Reactive Dye Degradation by AOPs; Development of a Kinetic Model for UV/H$_2$O$_2$ Process

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Dedicated to Prof. Dr. Đurđa Vasić-Rački on occasion of her 60th birthday

An application of UV/H$_2$O$_2$ process for the treatment of model wastewater containing organic reactive azo dye C.I. Reactive Blue 137 (RB137) was studied. The efficiency of applied process for decolorization and mineralization of RB137 model solution is discussed. The influence of operating process parameters, initial pH and initial concentration of H$_2$O$_2$, as well as initial dye mass concentration on process effectiveness was investigated. Both direct UV photolysis and OH radical attack were assumed as RB137 degradation mechanisms and a detailed kinetic model for dye degradation by UV/H$_2$O$_2$ process was proposed. The predicted system behavior was compared with experimentally obtained results of decolorization and mineralization of RB137 wastewater. A sensitivity analysis for the evaluation of importance of each reaction used in the model development was also included.

Key words:
Reactive dye, AOPs, UV irradiation, kinetic model, sensitivity analysis

Introduction

The control of water pollution is one of today's main areas of scientific activity. Organic synthetic dyes are the major industrial pollutants and water contaminants.[1] Over the past two decades, manufacturers and users of synthetic colorants have faced increasingly stringent regulations promulgated by agencies established to safeguard human health and the environment.[2] Among all dyes produced today worldwide a group of reactive dyes participates with a large portion. Reactive dyes are widely used in the textile industries because of its simple dyeing procedure and good stability during washing process.[3] The discharge of wastewaters from dye and textile industries introduced intensive color and toxicity to aquatic environment causing serious environmental problems.[4] Around 30 % of commercially available synthetic reactive dyes, consumed in textile processes, is lost in wastewaters and cannot be reused because they are hydrolyzed during the dyeing step.

In general, dyes can be removed from water using biological, physical, and chemical treatment processes. Due to the complex aromatic structure and stability of reactive dyes, conventional biological treatment methods are ineffective for degradation.[5] Chemical and photochemical methods such as Advanced Oxidation Processes (AOPs) are more promising and may be used to degrade bioresistant compounds. AOPs are a class of processes where short-lived, highly oxidizing species, like hydroxyl radicals, are produced. Formation of hydroxyl radicals can be enhanced by exposing an oxidant, e.g. hydrogen peroxide (H$_2$O$_2$) to ultraviolet (UV) light, so AOPs UV and UV/H$_2$O$_2$ present attractive alternatives for the treatment of wastewater containing reactive dyes.[1]

Engineering analysis relies heavily on the use of mathematical models for the forecasting of the environmental impacts and finding appropriate solutions of environmental problems. Mathematical models consist of one or more equations that describe or approximate the behavior of a system. Many of these models reflect the principles of mass and energy conservation. Others are based on empirical and/or theoretical approximations to the behavior of natural and engineered systems.

In this paper an application of UV/H$_2$O$_2$ processes for the treatment of model wastewater containing organic reactive dye of azo type C.I. Reactive Blue 137 (RB137) was studied. A mathematical model predicting system behavior was developed. Evaluation of importance of each reaction used in model development has been made on the basis of sensitivity analysis.

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Experimental section

Synthetic wastewater containing organic model pollutant was prepared using the commercial dye Cibacron Marine P2R-01, C.I. Reactive Blue 137 (RB137) (Fig. 1) obtained from Ciba-Geigy, and deionezed water; pH 7, conductivity less than 1 μS cm^{-1}. Other chemicals (H$_2$O$_2$, 30 %; sulfuric acid, > 95 %; and sodium hydroxide, p.a.) were supplied by Kemika, Croatia.
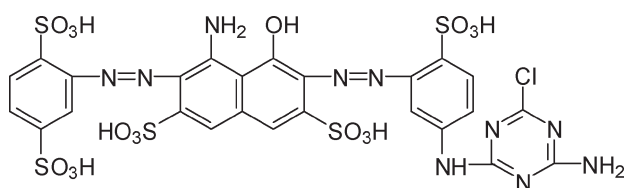

