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Degradation mechanism of Reactive Orange 113 dye by H_2O_2/Fe^{2+} and ozone in aqueous solution

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Abstract

The oxidative degradation of azo dye Reactive Orange 113 aqueous solution by H_2O_2/Fe^{2+} and ozone was investigated. The full decolorization is attained during the first minutes of oxidation process by H_2O_2/Fe^{2+} and ozone. The complete mineralization of aqueous solutions of Reactive Orange 113 dye cannot be achieved even under the optimal reaction conditions. Ozonation appeared more effective in comparison with Fenton's process. A tentative pathway for the oxidative degradation of Reactive Orange 113 dye were postulated.

Keywords: Reactive Orange 113; Fenton's process; Oxidation; Ozonation; Decolorization; Azo dye degradation

1. Introduction

Reactive Orange 113 is one of azo derivatives belonging to the overwhelming majority of synthetic dyes currently used in the industry. Commercial importance, the impact and toxicity of dyes that are released in the environment have been extensively studied [1]. Our knowledge concerning dyes behavior in the environment and health hazards involved in their use is still incomplete. Traditional wastewater treatments appeared ineffective because of the chemical stability of most dye pollutants making them the non-biodegradable compounds. 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. [1]. The efficiency of the various methods of dye removal, such as chemical precipitation, chemical oxidation, adsorption and their effects on biological treatment was reported in earlier papers [2,3]. Strongly dependent on oxidant type chemical oxidation pretreatment is a prerequisite condition of the subsequent activated sludge process [4].

Hydrogen peroxide can effectively decolorize dye wastewaters in the presence of Fe^{2+} sulphate [5,6]. 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 [7]. UV/H_2O_2 treatment can be successfully used for the decolorization of acid dyes, direct dyes, basic dyes and reactive dyes [8]. The influence of operating parameters on the decolorization of reactive dye by ozone has been studied in detail [9]. The results indicated that the decomposition rate increased with increasing pH and temperature [10].

This paper is focused on a study of Reactive Orange 113 aqueous solution neutralization by Advanced Oxidation Process (AOP) involving ozonation (O_3) and Fenton's (H_2O_2/Fe^{2+}) 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. Also, on the

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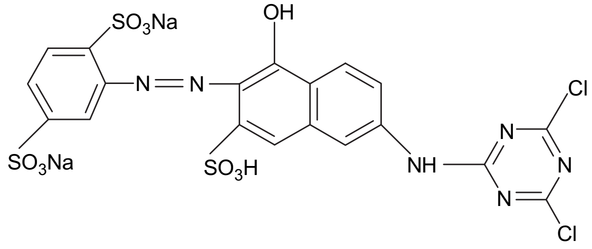
basis of GC–MS analysis a tentative mechanistic approach of Reactive Orange 113 dye decomposition of aqueous solution is postulated.

2. Experimental

2.1. Materials

Reactive Orange 113 is a synthetic product of aniline-2,5-disulphonate coupling with 6-*N*(3,5-dichloro-2,4,6-triazin)-amino-1-hydroxynapthaleno-3-sulphonate acid. This dye was obtained from Dyestuff Industry Works "BORUTA-KOLOR" and it is applied in tanning and textile industries. Molecular formula of Reactive Orange 113 is as follows:



