



PRETREATMENT OF AZO DYES USING OZONE

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ABSTRACT

Wastewaters produced in textile industrial processes contain organic dyes which are not easily amenable to biological treatment. Pretreatment with ozone is a promising method for oxidation of those dyes to more degradable compounds. The aim of this work is to assess the oxidation kinetics of a specific azo dye used in the textile industry, Orange II. Batch experiments were conducted in order to elucidate the oxidation route of the dye. Oxalate, formate and benzenesulfonate are found to be the oxidation intermediate compounds. A mathematical model which describes the dye elimination, the COD and BOD₅ variation, the amount of ozone reacted and the time evolution of the intermediate compounds has been developed. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

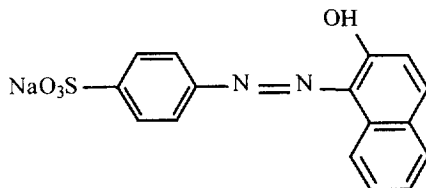
Azo-dye; intermediates; modelling; Orange II; ozonation; wastewater pretreatment.

INTRODUCTION

The wastewater discharged from dyeing processes in the textile industry exhibits low biochemical oxygen demand (BOD), high chemical oxygen demand (COD) and is highly coloured. Thus, the need for pretreatment by means of chemical oxidation is necessary, in order to produce more readily biodegradable compounds, and ozone is becoming more and more important as a very versatile and environmentally sound oxidation agent. Due to its high electrochemical oxidation potential (2.07 V), ozone is the strongest oxidant available and applicable, compared with for example hydrogen peroxide (1.77 V) which exhibits a more or less similar reaction behaviour (Kaulbach, 1996). Unlike other agents such as chlorine, oxidation with ozone leaves no toxic residues that have to be removed and disposed of, as the process yields only the products of the oxidation and oxygen.

Ozonation has been applied to many fields in water and wastewater treatment and has many abilities. Many investigators (Saunders *et al.*, 1983; Gilbert, 1987; Tzitzis *et al.*, 1994; Nobuyuki Takahashi *et al.*, 1994) have worked on ozone oxidation, however, rather little is known about the reaction intermediates formed and the ozonation kinetics. According to Scott and Ollis (1995) effective treatment of a particular wastewater can be attained by a combination of chemical and biological processes and the key to the efficiency of such a system is a better understanding of the mechanisms involved during the chemical oxidation step.

In this work a synthetic azo-dye, Orange II ($C_{18}H_{11}O_4NaSN_2$) has been chosen for study as a representative model compound found in textile industry wastewaters. Azo dyes represent the largest group of industrial dyes, both in number and amount produced (approximately one-half of the structures disclosed in CI). They are organic compounds containing azo groups ($-N=N-$) mainly bound to substituted benzene or naphthalene rings. Specifically, Orange II involves a sulfonic acid group which renders the dye water soluble and capable of dyeing wool and silk (Rys and Zollinger, 1972; Waring and Hallas, 1990). However, this group deactivates the structure towards electrophilic attack. This results in a marked resistance of the dye towards conventional biological treatment (Gould and Groff, 1987). The structure of the dye is shown in the following scheme.



The objective of this research is to develop a mathematical model that not only adequately describes the key parameters of interest i.e. BOD, COD, dye concentration and ozone, but accounts explicitly for the observed reaction intermediates as well. Since the ozonation reaction may produce unidentified intermediates as well, in a kinetic formulation these have to be appropriately lumped into other overall variables, such as total biodegradable COD. This approach allows both explicit kinetic representation of observed intermediates and adequate description of observed BOD and COD values.

MATERIALS AND METHODS

Materials

The experimental set-up used in this study is shown in Fig. 1. Ozone gas was generated using a Prominent ozone lab generator OL 0.5/50. Gas flow rate to the reactor was monitored using a flowmeter incorporated with the generator. The ozonation took place in a 1000 ml batch, magnetically stirred, reactor. Ozone gas was supplied at the bottom of the reactor through a sintered glass plate diffuser. In series with the reactor two ozone traps containing 2% potassium iodide solution (KI) were connected, in order to collect all ozone gas passing through the reactor unreacted. 95% pure Orange II (CI 15510) was obtained from the Aldrich Chemical Company. All the experiments were conducted at 25°C.