F i g . 1 – *Structure of C.I. Reactive blue 137*

All experiments were carried out in a 0.8 L batch glass annular water-jacketed photoreactor (Fig. 2). The irradiation source was a mercury lamp of 125 W (UV-C, 254 nm), UVP-Ultra Violet Products, Cambridge, UK, supplied by Hach Company, Loveland, CO, USA, which was placed in the inner quartz tube of the reactor. The incident UV-light flux by the reactor volume unit at 254 nm was measured by hydrogen peroxide actinometry.[5] Initial pH values and hydrogen peroxide concentration ranged
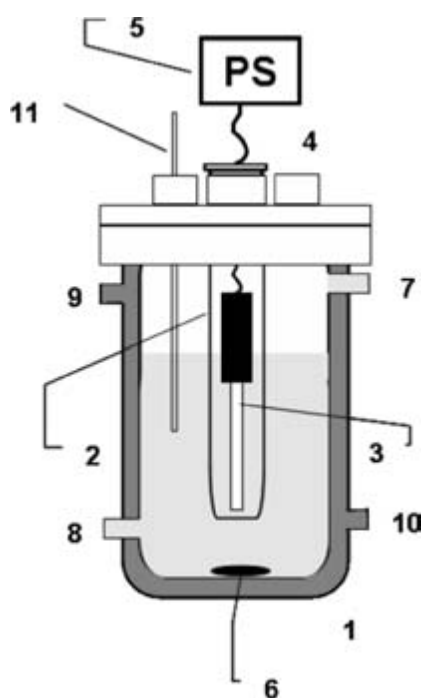

F i g . 2 – *Schematic diagram of photoreactor. (1) glass water-jacketed reactor, (2) quartz jacket, (3) UV lamp, (4) sampling port, (5) power supply (PS), (6) magnetic stirring bar, (7) and (8) solution inlet and outlet, (9) and (10) cooling water inlet and outlet, (11) thermometer*

from 3–11 and 2.5–20 mmol L^{-1}, respectively. The reaction mixture was magnetically stirred at 20 (± 0.2) °C. Model wastewater solution contained 20 or 80 mg L^{-1} of RB137 (0.5 L). The samples were taken from the reaction mixture after 2, 5, 10, 15, 20, 30, 40, 50 and 60 min, and thereafter immediately analyzed. All experiments were repeated three times and averages are reported.

The initial pH values were measured by handy-lab pH/LF portable pH/conductivity-meter, Schott Instruments GmbH, Mainz, Germany. The decolorization of RB137 solution was monitored by a Perkin Elmer Lambda EZ 201 UV/VIS spectrophotometer, USA, at the maximum absorption wavelength of 610 nm. The extent of RB137 mineralization was determined on the basis of total organic carbon (TOC) measurements, using TOC analyzer; TOC-V$_{CPN}$ 5000 A, Shimadzu, Japan.

Model formulation

The mathematical model for UV/H$_2$O$_2$ process, including 12 chemical species (ions, atoms and molecules) and 19 chemical reactions, was developed using chemical reactions and rate constants mostly from literature (Table 1.).[3,6–12] The developed model describes radical chain reactions which occur in the bulk during UV/H$_2$O$_2$ process. Both degradation mechanisms, direct UV photolysis of organic pollutant and OH radical attack to the organic pollutant, were included in the model formulation. The photolysis of H$_2$O$_2$ was assumed to be the only source of OH radicals generation. Model predicts dependence of system behavior on operating parameters of UV/H$_2$O$_2$ process, initial pH, and initial concentration of H$_2$O$_2$.

The general mass balance for a well-mixed, constant volume, and constant temperature batch reactor is given by:

$$\frac{dc_i}{dt} = -r_i \tag{1}$$

where c_i is concentration of specie i in the bulk and r_i is the bulk phase rate of the same specie.[13] Dye degradation was simulated by *Mathematica 5.0* (Wolfram Research, Champaigne, IL) using GEAR method, which finds the numerical solution to the set of ordinary differential equations. Values of rate coefficient of reactions 17 and 19, describing decolorization and mineralization of RB137 by OH radicals, respectively, were determined by trial and error method fitting the values into the model. Firstly, the model M1, which predicts RB137 degradation by UV irradiation, was developed and the quantum yield of RB137 was determined by trial and error method. In the next step, the model M1

T a b l e 1 – *The reactions, rate coefficients and quantum yields used for the kinetic modeling*