2.2. Apparatus and procedure

Experiments were carried out in a reactor with a constant capacity. At first a concentrated dye solution with a specified volume was implemented to the reactor, then pH was adjusted to the fixed value and proper amount of the Fe(II) ions ($FeSO_4$ solution) was added, next the reactor was filled with demineralized water to the volume of 100 cm^3. After stirring the reactor content, the initial absorbance (A_0) of the solution was determined. Next, the specified amount of an oxidant was added to the reactor and after 120 min of the experiment, final absorbance (A) was measured. The wavelength at maximal absorbance was located at 479 nm for Reactive Orange 113 solutions. Absorbances were measured by Hach Odyssey DR 2500 spectrophotometer produced by Hach Company. The degree of the solution decolorization was calculated on the basis of the following equation: $\alpha = (1 - A/A_0) \times 100\%$. Additionally, for samples in optimal conditions of process total organic carbon (TOC) and chemical oxygen demand (COD) were determined by means of dichromate method, and UV–vis spectra were recorded. TOC 505 Shimadzu analyzer was used to determine TOC. COD values were determined after 2 h of samples mineralization in Hach DRB 100 thermoreactor and by means of Hach Odyssey DR 2500 spectrophotometer according to procedure accepted by USEPA. The experiment was monitored by UV–vis spectrophotometer (UV-2401 PC Shimadzu). Experiments were carried out at room temperature by means of thermostat.

The ozonation experiments were carried out in a reactor containing aqueous solution of dye 60 mg/dm^3 saturated in oxygen containing about 17 ppm of ozone with volume velocity 15 dm^3/h. In the course of experimental run the following parameters were measured: concentration of ozone, redox potential and degree of decolorization.

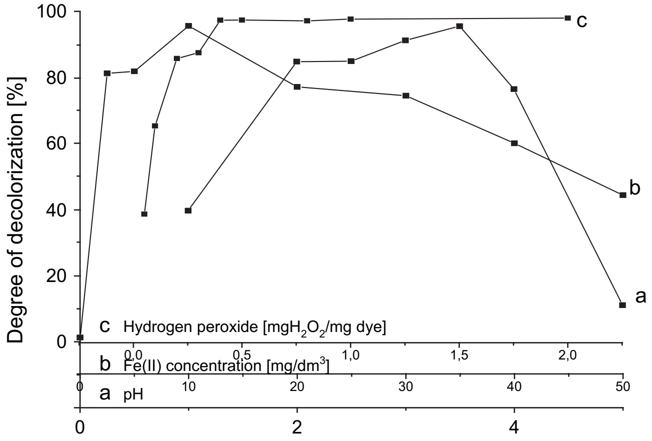


Fig. 1. A dependence of the degree of Reactive Orange 113 dye solution decolorization on H_2O_2 dose, and Fe^{2+} concentration and pH of aqueous solution after 2 h oxidation.

2.3. GC–MS analysis

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

The intermediates were collected and extracted, concentrated by SPE (solid phase extraction). Sample of dye (1 cm^3) was passed through the SPE and washed with 1 cm^3 water and eluted with 1 cm^3 methanol. The eluted solutions were collected and analyzed by GC–MS system. The GC conditions were as follows: initially, the oven temperature was maintained at 40 °C for 0.7 min, then it was increased to 80 °C at a rate of 10 °C/min, then to 280 °C at

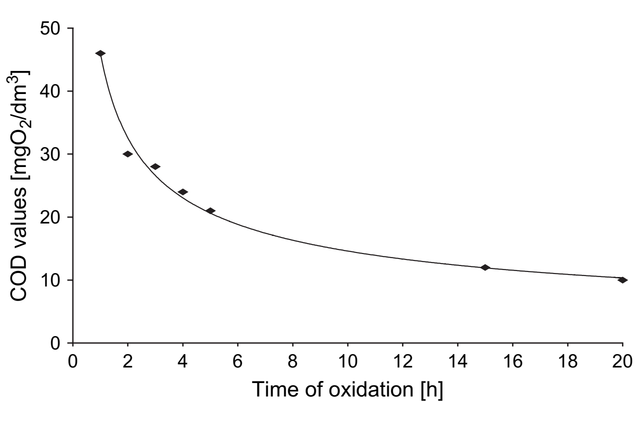


Fig. 2. COD values as function of oxidation time of Reactive Orange 113 dye solution by H_2O_2/Fe^{2+}.

