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Modeling of Ozonation of C.I. Reactive Black 5 through a Kinetic Approach

Abstract
C.I. Reactive Black 5 (RB5) is the most commonly used dye in the textile industry. Ozone is a strong oxidan that can decompose many barely degradable pollutants, including dyes. Although there are many literature reports devoted to the treatment of textile wastewater and dye solutions by ozone, the ozonation mechanism and modeling of the kinetics is still not well covered. In this work a kinetic model of the process of RB5 decolourisation by ozone has been proposed and validated on the basis of experimental data. The experiments were carried out in a liquid-liquid system to avoid mass transfer limitation. A model was established for acid reaction medium. The main RB5 reaction was direct oxidation of the dye with molecular ozone. The self-decomposition of ozone in liquid phase was taken into account and described by an empirical equation. The reaction rate constants of RB5 with ozone were estimated from the experimental data in the range of $(1.88 \pm 0.08) \times 10^4 - (2.53 \pm 0.10) \times 10^5 \, M^{-1}s^{-1}$ (invariant with initial dye concentration). An empirical equation $k_2' = 1.06 \times 10^8 (C_{OH^-})^{0.31}$ was built for the constant to make it dependent on the pH value. A solution of the non-linear inverse problem allowed for identification of the kinetic constants on the basis of the experimental data obtained. The model gave a good match between the prediction and experimental data for pH between 1.88 and 4.0.

Key words: *ozonation, C.I. Reactive Black 5, kinetic model, second-order kinetic constant with ozone, second-order kinetic constant with hydroxyl radical.*

Introduction

There are many literature reports where dyes were successfully decomposed using ozone and ozone-based Advanced Oxidation Processes (AOPs) in aqueous solutions [1-13], as well as in textile wastewater [14-22]. However, there are only a few publications focused on the determination of kinetic parameters [23 -25] or modeling of the kinetic [26-30]. In contrast to research concentrated only on the optimization of the treatment, modeling of the ozonation kinetics can be troublesome. The complexity of the process is the main reason causing difficulty. In most cases ozonation is proceeded in heterogeneous gas-liquid systems, for example in a bubble column reactor. Then the mass transfer of ozone from the gas to liquid phase can be the limiting stage, which can influence the global reaction rate. This problem can be skipped by using the liquid-liquid system during kinetic study, like in Olak-Kucharczyk & Ledakowicz's 2016 work [31]. In order to avoid this problem, the research presented was conducted in the liquid-liquid system.

The next problem that may occur is a high reaction rate. The oxidation of dyes by ozone is a rapid process. Second-order kinetic constants of these reactions can be found within 10^4 and $10^6 \, M^{-1} \, s^{-1}$ [23, 24, 28]. Testing of such fast chemical reactions requires specific measurement techniques, like competition kinetics or using the stopped-flow method [31]. Moreover the mass transfer limitation is more possible when very fast reactions occur in the gas-liquid ozone system, where the ozone absorption is much slower than the reaction.

Finally ozone characteristics is a very important issue. Ozone is a strong oxidant that, due to a high oxidative potential (2.07 V), can decompose many of barely degradable pollutants [32]. However, one of the main features of ozone is its instability in the gas phase as well as in the liquid phase. Many mechanisms of ozone decomposition have been presented since Wiess's work in 1934 [33]. The most popular mechanisms are SBH (Staehelin, Buhler and Hoigne) and TFG (Tomiyasu, Fukutomi and Gordon) [33]. Both consider ozone decomposition as a chain of reactions, including initiation, propagation and termination steps. The SBH mechanism, where the propagation step is an ozone reaction with OH^- ion, is the most popular one. However, the TFG mechanism, where ozone decomposition can start due to OH^- ion, as well as OH_2^- ion, is recognized as more reliable when the pH of the reaction medium is high. The more recent studies on the topic are based mostly on these two mechanisms with only slight modifications [34].

As far as the decomposition of ozone is concerned an empirical equation can be a way of describing the issue as well. Then the decomposition mechanism is not considered and the equation can give information about ozone decay. Based on experimental data, Qiu [35] noted that the decomposition of ozone follows the first order kinetic regime and proposed a formula for the rate constant which describes ozone decomposition for a very wide pH range [35].