#	Reaction	Ref.	k/L mol^{-1} s^{-1}	
			literature	used
1	$H_2O_2 + h\nu \rightarrow 2HO\bullet$	3, 6, 7	$\Phi = 0.5$ mol Einstein^{-1}	$\Phi = 0.5$ mol Einstein^{-1}
2	$HO\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O$	6, 8–11	1.2–4.5×10^7	4.5×10^7
3	$HO\bullet + HO_2^- \rightarrow HO_2\bullet + OH^-$	7, 9	7.5×10^9	7.5×10^9
4	$HO_2\bullet + H_2O_2 \rightarrow H_2O + HO\bullet + O_2$	7	3.0	3.0
5	$O_2\bullet^- + H_2O_2 \rightarrow OH^- + HO\bullet + O_2$	7	0.13	0.13
6	$2HO\bullet \rightarrow H_2O_2$	7-11	4.2-5.3×10^9	5.3×10^9
7	$HO_2\bullet + HO\bullet \rightarrow H_2O + O_2$	7-11	6.6×10^{11}	6.6×10^{11}
8	$2HO_2\bullet \rightarrow H_2O_2 + O_2$	6-11	8.3×10^5	8.3×10^5
9	$O_2\bullet^- + HO_2\bullet \rightarrow HO_2^- + O_2$	6-11	9.7×10^7	9.7×10^7
10	$O_2\bullet^- + HO\bullet \rightarrow HO^- + O_2$	7-11	1.0×10^{10}	1×10^{10}
11	$HO_2\bullet \rightarrow O_2\bullet^- + 2H^+$	6-11	1.58-7.9×10^5 s^{-1}	1.58×10^5 s^{-1}
12	$O_2\bullet^- + 2H^+ \rightarrow HO_2\bullet$	6-11	1.0×10^{10}	1.0×10^{10}
13	$HO\bullet + H_2O_2 \rightarrow O_2\bullet^- + H_2O$	8, 9	2.7×10^7	2.7×10^7
14	$HO_2^- + H^+ \rightarrow H_2O_2$	9	2.6×10^{10}	2.6×10^{10}
15	$H_2O_2 \rightarrow HO_2^- + H^+$	9	3.7×10^{-2} s^{-1}	3.7×10^{-2} s^{-1}
16	$RB137 + h\nu \Leftrightarrow RB137^* \rightarrow$ products 1	3		$\Phi = 4.2 \times 10^{-3}$ mol Einstein^{-1}
17	$RB137 + HO\bullet \rightarrow$ products 1	3, 6, 12		3.32×10^9
18	$OC + h\nu \Leftrightarrow OC^* \rightarrow$ products 2	3		$\Phi = 4.2 \times 10^{-3}$ mol Einstein^{-1}
19	$OC + HO\bullet \rightarrow$ products 2	3, 6, 12		2.68×10^8

RB137 – parent dye molecule   products 1 – colorless products
OC – organic content of dye solution   products 2 – inorganic products

was incorporated in the model M2 which predicts RB137 degradation by UV/H$_2$O$_2$ process.

In order to determine the sensitivity of the model output to input reaction rate constants and the importance of specific reactions, a parametric sensitivity analysis, as described in literature,[14,15] was used. The system of chemical reactions is represented by a vector **y** with N components, and is determined by solution of the differential equations

$$\frac{dy_j}{dt} = f_i(\mathbf{y},\phi,t) \qquad (2)$$

with initial conditions

$$y_i(0) = y_i^i \qquad (3)$$

where y_i is dependent variable, t the time, and ϕ is the vector containing m system input variables. For the kinetic model used in the present study, y_i is the average concentration in the bulk phase of species i, and ϕ is the vector of reaction rate coefficient. The general solution to equation (2) is

$$y_i = y_i(t,\phi). \qquad (4)$$

The sensitivity coefficients, $s(y_i; \Phi_j)$, determine how a small change in one reaction rate coefficient, or in general any model parameter, affects the dependent variables and are defined by

$$s(y_i;\phi_j) = \frac{\partial y_i(t,\phi_j)}{\partial \phi_j} \qquad (5)$$

Normalized sensitivity coefficients are defined as

$$S(y_i;\phi_j) = \left(\frac{\phi_j}{y_i}\right) s(y_i;\phi_j) \qquad (6)$$

For the current kinetic system, the following equations are solved simultaneously with the system ordinary differential equations representing the material balances:

$$\frac{ds_j}{dt} = \mathbf{J}(t)s_j + \frac{\partial f(t)}{\partial \phi_j} \qquad (7)$$

with initial conditions

$$s(y_i;\phi_j)\big|_{t=0} = \begin{cases} 0, & \phi_j \neq y_j^i \\ 1, & \phi_j \equiv y_j^i \end{cases} \qquad (8)$$
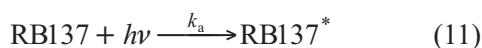
where

$$J(t) = \begin{bmatrix} \dfrac{\partial f_1}{\partial y_1} & \dfrac{\partial f_1}{\partial y_2} & \Lambda & \dfrac{\partial f_1}{\partial y_n} \\ \dfrac{\partial f_2}{\partial y_1} & \dfrac{\partial f_2}{\partial y_2} & \Lambda & \dfrac{\partial f_2}{\partial y_n} \\ M & M & O & M \\ \dfrac{\partial f_n}{\partial y_1} & \dfrac{\partial f_n}{\partial y_2} & \Lambda & \dfrac{\partial f_n}{\partial y_n} \end{bmatrix} \qquad (9)$$

and

$$\frac{\partial f(t)}{\partial \phi_j} = \begin{bmatrix} \dfrac{\partial f_1}{\partial \phi_j} \\ \dfrac{\partial f_i}{\partial \phi_j} \\ M \\ \dfrac{\partial f_i}{\partial \phi_j} \end{bmatrix} \qquad (10)$$