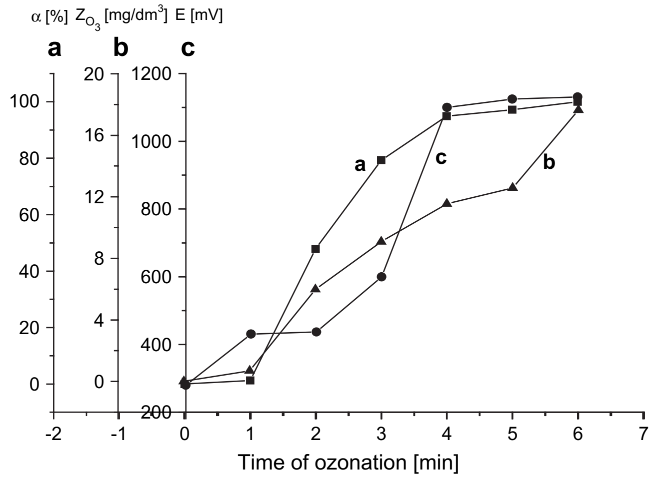


Fig. 3. A dependence of the ozonation parameters of dye solutions on ozonation time. α – Degree of decolorization (%); Z_{O_3} – ozone consumption (mg/dm^3); E – redox potential (mV).

4 °C/min. Helium was used as the carrier gas at a flow rate of 0.9 cm^3/min. The temperature of the MS transfer line was 280 °C. The MS source temperature was 230 °C. The MS quadrupole temperature was 150 °C, ionization was performed by electron ionization at 70 eV. Products were identified by comparing the mass spectra with that stored in NIST 98 Library.

3. Results and discussion

The influence of the experimental parameters such as hydrogen peroxide concentration (mg H_2O_2 per 1 mg of a dye), Fe^{2+} ion concentration and pH of solution on the effectiveness of solution decolorization are presented in Fig. 1. The degree of solution decolorization higher than 80% can be easily achieved after 2 h of dye solution oxidation. The effect of solution acidity was measured in pH range from 1 to 5. The degree of dye decolorization higher than 80% (curve a) were achieved in pH range 2–4. The effect of ferrous ions concentration was investigated in the range from 0 to 50 mg/dm^3 (curve b). 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 5–10 mg/dm^3. The increase of H_2O_2 concentration up to 0.4 mg per 1 mg of dye leads to 100% complete decolorization (curve c). Thus, the following parameters were chosen as optimal conditions for further experiments of Reactive Orange 113 oxidation: hydrogen peroxide concentration with the ratio of 0.4 mg H_2O_2 per 1 mg of a dye, Fe^{2+} ion concentration 10 mg/dm^3 and pH = 3.

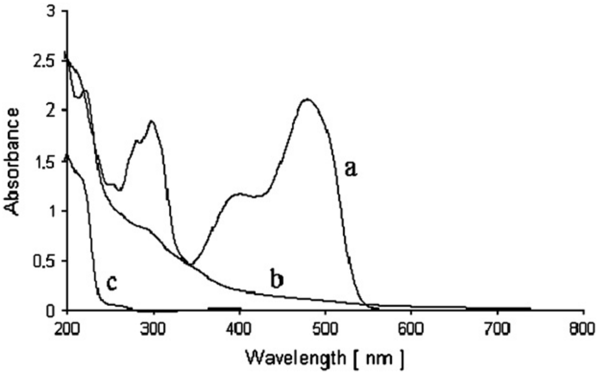


Fig. 4. UV–vis spectra changes of Reactive Orange 113 solutions before and after 2 h oxidation by H_2O_2 and O_3. a – Before decolorization; b – after decolorization by H_2O_2; c – after decolorization by O_3.

The application of the above optimal conditions of dye solution oxidation leads to the results of the influence of oxidation reaction time on chemical oxygen demand COD values which are presented in Fig. 2. After 5 h of reaction the reduction of COD initial value was about 70% and after 20 h more than 90% decrease of COD value was observed.