Moreove when ozone decomposes, the elution of free radicals takes place, especially in alkaline pH [32]. Therefo two pathways of pollutant decomposition during ozonation can be mentioned. The first one is direct oxidation by the ozone molecule and the second one is a reaction with the radical (indirect pathway). Reaction with ozone is a selective one. Ozone can react with molecule structures where a high electron concentration is present, like conjugated double bonds or nucleophilic centers. These kinds of chemical structures are characteristic of dyemolecules. Therefore dyes can be likely decomposed with ozone. However, free radicals, especially hydroxyl ones, are highly non selective and can easy decompose any organic substance, including dyes. It can be concluded that both direct (predominant in an acidic reaction medium) and indirect (predominant in alkaline reaction medium) mechanisms are possible [36]. Therefore within the parameters that can normally control a kinetic rate, like temperature or substrate concentration, in thecase of ozonation pH is the one, which can affect it the most.

The objective of this study was to build a reliable mathematical model to describe the kinetic of RB5 (Reactive

Black 5) decolourisation by ozonation in an aqueous solution. The model was tested in an acid reaction medium (pH between 1.88 and 6.1). In this pH the main reaction pathways were found by direct ozonolysis. Ozone decomposition was taken under consideration during modeling as well, described with an empirical equation based on Qiu's 1999 work [35]. The second-order reaction rate constants of RB5 with ozone were estimated from the experimental data. An empirical equation was built for the constant to make it dependent on the pH value. The invert problem wassolved to find the parameters of the model.

Experimental

Materials

In the kinetic study Reactive Black 5 (RB5) was used, obtained from Boruta-Zachem (Poland) as a purified reagent. The characteristics of this dye are presented in *Table 1*. The buffer components were H_3PO_4, KH_2PO_4 & Na_2HPO_4, all of which were A.R. grade, purchased from Chempur (Poland).
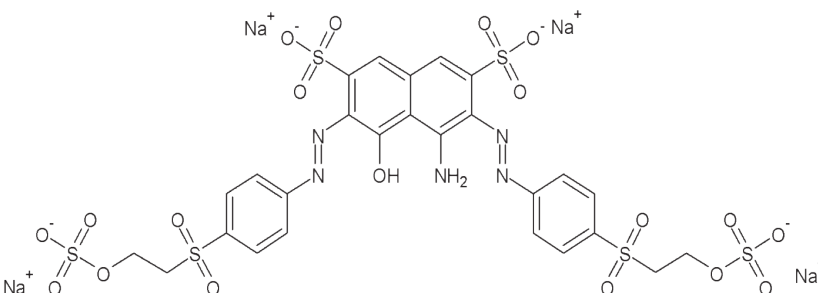
Analytical methods

Kinetic study. In order to avoid mass transfer limitation of ozone, a kinetic study was conducted in the liquid-liquid homogeneous system. Pre-ozoned buffer solutions were saturated with ozone in a bubble column with a capacity of 20 l. Ozone was fed into the reactor from the bottom with a ceramic diffuser – brandol 60®. The ozone was produced by a TOG-C8X TROGEN LTD generator, which was equipped with an integral compressor and oxygen concentrator. The ozone concentration in the gas phase at the inlet and outlet of the reactor was measured by an ozone analyzer – BMT 964, manufactured by BMT MESSTECHNIK GMBH (Germany). Circulation of the liquid phase was induced by a peristaltic pump. The gas effluents from the reactor passed through a scrubber filled with silica gel with an indicator in order to remove moisture contained in the gas, and was then directed to an ozone destructor. Ozone concentration was measured in the liquid phase with a Wallance & Tierman z VariSens™ flow cell (Evoqua Water Technologies GmbH, Germany).

Ozone solution, immediately after taking it from the bubble column, was added into dye solution placed in a spectrophotometer cuvette. The decay of RB5 was measured spectrophotometrically

at a maximum wavelength using a UV-VIS Jasco V-630 spectrophotometer (JASCO, Japan) with 0.01 s intervals. Ozone decomposition was investigated spectrophotometrically by absorbance measurement (λ_{max} = 254 nm) in a separate experiment. Each kinetic experiment was repeated from ten to fourteen times.

Determination of the stoichiometry. The stoichiometry of RB5 ozonation was investigated in a semibatch glass reactor (heterogeneous gas-liquid system) with a capacity of 1 l. Mixing in the reactor was performed with a magnetic stirrer (Wigo type ES 21). Ozone was produced by an Ozonek Ozone Generator (Poland) fed with oxygen from a compressed gas cylinder (O_2 purity 99.5%). O_3 concentrations at the inlet and outlet of the reactor were measured with a BMT 963 Vent ozone analyser (this was the basis for absorbed ozone dose calculations).

Calculations were performed using Origin 9.1 version Pro software. Mathematical modeling was conducted with MAT-LAB software.