Results and discussion

The first set of experiments was directed to the investigations of the efficiency of direct UV photolysis for RB137 degradation in model wastewater (20 mg L^{-1}) and development of mathematical model which predicts investigated system behavior. In the case of treatment with UV irradiation, organic substrate RB137 is degraded under illumination through the mechanism shown by equations (1), (2) and (3):[3]

$$RB137 + h\nu \xrightarrow{k_a} RB137^* \qquad (11)$$

$$RB137^* \xrightarrow{k_b} RB137 \qquad (12)$$

$$RB137^* \xrightarrow{k_c} products \qquad (13)$$

where degradation efficiency of organic dyes by direct photolysis is dependent upon reactivity and photosensitivity of the dye. Rate coefficients of reactions (11), (12) and (13) are summarized in term $[k_a(1 - k_b/(k_b + k_c))]$ and can be defined as quantum yield of RB137 (Table 1, #16). The used model M1 is a modified version of the so-called "LL model", a semiempirical model based on the Lambert's law, proposed in the literature:[3]

$$r_{UV} = -\frac{\lim dc_j}{\lim dt} =$$

$$= \phi_i F_i I_0 [1 - \exp(-2.303 L \sum \varepsilon_j c_j)] \qquad (14)$$

being $F_i = \dfrac{\varepsilon_i c_i}{\varepsilon_j c_j}$

where Φ_i, ε_i, I_0 and L stand for the quantum yield and the molar absorption coefficient of specie i, the incident photon flux by reactor volume unit and the effective optical path in the reactor, respectively. *Gimeno* et al.[16] proposed that, if only the beginning of the photolysis process was considered, almost all radiation was adsorbed by the parent compound i, and that no other generated intermediates j competed for the absorption of photons. In the latter case, it followed that $\varepsilon_i c_i \approx \varepsilon_j c_j$ and $F_i \approx 1$. Consequently, the equation (14) could be modified as:

$$r_{UV} = -\frac{\lim dc_i}{\lim dt} = \qquad (15)$$

$$= \phi_i I_0 [1 - \exp(-2.303 L \sum \varepsilon_j c_j)]$$

Once I_0, $3.68 \cdot 10^{-6}$ Einstein L^{-1} s^{-1}, and L, 3 cm, were known by actinometry experiments, the quantum yield of the specie i could be calculated. The value of molar absorption coefficient of RB137, $\varepsilon_{RB137} = 18\ 123.9$ L mol^{-1} cm^{-1}, was calculated from the equation (16) by measuring absorbance of the RB137 solution at 254 nm. Absorbance A, can be expressed as a:

$$A = \varepsilon\ c\ l \qquad (16)$$

where ε is the molar absorption coefficient with dimensions $1/(concentration \times length)$, and l is the cell path length.[17] The value of quantum yield of RB137, $4.2 \cdot 10^{-3}$ mol Einstein^{-1}, was determined by trial and error method inserting values into the model M1, given by equation (15), with simultaneous comparison of predicted and experimentally obtained data for RB137 decolorization. From Fig. 3 a good accordance between data for color and TOC removal predicted by the model used and data obtained experimentally during the treatment of RB137 model solution by UV photolysis process can be observed. Minor discrepancy between predicted and observed TOC removal, may be attributed to the formation of by-products with different quantum yields which was not included in the modeling. From Fig. 3 it can be seen that decolorization of RB137 model solution reached 97.6 % after a one-hour treatment by UV process. However, very low mineralization extent with maximal 5.9 % of TOC removal was demonstrated. Such behavior of the studied system was expected due to the fact that decolorization to the certain level enables the progress of mineralization.[18]

When UV radiation was combined with a powerful oxidant H$_2$O$_2$, degradation efficiency of the organic dye RB137 was significantly enhanced due
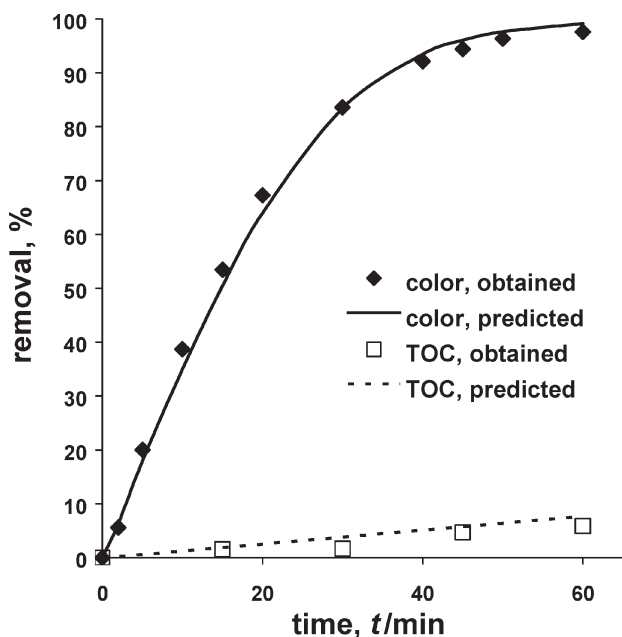
F i g . 3 – *The efficiency of direct photolysis for the degradation of RB137, the comparison of data predicted by model and those experimentally obtained (γ (RB137) = 20 mg L⁻¹, pH 5.5)*