The ozonation result of aqueous solutions of Reactive Orange 113 concentration is 60 mg/dm^3. The time necessary to achieve full decolorization $\alpha = 100\%$ was 6 min. Also, ozone consumption and redox potential are presented in Fig. 3.

The comparison of UV–vis spectra of Reactive Orange 113 aqueous solutions before and after 2 h of oxidation by hydrogen peroxide and ozone is presented in Fig. 4. Both processes were performed at the optimal conditions which were chosen after preliminary measurements. The spectra of dye initial solution represent UV bands characteristic for —N=N— (478 cm^{-1}) and are related to the benzene and naphthalene rings bonded to the —N=N— group (253, 281 and 297 cm^{-1}) [11–13]. The dramatic changes of UV spectra represent a disappearance of both azo and aromatic groups during the degradation of Reactive Orange 113 dye. Ozone treatment appears much more efficient than Fenton's process.

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 solutions of Reactive Orange 113 dye are presented in Table 1.

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 Reactive Orange 113 dye solution

Name of dye	Before oxidation		After oxidation by H_2O_2		After oxidation by O_3		H_2O_2		O_3	
	COD (mg O_2/dm^3)	TOC (ppm)	COD (mg O_2/dm^3)	TOC (ppm)	COD (mg O_2/dm^3)	TOC (ppm)	η_{COD} (%)	η_{TOC} (%)	η_{COD} (%)	η_{TOC} (%)
Reactive Orange 113	50	263	30	181	28	168	40	31	44	36

η – denotes the reduction of TOC and COD values (%).

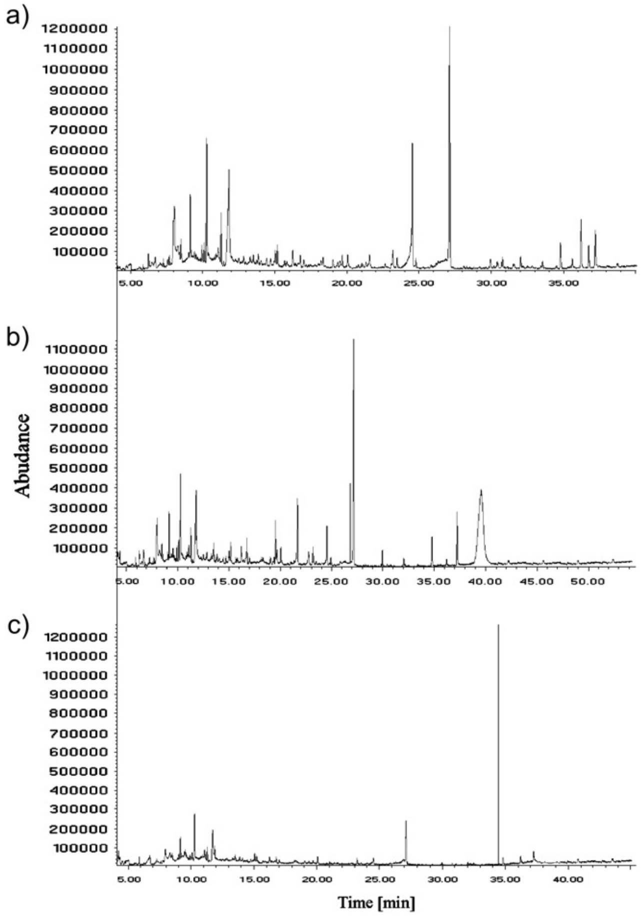


Fig. 5. Total ion GC–MS chromatogram of Reactive Orange 113 oxidative decomposition products. a – Before oxidation; b – after H_2O_2 oxidation; c – after O_3 oxidation. The major peaks are identified in Table 2.

Results of TOC analysis indicate that organic compounds are not completely oxidized to CO_2. The decreases of TOC values were 31 and 36% after 2 h oxidation by H_2O_2 and ozone, respectively. The reductions of COD values were about 40% by hydrogen peroxide and 44% by ozone treatment.