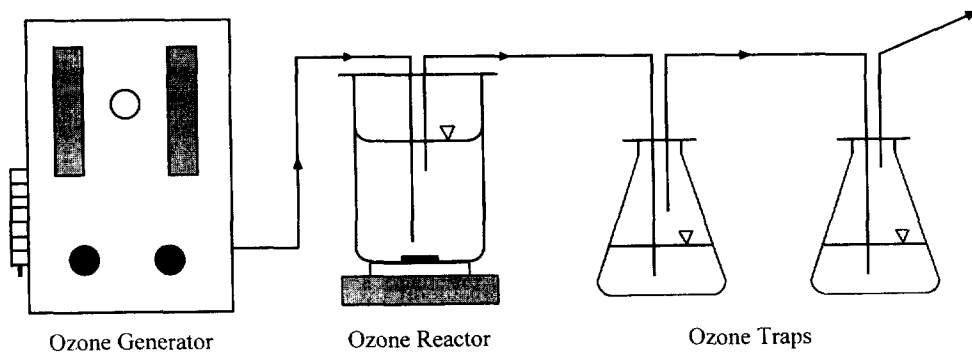


Figure 1. Experimental apparatus.

Analytical methods

Dye concentration was determined spectrophotometrically in the visible region and at the maximum wavelength, using a Milton Roy Spectronic 601 Spectrophotometer. For the Orange II the maximum wavelength is at 480nm. Ozonation intermediates were analysed by a Dionex DX-300 ion chromatograph, with an Ionpac AS11 analytical column and a CDM-3 conductivity detector. The elution was gradient using deionized water and NaOH 100 mM at a flow rate of 2 ml/min.

Ozone concentrations in the feed and in the reactor effluent were determined for each ozonation sequence using the iodometric procedure (APHA, Standard Methods for the Examination of Water and Wastewater, 1975). The difference between the ozone quantity produced by the ozone generator (measured before and after ozonation) corresponds to the ozone quantity which reacts with the dye.

BOD₅ measurements were performed by a VELD manometric apparatus and a refrigerated thermostat FTC90 for the incubation at 20°C of BMS 6, while COD analyses were carried out with a Hach 45600 COD reactor and a DR/2000 spectrophotometer.

Model parameter estimation

A key modelling step is the estimation of model parameters in a way that the model predicted response of a variable is as representative as possible of the actual experimentally observed one. Various least-squares fitting procedures are often used for the optimal evaluation of the kinetic parameters based on minimization of the squared differences between the experimental and calculated variables. The traditional goal of such a method is the selection of a parameter that minimizes the sum of absolute residuals. However, when the magnitude of the dependent variables varies widely, as is often the case, the minimization of the sum of relative residuals is the proper choice (Sáez and Rittmann, 1992). The objective of minimization is therefore expressed as:

$$\min \sum_i^m w_i \left[\sum_j^{n_i} (y_{\text{ex},j}^i - y_{\text{calc},j}^i)^2 \right] \quad (1)$$

where

- m = number of dependent variables
- n_i = number of experimental observations of the dependent variable i
- $y_{\text{ex},j}^i$ = experimental observation of the dependent variable i
- $y_{\text{calc},j}^i$ = model-predicted value for the dependent variable i
- w_i = suitable normalizing weight factor.

Normally, as a weight factor the inverted variance σ^2 of the measured variable, i.e. $w_i = 1/\sigma_i^2$ is chosen. However, when reliable variances are not available, the inverse of the squared maximum value of each measured variable may be used in order to minimize the relative residuals instead of the absolute ones. Additionally, a properly weighted sum of residuals is obtained only by dividing the sum with the number of measurements for each dependent variable. Therefore (1) is used in the form of:

$$\min \sum_i^m \frac{1}{(y_{\text{ex},i}^{\text{max}})^2 n_i} \left[\sum_j^{n_i} (y_{\text{ex},j}^i - y_{\text{calc},j}^i)^2 \right] \quad (2)$$

The least-squares fitting procedure used in the present work for the estimation of model rate constants and stoichiometric parameters is the Nelder-Mead simplex algorithm (Dennis and Woods, 1987).