Results and discussion

Stoichiometry of BR5 reaction with ozone

The stoichiometric factor for the reaction between the RB5 and ozone was experimentally determined. The pH of the reaction medium was set at 2 with aphosphate buffer to avoid a secondary reaction of the ozone. The initial concentration of RB5 was equal 5.05×10^{-4} M. The reactor was fed with an ozone-oxygen mixture. The ozone dose transferred into the liquid phase was calculated as the difference between the gas at the inlet and outlet at a specific time. The values

of Δn_{RB5} and Δn_{O3} were monitored during the reaction time and the stoichiometric factor $z_1$was calculated as follows:

$$z_1 = \frac{\Delta n_{O3}}{\Delta n_{RB5}} \qquad (1)$$

In *Figure 1* the values of z_1 are presented. It can be noticed that the stoichiometric factor z_1 is very high, equal to 10.6. This result is very close to that obtained by Kusvuran et al., 2010 [37].

The results presented indicate that as long as the colour in the reaction mixture could be observed, c. a. eleven moles of ozone could react with one mole of RB5. The RB5 has a complex molecule and the reaction mechanism may be very complex as well. Because the RB5 samples were contaminated by excipients and many impurities, attempts were made to apply chromatography coupled with mass spectrometry (UHPLC/MS) to analyse intermediates in the reaction mixture. However, the results were notsatisfactory and the detailed decomposition mechanism could not be developed. Thereforeonly a general observation could be made for the possible degradation pathway.

According to many literature reports, like Colindres et al., 2010 [2] and Bamperng et al. 2010 [3], the decolourisation of dyes is supposed to be the the dominant phenomenon in the initial phase of the ozonation process. This observation was reported in the authors' previous work as well [38]. The easiest explanation for decolourisation could be the direct attack of ozone on the chromophore of the dye. RB5 is a di-azo dye based on H-acid. The most possible places for ozone attack in the chromophore of RB5 are the azo bonds. Next eight molecules of ozone can likely react with C=C bonds

Table 1. Characteristics of RB5.

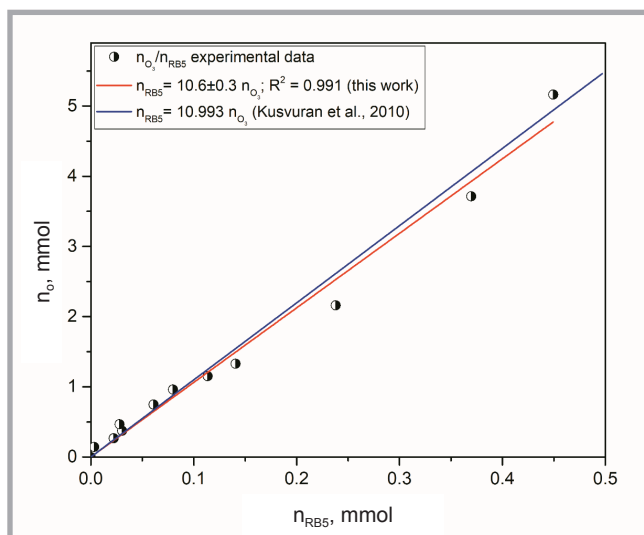| Name	CI No.	CAS No.	Molecular weight, g/mol	λ_{max}, nm	Type
RB5	Reactive Black 5	12225-25-1	991.8	596	azo

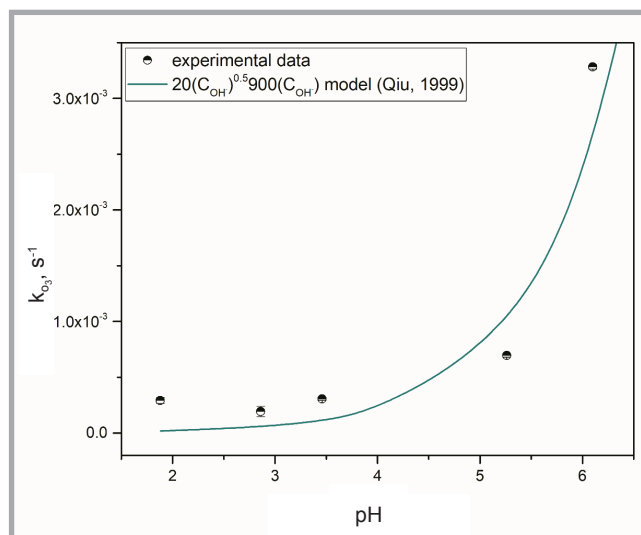**Figure 1.** *Stoichiometric relationship between ozone and RB5 dye.*

Figure 2. *First order rate constants of ozone self-decomposition versus pH of the medium.*

in vinylosulfone groups. Therefore when decolourisation takes place, the simultaneous reaction of ozone with the chromophore and vinylosulfone groups of RB5 cannot be excluded. These observations were postulated by Kusvuran et al., 2010 [37] as well. Moreover, Lopez-Lopez et al, 2007 [25] noted that the molecular structure of dyes was related to ozone consumption and that the electrophilic attack of ozone on the olefins groups cannot be excluded during decolourisation.