Table 2
GC–MS analyses of fragmentation products

No	Retention time on GC	Compound identified by MS	Formula	M_W
1	6.30	Oxime-, methoxy-phenyl	$C_8H_9NO_2$	151
2	8.30	Octanal	$C_8H_{16}O$	128
3	9.20	3-*tert*-Butyl-5-chloro-2-hydroxybenzophenone	$C_{17}H_{17}ClO_2$	288
4	10.14	α-Methylbenzylalcohol	$C_8H_{10}O$	122
5	10.30	Acetophenone	C_8H_8O	120
6	11.30	Nonaldehyde	$C_9H_{18}O$	142
7	11.80	Butylethylacetic amide	$C_8H_{16}O_2$	144
8	24.53	2,6-Di-*tert*-butyl-4-methyl phenol	$C_{15}H_{24}O$	220
9	27.04	1,2-Benzenedicarboxylic acid, diethylester	$C_{12}H_{24}O_4$	222
10	36.21	Pentadecanoic amide	$C_{17}H_{34}O_2$	270
11	37.24	Benzenopropenoic amide	$C_{18}H_{28}O_3$	292

The intermediate compounds of Reactive Orange 113 dye degradation were characterized. We used GC–MS system to directly examine the intermediate product mixtures. The degradation products of the Reactive Orange 113 demonstrate some substituted aromatic compounds which are shown in Fig. 5, containing typical GC chromatogram and these peaks were identified by MS analysis and typical compounds are listed in Table 2.

The main intermediate compounds of dye Reactive Orange 113 degradation are presented as GC chromatogram in Fig. 5a. The major peaks were identified by GC–MS analysis and the most important compounds are listed in Table 2.

From mono-substituted benzene we obtained acids and aldehydes. From substitute napthalene decompose on substitute benzene and then to alcohols, after hydrogen peroxide oxidation we can show in Fig. 5b. After ozone oxidation we obtained hydrocarbons from 3,6-dichloro-2,4,8-triazin which are presented in Fig. 5c.

Based on our results a tentative pathway for the degradation of Reactive Orange 113 dye was postulated and this mechanism is presented in Fig. 6.

We believe that the identified compounds are the degradation products of Reactive Orange 113 oxidation. In the very first step of degradation the azo bonds Ar–N=N–Ar′ lose unsaturated character that is being transformed into hydroxyl structure and further oxidation leads to –N–N– bond splitting and nitro group formation and mono- or multi-substituted benzene and naphthalene compounds are produced. Further oxidation gives rise to the opening of an aromatic ring to the formation of alcohols, aldehydes, carboxylic acids. Finally, the mineralization of dye leads to produce carbon dioxide and water.

4. Conclusion

Hydrogen peroxide and ozone oxidation processes for dye were very efficient, because almost total decolorization for optimal reaction parameters were obtained. The full 100% decolorization is attained during first minutes of oxidation process by H_2O_2/Fe^{2+} and ozone at room temperature.

Degradation efficiency for hydrogen peroxide and ozone was strongly dependent on pH value and was the highest for $pH = 3.0$ and $pH = 2.4$, respectively. Hydrogen peroxide degradation conditions prove that reaction proceeds according to the mechanism of Fenton's process, which requires the presence of Fe(II) ions and low pH of the reaction environment.

The complete mineralization of aqueous solutions of Reactive Orange 113 dye cannot be achieved even under the optimal reaction conditions. Ozonation appeared more effective in comparison with Fenton's process.

The investigated dyes were characterized by a large resistance to action of both the oxidants, because their effective decolorization required in room temperature. Hydrogen peroxide used in Fenton's process has caused greater degradation of examined dyes taking into consideration the values of reduction indicators TOC and COD. It can be partially confirmed by the analysis of UV–vis spectra.