to OH radical production caused by the photolysis of H_2O_2, (Table 1, #1).[3] In all experiments where UV radiation was combined with hydrogen peroxide as an additional oxidizing agent, the complete bleaching was achieved rather fast, $t < 10$ minutes of treatment (results are not shown). Complete decolorization and partial mineralization was achieved after a one-hour treatment by UV/H_2O_2 process through entire investigated range of hydrogen peroxide concentrations (Fig. 4). These results indicate
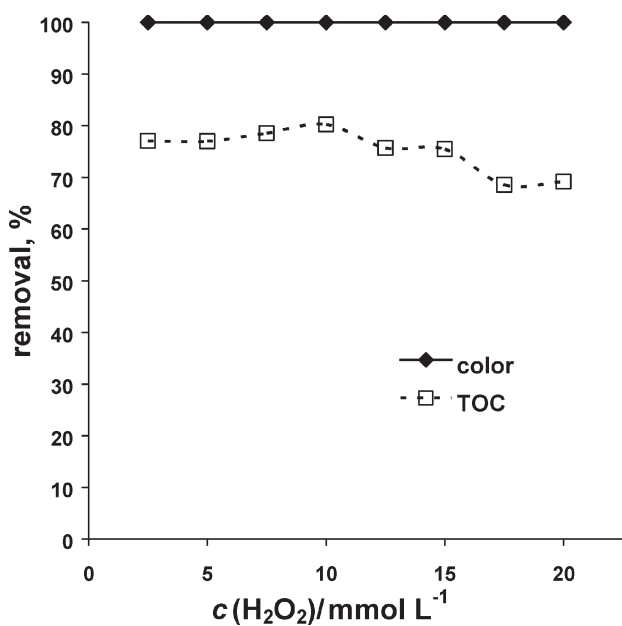
that oxidation products still have an organic nature, i.e. only partial mineralization was achieved. With an increase of initial H_2O_2 concentration from 2.5 to 10 mmol L⁻¹, mineralization extent also increased, but very slightly, from 77.1 % to the maximum of TOC removal of 80.2 %. Further increase of H_2O_2 initial concentration from 10 mmol L⁻¹ to 20 mmol L⁻¹ decreased the mineralization extent from 80.2 % to 68.6 %. Hence, 10 mmol L⁻¹ H_2O_2 was chosen as the optimal concentration for RB137 degradation by UV/H_2O_2 photooxidation. Slight enhancement of mineralization extents in the first part of the range of initial H_2O_2 concentration studied (2.5–10 mmol L⁻¹), could be contributed to an increase of OH radical concentration in the bulk according to the mechanism shown in Table 1, #1. Decrease of RB137 degradation efficiency by UV/H_2O_2 process with further increasing of the initial H_2O_2 concentration could be the result of H_2O_2 bulk concentration higher than 10 mmol L⁻¹. When hydrogen peroxide is in excess, it behaves as a scavenger, consequently lowering the hydroxyl radicals concentration (Table 1, reactions #2, #7, #10 and #13) and decreasing the overall mineralization efficiency of the applied process.[6,19]

The reactivity of hydrogen peroxide depends on pH of the medium. Therefore, additional set of experiments was performed in order to determine the most effective initial pH for RB137 decolorization and mineralization at initial H_2O_2 concentration of 10 mmol L⁻¹. Effect of initial pH was studied in the pH range 3–11. As presented in Fig. 5, mineralization extent increased with the increase in pH value, from 69.3 % TOC removal at pH 3, to
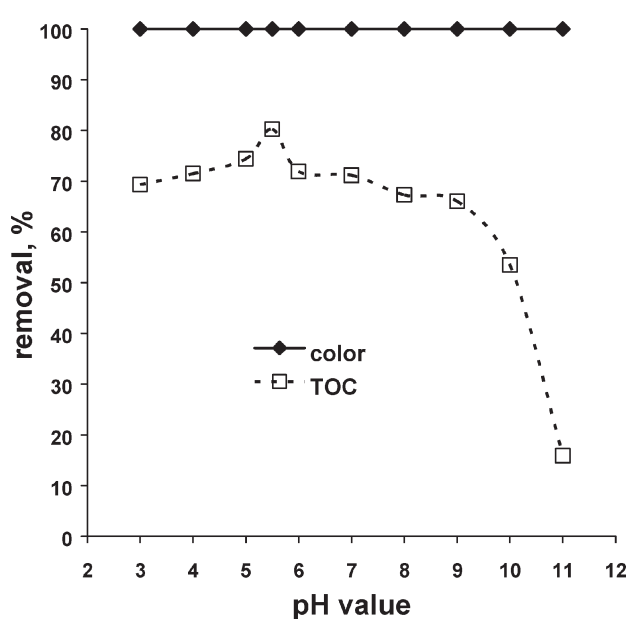

