final products (CO_2 and H_2O). The UV–VIS spectra, presented in Fig. 6, seem to confirm the destruction of aromatic rings and the chromophoric groups in the dye molecule during decolorisation by H_2O_2 and NaOCl [9].

3.4. Biological assessment of the effectiveness of dye degradation – the inhibition test

The results of the test for inhibition of oxygen consumption by activated sludge are presented in Fig. 7. It is apparent that the dye before oxidation did not inhibit the consumption of oxygen by activated sludge. In addition, a rather positive stimulated effect of oxygen consumption for microorganisms can be inferred after oxidation by hydrogen peroxide and sodium hypochlorite.

3.5. GC/MS analysis of Acid Brown 349 dye

The degradation products formed during the photo-oxidation processes were analyzed by the GC/MS technique and identified by interpretation of their fragment ions in the mass spectra. The main compounds detected in the solution of Acid Brown 349 are presented in Fig. 8a and Table 4. The degradation products were identified by their molecular ion and mass spectrometric fragmentation peaks. Two of the degradation products are in methylated form because methanol reacts easily with the carboxyl group to produce esters at high temperature during the measurement. A possible mechanism for the formation of these degradation products is shown in Fig. 10. We found that the first step of the degradation is cleavage of the azo bond in the dye molecule, and mono or multi substituted benzene and naphthalene rings are produced. Next, oxidation causes opening of a benzene and naphthalene ring leading to the formation of carboxylic acids, aldehydes and alcohols. After ozone oxidation we obtained alcohols from 2-amino-6-naphthalenesulfonic acid (Fig. 8c). Finally, the mineralization of the dye results in carbon dioxide formation.

3.6. TG–DTA–MS analysis of Acid Brown 349 dye

Fig. 9 presents the results of the thermal degradation of Acid Brown 349 in air as TG, DTG and DTA profiles (upper part) and selected MS curves showing typical gaseous products of the dye oxidative decomposition (lower part). The thermal oxidation of Acid Brown 349 in air can be divided into three steps:

- In the temperature range 25–220 °C, the weight loss on the TG curve of about 4% is accompanied by an exothermic DTA effect and evolution of water as shown in the MS curve (H_2O, $m/z = 18$). This behavior confirms the high moisture content of the commercial dye sample.
- In the temperature range 220–540 °C, the weight loss on the TG curve $\Delta m \approx 68\%$ represents two step major and highly complex decomposition steps, accompanied by two strongly overlapping DTG peaks and highly exothermic DTA effects. The selected MS curves representing the evolution of CO_2, C_6H_6, fragments of alkanes C_3H_4 and C_4H_3, fragment of ammonia NH, NO, H_2O and SO_2 are included.
- In the temperature range above 540 and up to 1000 °C, further but incomplete weight loss on the TG curve finally reaches about 80% of total mass lost and proves that burning of the residual carbon deposit is represented by the CO_2 evolution.

Table 4
GC–MS analyses of fragmentation products.

No.	Retention time	Compound identified by MS	Formula	M_W	The major ions (m/z)
1	25.93	2-amino-6-naphthalenesulfonic acid	$C_{10}H_{17}O_3SN$	223	142, 223, 115, 130, 158
2	28.43	Butanoic acid, 2-propenylester	$C_7H_{12}O_2$	128	43, 71, 39, 128, 57
3	29.77	Tetradecanoic acid methylester	$C_{15}H_{30}O_2$	242	74, 87, 55, 143, 242
4	31.10	1,2-benzenedicarboxylic acid	$C_8H_6O_4$	166	104, 76, 18, 148, 76