EXPERIMENTAL RESULTS AND KINETIC MODELLING

In order to elucidate the oxidation route of Orange II, a batch experiment was performed with an initial dye concentration of 0.5 g/l, neutral pH and temperature 25°C. The products which were identified using the ion chromatograph (gradient elution) are oxalate, formate and benzenesulfonate. The retention times were 3.6, 0.8 and 3.2min respectively. During the same experiment BOD₅ and COD measurements were conducted as well. An increase in the BOD₅ values, accompanied by a corresponding decrease in the COD values was observed (BOD₅ : COD ratio increased), indicating the conversion of the dye molecule to more readily biodegradable compounds.

For the elucidation of the kinetics of ozonation of the intermediate products, two additional experiments were carried out.

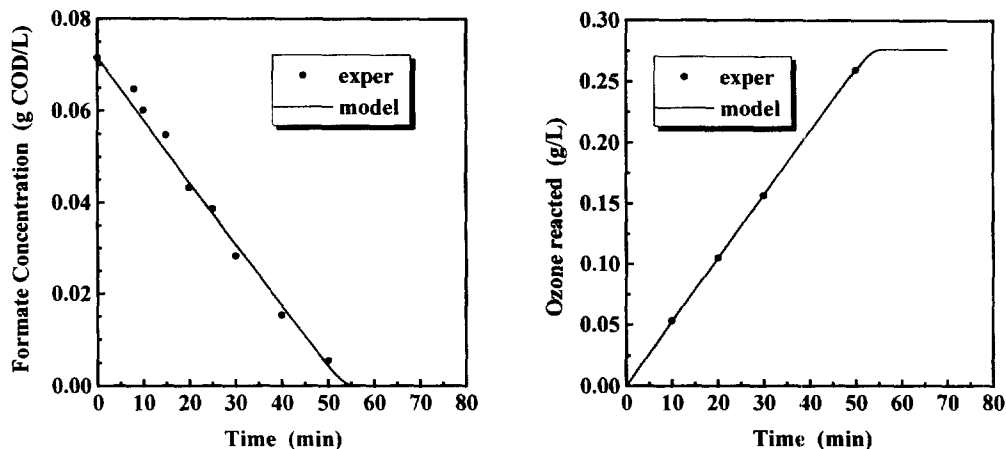
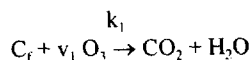


Figure 2. Experimental and model prediction profiles of formate and ozone reacted.

Ozonation of formate

A buffered solution (pH≈7) of formic acid at the initial concentration of 200 mg/l was ozonated at 25°C. Ozone production was 7.5 mg l⁻¹ min⁻¹. Formate concentration and quantity of ozone reacted are shown in Fig.2. As observed, formate concentration was completely eliminated within 60 min of ozonation. A kinetic model which describes the elimination of formic acid and the amount of ozone reacted was developed as follows. Formic acid reacts with ozone according to the reaction:



Assuming mass action kinetics for this reaction, and accounting for ozone transfer from the gas to the liquid phase with mass transfer coefficient $k_1 a$ (dimensionless), the following equations may be written:

- formate* :

$$\frac{dC_f}{dt} = -k_1 \cdot C_f \cdot C_{O_3(liq)} \quad (3)$$

- ozone* :

$$\frac{dC_{O_3(liq)}}{dt} = \frac{q_g}{V_l} \cdot k_1 a \cdot (C_{O_3(gas)}^0 - H \cdot C_{O_3(liq)}) - \nu_1 \cdot k_1 \cdot C_f \cdot C_{O_3(liq)} \quad (4)$$

where q_g is the air flow velocity (l/min), V_1 is the reactor volume (l), and H is the Henry's law constant.

Using nonlinear least-squares fitting of the experimental data to the model described by eqs. (3) and (4) the optimal values for the rate constant k_1 , the stoichiometric coefficient v_1 and the dimensionless ozone mass transfer coefficient k_{1a} were found to be:

$$\begin{aligned}k_1 &= 319.13 \text{ (g/l)}^{-1} \text{ min}^{-1} \\v_1 &= 3.864 \\k_{1a} &= 0.707\end{aligned}$$

As observed in Fig. 2 these parameters give an excellent fit to the experimental data.