It should be noted that all of these observations are true at the initial phase of the process, when the colour can still be observed. When further decomposition of RB5 took place, the stoichiometric factor was even greater (results not shown in the work).

Kinetic of self-decomposition of ozone

The ozone molecule is unstable and decomposes easily with the elution of free radicals. An empirical equation can be a way of describing this issue. Based on the experimental data presented by Qiu, 1999 [35], it was noted that the decomposition of ozone follows the first order kinetic regime according to *Equation (2)*:

$$r_D = -\frac{dC_{O3}}{dt} = k_D C_{O3} \quad (2)$$

where k_D is the kinetic constant, which depends on the OH⁻ ion concentration according to *Equation (3)*:

$$k_D = 20(C_{OH-})^{0.5} + 900\,(C_{OH-}),\ s^{-1} \quad (3)$$

This empirical formula was established by Qiu, 1999, for a very wide range of pH values, between 2.0 and 13.5 [35].

The experiment in this study was carried out within a pH range of 1.88 and 6.1. *Figure 2* shows that the first order rate constants of decomposition of ozone in water obtained in present work could be successfully described by *Equation (3)*. Therefore the empirical formula proposed by Qiu, 1999, was used in this study to build a model of the ozonation of BR5.

Kinetics of RB5 oxidation with ozone

During the kinetic study, the colour decay of RB5 was observed spectrophotometrically at $\lambda = 596$ nm. The RB5 absorbed the irradiation in the wavelength region of ozone detection as well. It was impossible to monitor the concentration of ozone during the process. Therefore, to ensure the pseudo-first order regime of the reaction with respect to RB5, a high initial concentration of ozone was used (1.04×10^{-4} M). At the same time, lower concentrations of RB5 (between 4.7×10^{-6} and 1.6×10^{-5} M) were applied, respectively. An experiment was carried out in an acid medium, where direct ozonolysis takes place. Six pH values between 1.88 and 6.1 were examined. To avoid the mass transfer limitation, the kinetic of RB5 decolourisation was performed in homogeneous aqueous system.

The experimental data were described by the exponential decay function ($y = y_\infty + y_0 \cdot \exp(-kt)$) at the initial reaction phase, and the apparent pseudo-first order constants $k_{app}(s^{-1})$ were determined as the slope of the function as in the works's of Turhan et al., 2012 [39], Gomes et al., 2012 [23] & Gomes et al., 2010 [24]. The rate constants of

RB5 decay were investigated at each pH and initial dye concentration. *Figure 3.a* presents that the ozonation of RB5 in the initial reaction phase followed a pseudo-first order regime for various pH values. Moreover an increase in the constant values with an increasing initial BR5 concentration could be observed. Therefore it can be concluded that ozone was in excess during the initial phase of the reaction [25]. *Figure 3.b* shows the second order constants $k_2(M^{-1}s^{-1})$ vs pH. The values of the second order constants increase with increasing pH values, being between 1.88×10^4 and $2.53 \times 10^5 \,M^{-1}s^{-1}$. The values, found in this experiment are in the agreement with those in the literature [23, 24, 29, 39]. Based on the plot presented in *Figure 3.c*, an empirical equation $k_2' = 1.06 \times 10^8 (C_{OH^-})^{0.31}$ was built for the constant to make it dependent on the pH value (by the regression method). The equation exhibited the best fit for pH values between 1.88 and 4.0.
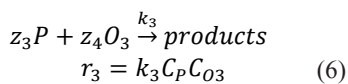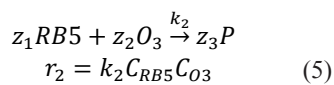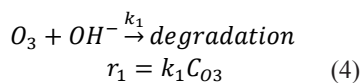
Modeling of ozonation process

As far as ozonation is concerned, the oxidation mechanism of the dyes can be a complex issue. Firstly as has been shown in the previous section, RB5 is a complex chemical compound with high molecular weight and numerous double bonds, which can likely react with ozone. Even though decolourisation was observed during the experiment, simultaneous decomposition could not be excluded (section 3.2). Secondly the RB5 can react with ozone rapidly and a specialist measurement method is needed to monitor the reaction rate (a high-speed spectrophotometer was used during the experiment).