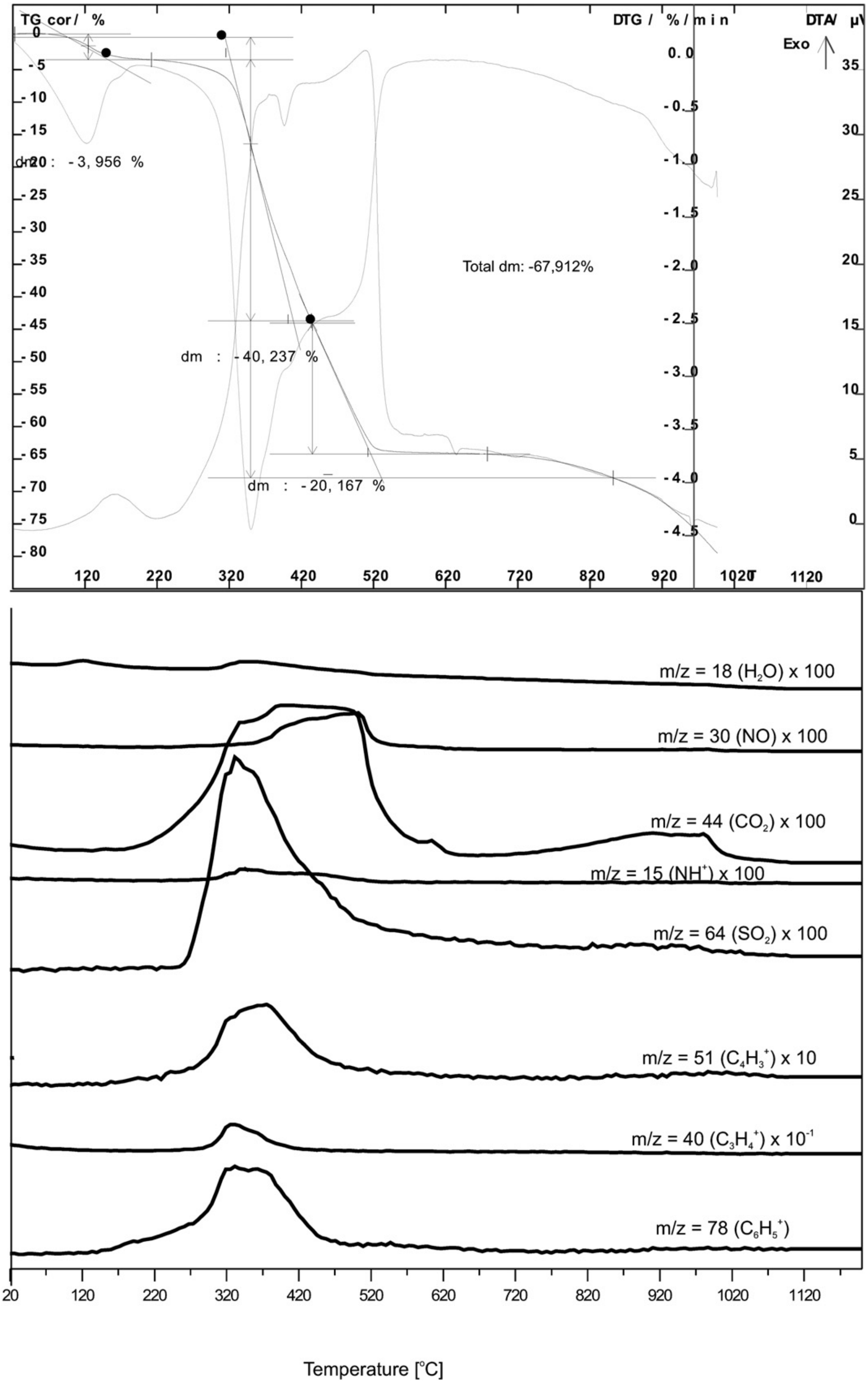

Fig. 9. The thermal degradation in air is presented as the TG, DTG and DTA profiles (upper part) and selected MS curves showing typical gaseous products from Acid Brown 349 oxidative decomposition (lower part).

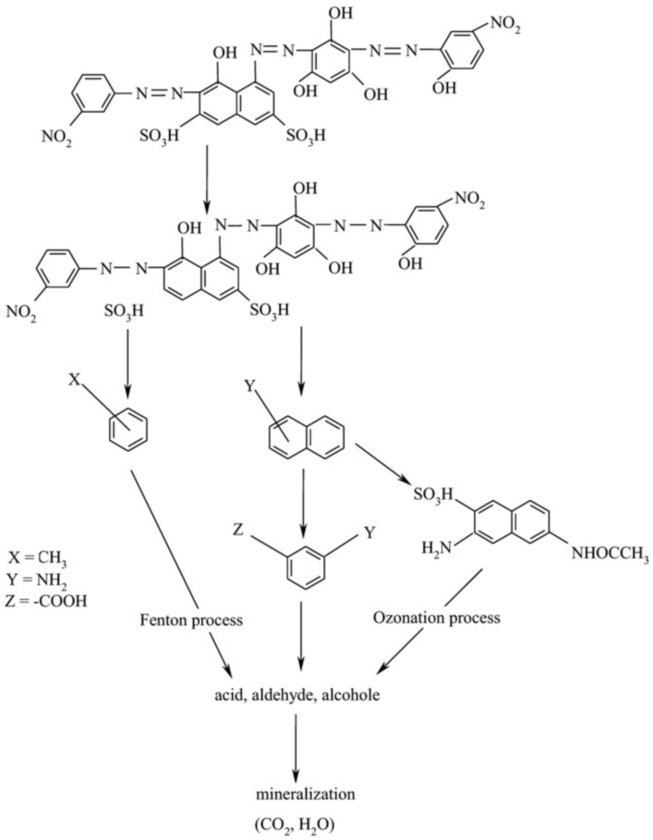

Fig. 10. Tentative pathway of for the oxidative degradation of Acid Brown 349.

Taking into account the overall stoichiometry of Acid Brown 349 complete oxidation one might expect 100% of dye mass loss, as follows:

$$C_{28}H_{18}O_{15}N_8S_2 + 42.5O_2 \rightarrow 28CO_2 + 9H_2O + 8NO_2 + 2SO_2$$

The missing mass loss, about 20%, is attributed to unburned carbon and residual solid sample contamination such as NaCl introduced during the commercial dye preparation.

4. Conclusions

The oxidation processes for C.I. Acid Brown 349 with hydrogen peroxide and sodium hypochlorite are very efficient, as almost complete decolorisation using optimal reaction parameters was obtained. The degradation efficiency with hydrogen peroxide was strongly dependent on pH, being greatest at pH 2.5. The efficiency achieved using sodium hypochlorite was considerably lower. Dye degradation using hydrogen peroxide was carried out with at the optimal concentration of ferrous ions (20 mg L^{-1}); for sodium hypochlorite, the presence of Fe(II) ions was unnecessary.

The aqueous dye solution appeared to be very resistant to the action of both oxidants, as its effective decolorisation required a temperature of 40 or 60 °C. Hydrogen peroxide used in Fenton's process imparted greater degradation of the dye taking in terms of both TOC and COD indicators. The oxidation of the dye by hydrogen peroxide and sodium hypochlorite imparted a positive effect on the microorganisms within activated sludge. A tentative mechanistic pathway for the oxidative degradation of the dye in aqueous solution was described.

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