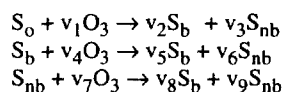
Ozonation of oxalate

Another experiment was carried out using a buffered solution ($\text{pH} \approx 7$) of oxalic acid at the initial concentration of 190 mg/l. Ozone production was 7.1 mg/l min. It was observed that oxalate is not susceptible to oxidation by ozone.

Ozonation of benzenesulfonate was not attempted, since one mole of benzenesulfonate was found to be generated per mole of Orange II, in the ozonation experiment of the azo-dye.

A mathematical model based on the assumption that Orange II (S_o , expressed in COD units) is oxidized to biodegradable and nonbiodegradable compounds expressed as S_b and S_{nb} in COD units respectively, has been developed in the past (Liakou *et al.*, 1997). Both biodegradable and nonbiodegradable compounds lumped in the form of S_b and S_{nb} respectively, are assumed to react further with ozone, yielding more of the same but with different stoichiometry. This holistic approach provides a kinetic framework in terms of measurable quantities, without it being necessary to have detailed knowledge of the intermediate compounds.

Thus the reactions which take place during the ozonation are assumed to be:



where the kinetic rate constants are k_1 , k_2 and k_3 respectively.

Measurable quantities, namely the concentration of the dye (C_A), the COD and the BOD_5 can be correlated with S_o , S_b and S_{nb} as follows:

$$\begin{aligned}C_A &= aS_o \\ \text{COD} &= S_o + S_b + S_{nb} \\ \text{BOD}_5 &= bS_b\end{aligned}$$

The rate equations can be written as follows:

- *Orange II* :

$$\frac{dC_A}{dt} = -l_1 \cdot C_A \cdot C_{O_3(\text{liq})}$$

- *BOD₅* :

$$\frac{d(\text{BOD}_5)}{dt} = l_5 \cdot C_A \cdot C_{O_3(\text{liq})} + l_6 \cdot (\text{BOD}_5) \cdot C_{O_3(\text{liq})} + l_7 \cdot (\text{COD}) \cdot C_{O_3(\text{liq})}$$

- *COD* :

$$\frac{d(\text{COD})}{dt} = l_8 \cdot C_A \cdot C_{O_3(\text{liq})} + l_9 \cdot (\text{BOD}_5) \cdot C_{O_3(\text{liq})} + l_{10} \cdot (\text{COD}) \cdot C_{O_3(\text{liq})}$$

- *ozone* :

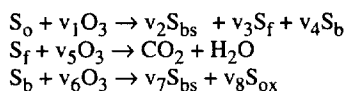
$$\frac{dC_{O_3(\text{liq})}}{dt} = \frac{q_g}{V_l} \cdot k_1 a \cdot (C_{O_3(\text{gas})}^0 - H \cdot C_{O_3(\text{liq})}) - l_2 \cdot C_A \cdot C_{O_3(\text{liq})} - l_3 \cdot (\text{BOD}_5) \cdot C_{O_3(\text{liq})} - l_4 \cdot (\text{COD}) \cdot C_{O_3(\text{liq})}$$

where l_i are the parameters of the model, directly related to the stoichiometric factors v_i , the kinetic rate constants k_i , and the conversion factors 'a' and 'b' each time.

This model is expressed directly in terms of readily measurable quantities. The values of the kinetic parameters estimated from the experimental data using least-squares were :

$$\begin{aligned} l_1 &= 21.216 \text{ (g/l)}^{-1} \text{ min}^{-1} & l_6 &= 0.956 \text{ (g/l)}^{-1} \text{ min}^{-1} \\ l_2 &= 6.957 \text{ (g/l)}^{-1} \text{ min}^{-1} & l_7 &= 0.1484 \text{ (g/l)}^{-1} \text{ min}^{-1} \\ l_3 &= -12.424 \text{ (g/l)}^{-1} \text{ min}^{-1} & l_8 &= -3.262 \text{ (g/l)}^{-1} \text{ min}^{-1} \\ l_4 &= 3.7103 \text{ (g/l)}^{-1} \text{ min}^{-1} & l_9 &= -12.141 \text{ (g/l)}^{-1} \text{ min}^{-1} \\ l_5 &= 0.322 \text{ (g/l)}^{-1} \text{ min}^{-1} & l_{10} &= -0.832 \text{ (g/l)}^{-1} \text{ min}^{-1} \\ & & k_1 a &= 2.971 \end{aligned}$$