Thirdly ozone is not stable in the liquid phase (water), and decomposes especially in an alkaline medium. Therefore the most general reaction mechanism consists of two contributions: direct oxidation by ozone in an acid medium and indirect oxidation by free radicals (HO• mainly) in an alkaline medium.

The main idea of the work was to develop a simplified mathematical model with a low number of parameters. To describe the complex process of dye decolourisation by a such a simple model, only a global approach can be used. Therefore the reaction between the ozone and RB5 was the only one considered. In order to eliminate a secondary reaction of ozone and the influence of free radicals on the process, an experiment was carried out in an acid reaction medium. Ozone decomposition was taken into account using the empirical equation proposed by Qiu, 1999 [35].

Given all the assumptions, the overall ozonation scheme is given as follows:

$$O_3 + OH^- \xrightarrow{k_1} degradation$$
$$r_1 = k_1 C_{O3} \qquad (4)$$

$$z_1 RB5 + z_2 O_3 \xrightarrow{k_2} z_3 P$$
$$r_2 = k_2 C_{RB5} C_{O3} \qquad (5)$$

$$z_3 P + z_4 O_3 \xrightarrow{k_3} products$$
$$r_3 = k_3 C_P C_{O3} \qquad (6)$$

Mass balance

Due to the fact that ozonation took place in the liquid-liquid homogeneous system and the volume of the reaction mixture was constant, the mass balance was based only on **Equations (4-6)** and describes the chemical reactions in the system. After taking into account the stoichiometry of the reactions, the mass balance can be obtained from **Equations (7-9)**:

$$\frac{dC_{O3}}{dt} = -r_1 - z_2 r_2 - z_4 r_3 \qquad (7)$$

$$\frac{dC_{RB5}}{dt} = -z_1 r_2 \qquad (8)$$

$$\frac{dC_P}{dt} = z_1 r_2 - z_3 r_3 \qquad (9)$$

Which can be rewritten more precisely as follows:

$$\frac{dC_{O3}}{dt} = -k_1 C_{O3} - z_2 k_2 C_{RB5} C_{O3} - z_3 k_3 C_P C_{O3} \qquad (10)$$

$$\frac{dC_{RB5}}{dt} = -z_1 k_2 C_{RB5} C_{O3} \qquad (11)$$

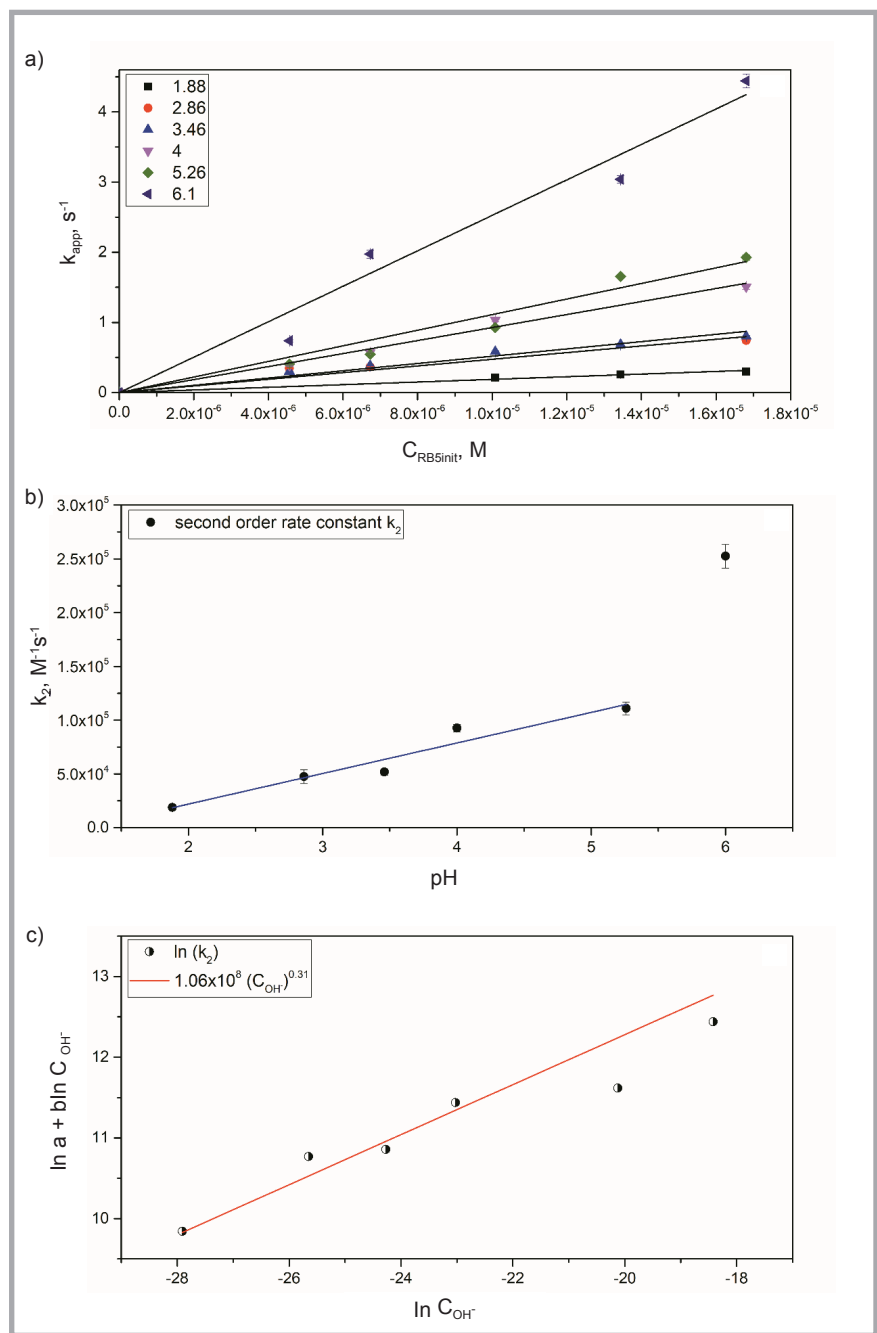$$\frac{dC_P}{dt} = z_1 k_2 C_{RB5} C_{O3} - z_3 k_3 C_P C_{O3} \qquad (12)$$