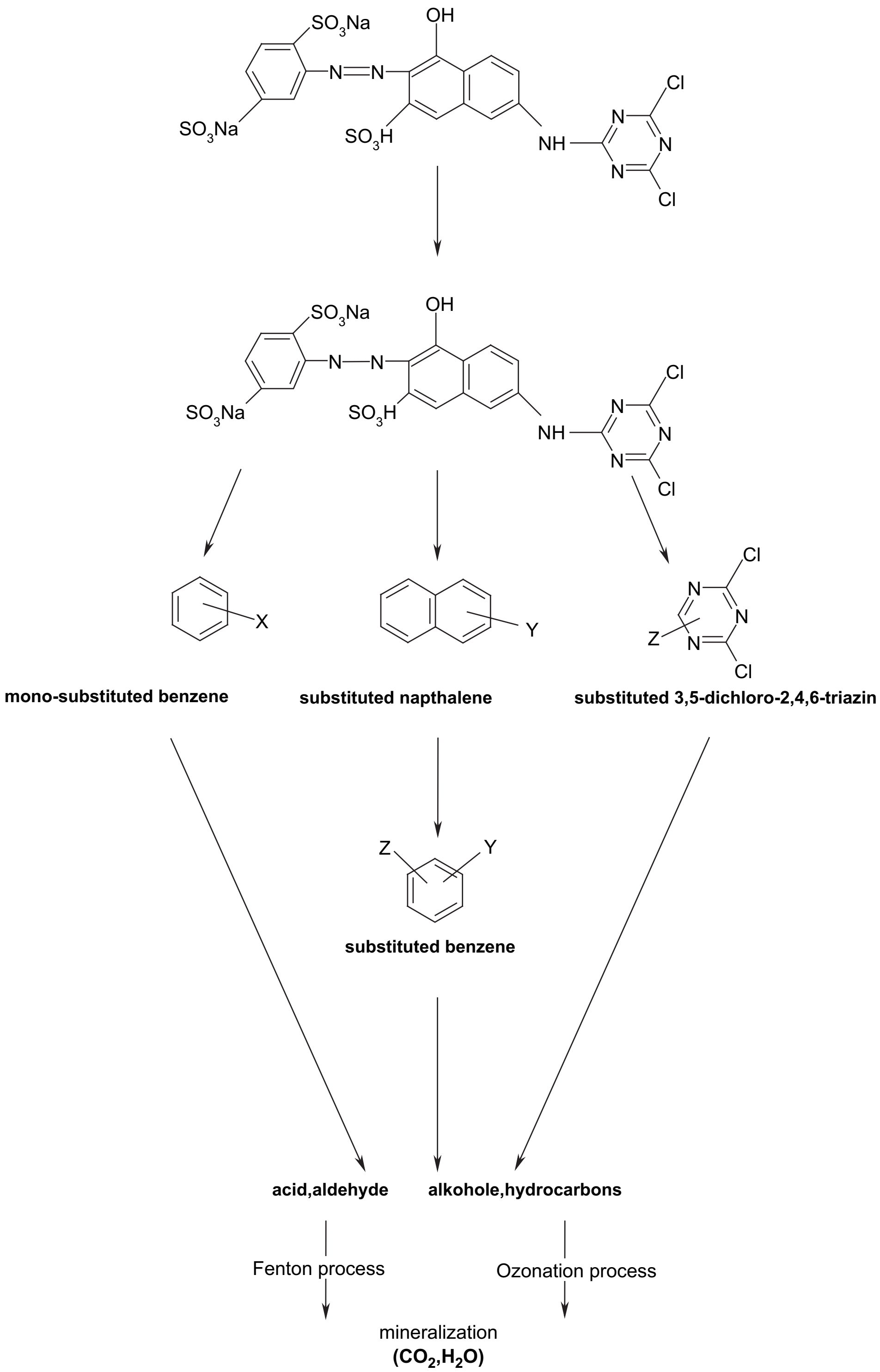


Fig. 6. Tentative pathway of Reactive Orange 113 oxidative degradation.

A tentative pathway for the degradation of Reactive Orange 113 dye was postulated.

Acknowledgements

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