The next step was to develop a more detailed model which accounts explicitly for the intermediate products of the dye oxidation. The reactions that are assumed to take place are:



where S_O , S_{bs} and S_b are the concentrations (expressed in COD units) of Orange II, benzenesulfonate and biodegradable compounds (excluding formate) respectively. The kinetic rate constants for the above reactions are k_1 , k_2 and k_3 respectively.

The total COD is simply the sum of the S_i variables since these are given directly in equivalent COD units. Oxalate was found to contribute linearly to the observed BOD within the range of interest with a constant $b_1=1$. This was not the case for benzenesulfonate and formate which exhibit a saturation within the range of interest. Consequently the total BOD may be correlated with the concentration of the different species as follows:

$$\begin{aligned} \text{COD} &= S_O + S_{ox} + S_{bs} + S_f + S_b \\ \text{BOD} &= b_1 S_{ox} + 12.99 \cdot 10^{-3} S_{bs} / (0.67 \cdot 10^{-3} + S_{bs}) + 38.28 \cdot 10^{-3} S_f / (8.93 \cdot 10^{-3} + S_f) + b_2 S_b \end{aligned}$$

The rate equations may be written as follows:

- *Orange II*:

$$\frac{dS_O}{dt} = -k_1 \cdot S_O \cdot C_{O_3(\text{liq})}$$

- *benzenesulfonate*:

$$\frac{dS_{bs}}{dt} = v_2 \cdot k_1 \cdot S_O \cdot C_{O_3(\text{liq})} + v_7 \cdot k_3 \cdot S_b \cdot C_{O_3(\text{liq})}$$

- *oxalate:*

$$\frac{dS_{ox}}{dt} = v_8 \cdot k_3 \cdot S_b \cdot C_{O_3(liq)}$$

- *formate:*

$$\frac{dS_f}{dt} = v_3 \cdot k_1 \cdot S_o \cdot C_{O_3(liq)} - k_2 \cdot S_f \cdot C_{O_3(liq)}$$

- *other biodegradable intermediate compounds:*

$$\frac{dS_b}{dt} = v_4 \cdot k_1 \cdot S_o \cdot C_{O_3(liq)} - k_3 \cdot S_b \cdot C_{O_3(liq)}$$

- *ozone:*

$$\frac{dC_{O_3(liq)}}{dt} = \frac{q_g}{V_1} \cdot k_1 a \cdot (C_{O_3(gas)} - H \cdot C_{O_3(liq)}) - v_1 \cdot k_1 \cdot S_o \cdot C_{O_3(liq)} - v_5 \cdot k_2 \cdot S_f \cdot C_{O_3(liq)} - v_6 \cdot k_3 \cdot S_b \cdot C_{O_3(liq)}$$

The best values of the undetermined rate constants and the stoichiometric coefficients using least-squares fitting to the experimental data are:

$$\begin{aligned} k_3 &= 3.7404 \text{ (g/l)}^{-1} \text{ min}^{-1} \\ v_2 &= 0.1216 \\ v_3 &= 0.0257 \\ v_4 &= 0.5410 \\ v_6 &= 1.606 \\ v_7 &= 0.5194 \\ v_8 &= 0.0381 \\ k_1 a &= 1.137 \\ b_2 &= 0.0558 \end{aligned}$$

The values of k_1 , v_1 , k_2 and v_5 were not included in the least-squares optimization procedure, as they were determined independently from the previous experiments. Fig. 3 shows the ability of the model to fit the experimental data. A satisfactory fit is observed for most variables with the exception of oxalate and formate which, however, are present only in very small amounts and as a result these measurements are highly susceptible to experimental error.