Figure 3. Values of the rate constant of reaction between RB5 and ozone: a) pseudo-first order apparent constants vs initial concentration of RB5, b) second order constants vs pH, c) constant's dependence on pH value by regression method.

Estimation of model parameters

The system of differential **Equations (10-12)** have been integrated numerically with the Rosenbrock method by MATLAB solver. The initial parameters as well as the rate constants obtained for the model are presented in **Table 2**.

The equations of the model were solved for six pH values. The concentrations of OH^- anions corresponding to pH and concentrations RB5 between 4.7×10^{-6} and 1.6×10^{-5} M, as well as, the concentration of ozone equal to 1.04×10^{-4} M

were initial values for modeling. The stoichiometry factor was 0.1 for RB5, 1 for P (by-product) and 1 for ozone. Values of the rate constants for the reaction RB5-ozone were calculated directly from the experimental data (k_2) and from the correlative equation in dependance on pH (k_2'). The value of the constant rate between P and ozone (k_3) was obtained from model optimization by solving the inverse problem with MATLAB computing script. The optimization method was carried out with the use of the 'fminsearch' MATLAB function.
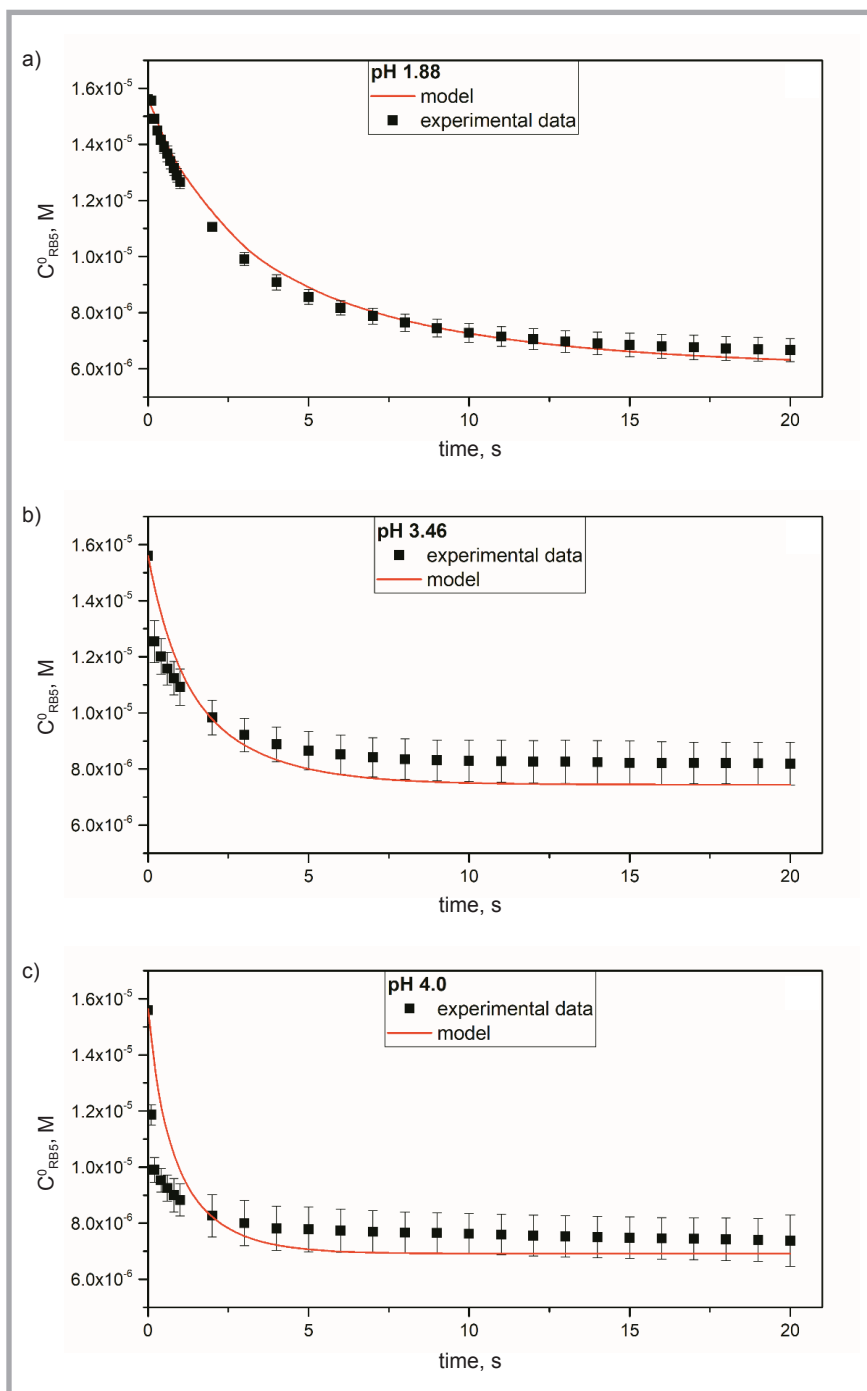
Figure 4. *Kinetics of the decolourisation of BR5 measured and calculated from the model: a) pH = 1.88, b) pH = 3.46, c) pH = 4.0 (initial concentration of RB5 = 1.65 × 10⁻⁵ M, initial concentration of ozone = 1.04 × 10⁻⁴ M).*