F i g . 4 – *Influence of the initial H_2O_2 concentration on RB137 decolorization and mineralization efficiency of UV/H_2O_2 process after a one-hour treatment (pH 5.5, γ (RB137) = 20 mg L⁻¹)*

F i g . 5 – *Influence of the initial pH value on RB137 decolorization and mineralization efficiency of UV/H_2O_2 process after a one-hour treatment (c(H_2O_2) = 10 mmol L⁻¹, γ(RB137) = 20 mg L⁻¹)*

80.2 % TOC removal at pH 5.5. With a further increase of pH value to neutral and low basic range, TOC removal was slightly decreased to values between 66.1–71.9 %. An increase of pH in strong basic range caused significant decrease in TOC removal, particularly at pH 11, where only 15.9 % of organic content was mineralized. The constant decrease in TOC removal in the alkaline medium (especially at pH 10 and pH 11) is due to the formation of oxidizing species such as hydroperoxy anion, HO_2^-, which is the conjugated base of H_2O_2. HO_2^- consumes OH radical, (Table 1, #3), consequently lowering the mineralization extent.[6,19] Therefore, the optimal operating parameters for degradation of RB137 model solution of 20 mg L^{-1} by UV/H_2O_2 process, where 80.2 % of TOC removal and complete decolorization were achieved, were established to be 10 mmol L^{-1} of initial H_2O_2 concentration and pH 5.5.

Decolorization and mineralization kinetics of RB137 model solution (20 mg L^{-1}) by UV/H_2O_2 at optimal process conditions is presented in Fig. 6, where experimental data are compared with data predicted by the mathematical model developed. In UV/H_2O_2 model development, the existence of both degradation mechanisms, direct photolysis of RB137 and OH radical attack, were assumed in the system studied. The reaction of direct photolysis of H_2O_2 (Table 1, #1) was considered as crucial i.e. as a main source of OH radical generation. The additional set of specific radical reactions (Table 1, #2–15) which occur during UV/H_2O_2 process in the bulk, was taken into account in the model develop-

ment. The photolysis of H_2O_2 and consequent OH radical generation was expressed by equation (15), with the values of molar absorption coefficient of hydrogen peroxide, $\varepsilon_{H2O2} = 18.6$ L mol^{-1} cm^{-1}, and quantum yield of hydrogen peroxide, $\Phi_{H2O2} = 0.5$ mol Einstein^{-1}, taken from the literature.[3] Dye degradation by OH radicals is described by reactions #17 and #19 (Table 1). The rate coefficients for decolorization, $k_{\#17} = 3.32 \cdot 10^9$ L mol^{-1} s^{-1}, and mineralization, $k_{\#19} = 2.68 \cdot 10^8$ L mol^{-1} s^{-1}, were determined by trial and error method fitting the values into the model M2.

Good accordance between experimental data for both decolorization and mineralization of RB137 and those predicted by the model developed for UV/H_2O_2 process, can be observed. The values of reaction rate coefficients #17 and #19 obtained fall within the range of rate coefficients of OH radical reactions with organic substrates reported in the literature by several authors. In our previous study dealing with kinetics of Fenton type processes, a similar value of the rate coefficient for the reaction of organic content and OH radical was determined.[20] *Arslan-Alaton* et al.[21] stated that the rate coefficient of reaction between OH radical and organic pollutant, ranges between 10^8–10^{11} L mol^{-1} s^{-1}. Moreover, *Padmaja* and *Madison*[22] reported that the reaction of the hydroxyl radical with azobenzene, the simplest azo dye, is diffusion-controlled reaction with the second order rate coefficient of $2 \cdot 10^{10}$ L mol^{-1} s^{-1}. However, in this work, complete bleaching of RB137 was obtained in less than 10 min of treatment, while the complete mineralization was not achieved even after a 1 h treatment. The result indicates significantly higher susceptibility of azo bond in chromogen of RB137 to OH radical attack, in comparison to byproducts formed, e.g. triazine structure as well as mono- and di-substituted benzenes and naphtoles.[23] Although both mechanisms, direct photolysis and OH radicals attack, are responsible for the degradation of organic compounds by UV/H_2O_2 process, OH radicals mechanism is considered as predominant, due to the constant OH radical supply throughout H_2O_2 decomposition promoted by UV light.[3,12] It could be expected that the degradation of organic pollutants over direct photolysis mechanism plays a significant role only when complete amount of added hydrogen peroxide is consumed, which was not the case in this study.