CONCLUSIONS

The azo dye Orange II was oxidised using ozone. The key intermediates were identified and a detailed mathematical model describing their evolution in time was developed. The model proved satisfactory in fitting the experimental data and may be used for designing pretreatment with ozone.

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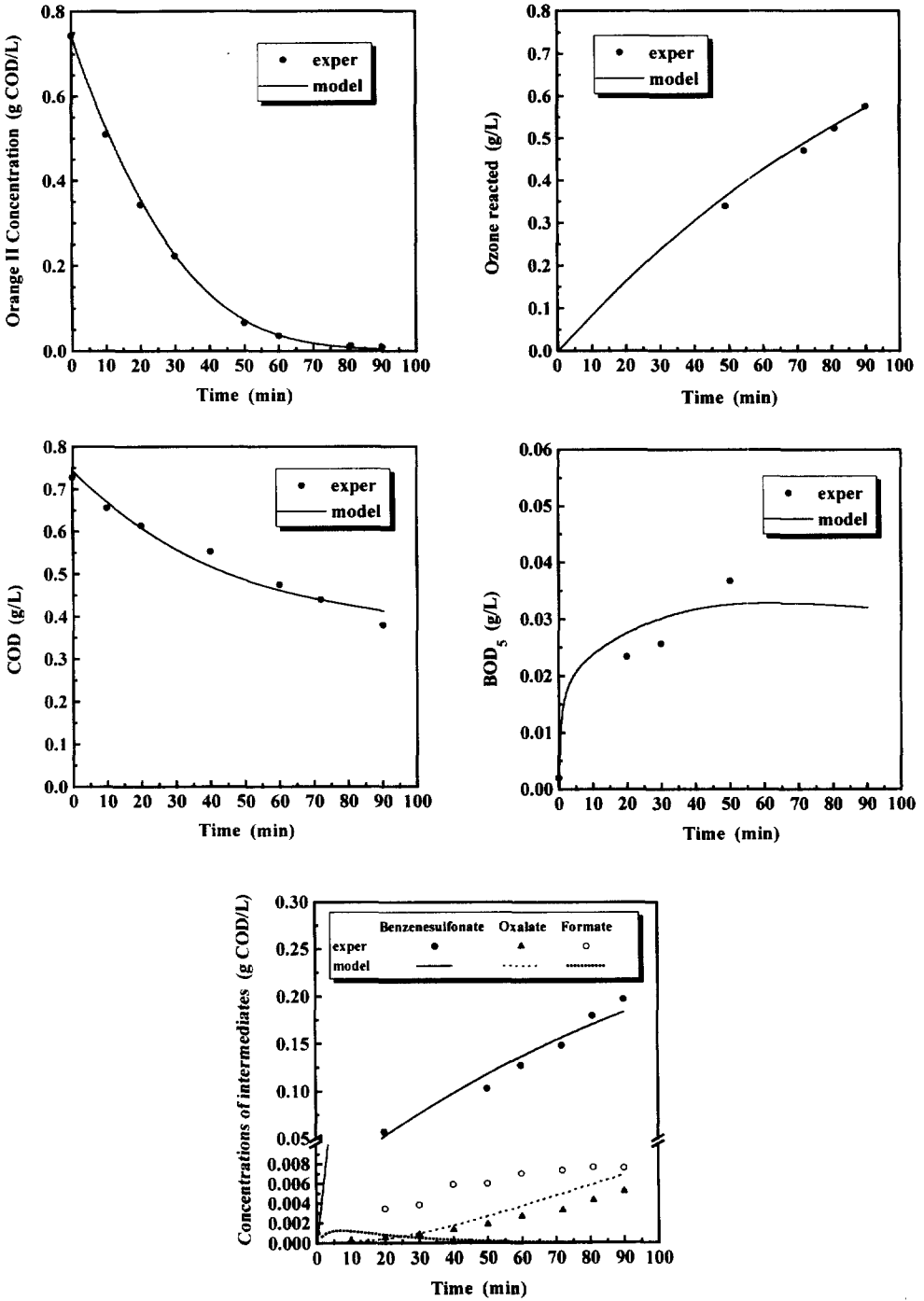


Figure 3. Experimental and model prediction profiles of Orange II, ozone reacted, BOD, COD and intermediate compounds.

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