It can be noticed that values of k_2 and k_2' are different, however their values correspond to each other, especially for pH between 1.88 and 4.0. The value of the constant rate between P and ozone (k_3) was estimated for pH 1.88, where the mechanism of the reaction was typically molecular, and used for pH values up to 4.0.

Evaluation of the model
In ***Figure 4*** the kinetics of BR5 decolourisation by ozone for pH equal to: a) 1.88, b) 3.46 and c) 4.0 are shown. The matching between the experimental data point and the model are satisfactory. The RB5 degree of conversion can be quite successfully predicted by the model in all cases. This information can be very useful from a practical point of view. At the same time, it can be noticed that with increasing pH the agreement between the experimental data point and the model gets worse at the initial phase of the process, which can be explained by the appearance of free radicals. When pH is higher than 4.0 the indirect oxidation mechanism becomes more relevant and is not included in the model. Based on these results, it can be concluded that a highly complex process like RB5 decolourisation can be successfully described using a simplified model with a low number of parameters. It can be a practical and useful approach to predict the colour decay of dye in acid pH as long as a direct oxidation with ozone is the main mechanism of the process.

Figure 5 shows how the model describes experimental data when the initial RB5 concentration changes The initial concentrations of RB5 between 7.7×10^{-6} and 1.6×10^{-5} M were tested. The pH was equal to 1.88 for all samples. In all cases the same parameters were used (except the initial RB5 concentration). The model successfully described experimental data for various initial RB5 concentrations. Therefore it can be concluded that