Validity of the model developed for degradation of RB137 was tested at different initial conditions, i.e. initial dye concentration and initial H_2O_2 concentration. Fig. 7 presents comparison of experimental data and mathematical model for decolorization and mineralization of RB137 by UV/H_2O_2 process. For this purpose experiments were performed at initial
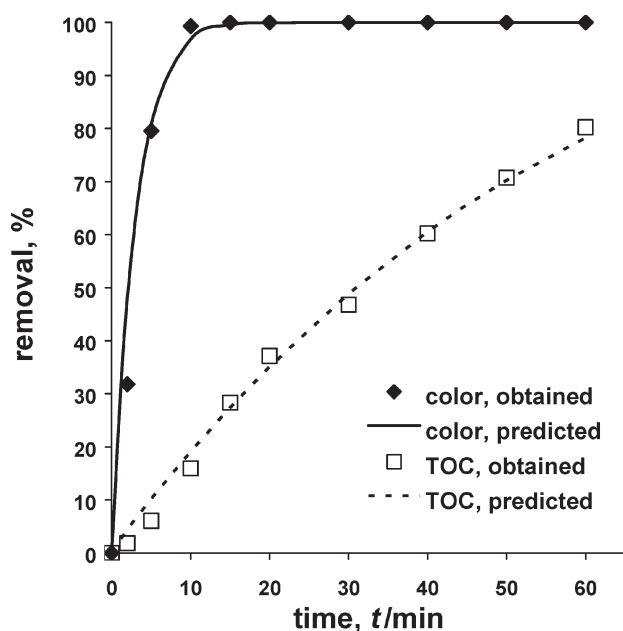

F i g . 6 – *Comparison of mathematical model and experimental results for decolorization and mineralization of RB137 dye solution during a one-hour treatment by UV/H₂O₂ process (pH 5.5, c(H₂O₂) = 10 mmol L⁻¹, γ(RB137) = 20 mg L⁻¹)*
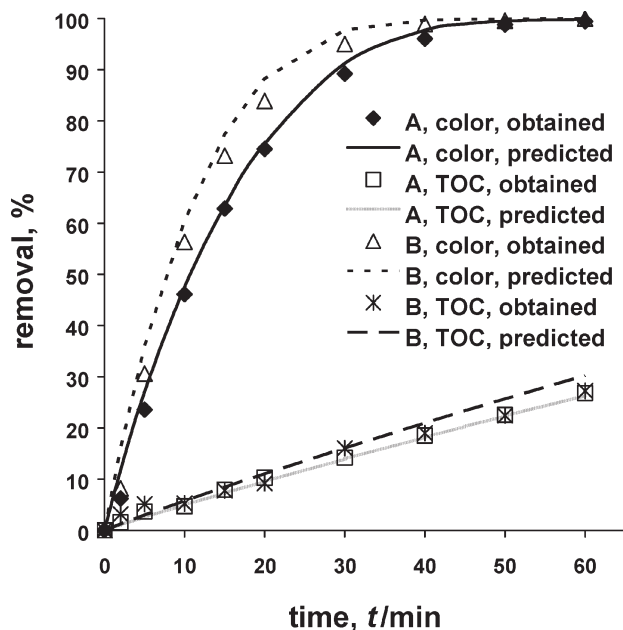
F i g . 7 – *Comparison of mathematical model and experimental results for decolorization and mineralization of RB137 dye solution during a one-hour treatment by UV/H$_2$O$_2$ process A (pH 5.5, c(H$_2$O$_2$) = 10 mmol L^{-1}, γ(RB137) = 80 mg L^{-1}) and B (pH 5.5, c(H$_2$O$_2$) = 40 mmol L^{-1}, γ(RB137) = 80 mg L^{-1})*

F i g . 8 – *The peak values of the dimensionless sensitivity coefficients for the concentration of organic content (TOC) with respect to reaction rate constant for the chemical reactions used in kinetic modeling*

RB137 mass concentration of 80 mg L^{-1} and initial H$_2$O$_2$ concentrations of 10 mmol L^{-1} and 40 mmol L^{-1}. In the model M2, developed previously, only the quantum yield of hydrogen peroxide was modified, due to the knowledge that its value depends strongly on solution transparency and clearness.[3] In both cases a good accordance between the model and the experimentally obtained data is observed.

Results of the sensitivity analysis, presenting the peak values of non-dimensional sensitivity coefficients for the concentration of organic content of dye solution (OC, expressed by the means of TOC parameter) with respect to the reaction rate coefficient for the chemical reactions used in kinetic modeling are given in Fig. 8. The most important parameter studied here is how small change in each reaction rate changes the rate of mineralization of RB137 organic content. Positive results of the normalized sensitivity coefficient for OC indicate that if the particular reaction rate coefficient was increased, a higher OC concentration would occur, showing that the rate of OC oxidation would be lower. On the other hand, negative values of the OC sensitivity coefficients indicate that rate of OC oxidation is increasing with an increase in the reaction rate. What is important, the sensitivity analysis shows the magnitude of the increase or decrease in OC oxidation, and therefore describes the significance of the specific reaction. The value for the normalized sensitivity coefficients described by equation (6) gives the order of magnitude of the change in concentration if the given reaction parameter changes by an order of magnitude. Hence,
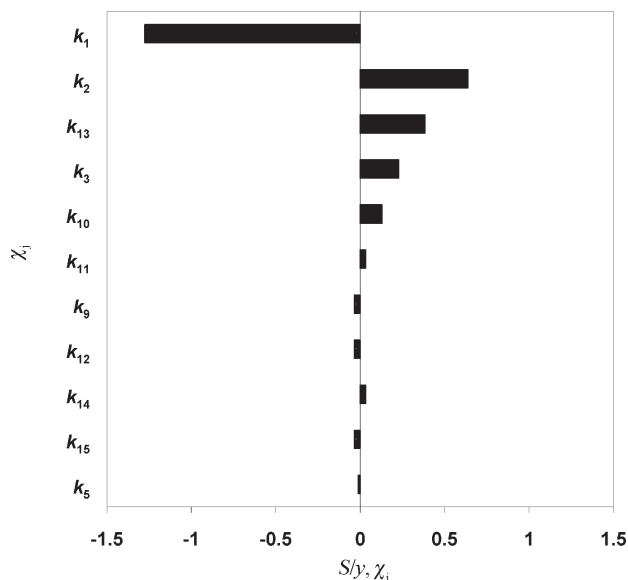
if the value of sensitivity coefficient for OC is 1, that would indicate that if reaction rate were increased by 1 order of magnitude, the value of OC concentration would be 1 order of magnitude higher than the original reaction rate.[9, 14, 15] In this study, sensitivity analysis showed that the most important reaction in the investigated system, besides reaction of direct photolysis of RB137 (Table 1, #18) and reaction between organic content of RB137 solution and OH radicals (Table 1, #19), is reaction #1 (Table 1), which describes photolysis of H$_2$O$_2$ and consequent production of OH radicals with the value of normalized sensitivity coefficient of –1.27 (Fig. 8). That means if the rate of OH radical production over H$_2$O$_2$ photolysis increased in reaction #1, the concentration of OC would decrease, thus giving a negative sensitivity coefficient. That system behavior was expected due to the fact that reaction represents, source of OH radicals, species responsible for mineralization of RB137. Other important reactions according to sensitivity analysis are #2 and #13 that describe a scavenging nature of H$_2$O$_2$ towards OH radicals, with positive values of normalized sensitivity coefficients 0.64 and 0.38. The values of normalized sensitivity analysis of reactions #3 and #10 that describe consumption OH radicals in radical chain reactions are found to be > 0.1, and it could be assumed that those reactions are also a part of group of important reactions in developed mathematical model. Values of normalized sensitivity coefficients of other reactions which are included in model development and that are not presented in Fig. 8, ranged between 10^{-5}–10^{-8}. Those reactions are considered to be less important.

Conclusion

In this study, degradation of commercial reactive dye RB137 by UV/H_2O_2 process was investigated. Influence of operating parameters, pH and initial H_2O_2 concentration, were investigated and discussed on the basis of UV/VIS and TOC measurements. The experimentally obtained results showed that UV/H_2O_2 process is suitable for effective treatment of model wastewater containing organic reactive azo dye RB137. Complete bleaching of RB137 model wastewater was obtained at both initial dye concentrations. The highest degree of mineralization, 80.2 % of TOC removal, was obtained in the case of initial dye mass concentration 20 mg L^{-1}, pH 5.5 and initial H_2O_2 concentration of 10 mmol L^{-1}. A kinetic model for the degradation of RB137 model wastewater by UV/H_2O_2 process was developed. Both degradation mechanisms of RB137, OH radical attack and direct photolysis, were considered. The model included also a set of radical chain reactions between inorganic species in the bulk specific for UV/H_2O_2 process. Validity of developed model was confirmed by the successful prediction of experimentally obtained results at different initial conditions. On the basis of the parametric sensitivity analysis performed, the importance of each chemical reaction included in model development was established.

N o m e n c l a t u r e

A – absorbance
c – concentration, mmol L^{-1}
I_0 – incident photon flux by reactor volume unit, Einstein L^{-1} s^{-1}
k – second order reaction rate coefficient, L mol^{-1} s^{-1}
l – cell path length, cm
L – effective optical path in the reactor, cm
r – reaction rate, mol L^{-1} s^{-1}
S – normalized sensitivity coefficients
t – time, min
γ – mass concentration, mg L^{-1}
ε – molar absorption coefficient, L mol^{-1} cm^{-1}
Φ – quantum yield, mol $Einstein^{-1}$

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