Table 2. *Initial parameters and rate constants obtained for the model.*

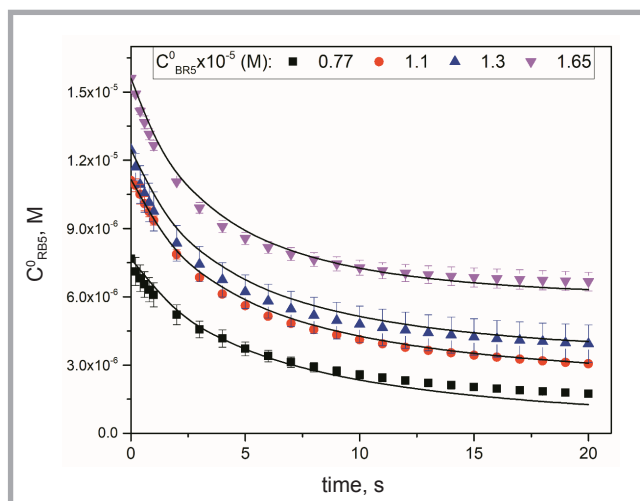| Parameter	Values					
pH	1.88	2.68	3.46	4.0	5.26	6.1
C_{OH^-}, M	7.59×10^{-13}	4.79×10^{-12}	2.88×10^{-11}	1.0×10^{-9}	1.82×10^{-9}	1.26×10^{-9}
C_{0O3}, M	1.04×10^{-4}					
z_1	0.1					
z_2, z_3, z_4	1					
k_1, s⁻¹	$20(C_{OH^-})^{0.5} + 900(C_{OH^-})$					
k_2, M⁻¹·s⁻¹	$(1.88\pm0.08) \times 10^4$	$(4.75\pm0.64) \times 10^4$	$(5.19\pm0.29) \times 10^4$	$(9.27\pm0.34) \times 10^4$	$(1.11\pm0.06) \times 10^4$	$(2.53\pm0.10) \times 10^5$
k_2', M⁻¹·s⁻¹	1.85×10^4	3.73×10^4	5.73×10^4	8.41×10^4	2.06×10^5	3.5×10^5
k_3, M⁻¹·s⁻¹	9.4×10^3				–	

the values of rate constants k_2 and k_3 (***Table 2***) obtained were invariant from the initial dye concentration.

The RB5 concentration was the only variable that could be measured within the process; but the model can give a prediction of ozone and by-product P concentrations over time. ***Figure 6.a*** presents RB5 decay. The model gave a good match between prediction and experimental data. ***Figure 6.b*** shows ozone decay over time. It can be noticed that it was in excess only at the initial phase of the process. Although the ozone was used in more than ten times higher concentration than for the RB5, the high stoichiometry factor and very fast simultaneous reaction with by-product P resulted in its fast consumption. ***Figure 6.c*** presents how the model predicted the concentration of by-product P. This concentration increased rapidly from 0 up to the maximum value and then consequently decreased because of a consecutive reaction of P with ozone. It can be concluded that by-product P appeared when RB5 had been decomposed, and was oxidised very fast to the next by-products. Both RB5 and P cannot be decomposed entirely due to the use of ozone.

Conslusions

Based on the results of the work, it can be concluded that the main objective has been achieved and the highly complex process of RB5 ozonation was successfully described by the simplified model with a low number of parameters. The model gave a good match between prediction and experimental data for pH values from 1.88 to 4.0, where the direct oxidation of RB5 by the ozone molecule was the main pathway of dye decomposition. At the same time it was shown at which pH value the ozonation pathway starts to change from direct (oxidation by ozone only) to mixed (simultaneous oxidation by ozone and free radicals). The model predicted the degree of RB5 conversion within the process, which can be useful from a practical point of view. The reaction rate constants of RB5 with ozone have been found in this work. Their values estimated from experimental data were between $(1.88 \pm 0.08) \times 10^4$ and $(2.53 \pm 0.10) \times 10^5$ M^{-1}s^{-1} (for pH = 1.88 – 6.1). Moreover an empirical equation $k_2' = 1.06 \times 10^8 (C_{OH^-})^{0.31}$ was built for the constant to make it dependent on the pH value. The results of the work indicated that the rate constants were invariant with the initial dye concentration.

Although the results of modeling were satisfactory, the model can be used only in acid pH up to 4.0. Therefore further research should be developed to include the influence of free radicals on the process. Then determination of the rate constant of the reaction between RB5 and the hydroxyl radical as well as its stoichiometry would be the main challenge.

Figure 5. *Kinetics of the decolourisation of BR5 measured and calculated from the model for initial concentrations of RB5 = 7.7 × 10⁻⁶, 1.1 × 10⁻⁵, 1.3 × 10⁻⁵ and 1.6 × 10⁻⁵ (pH = 1.88, initial concentration of ozone = 1.04 × 10⁻⁴ M).*
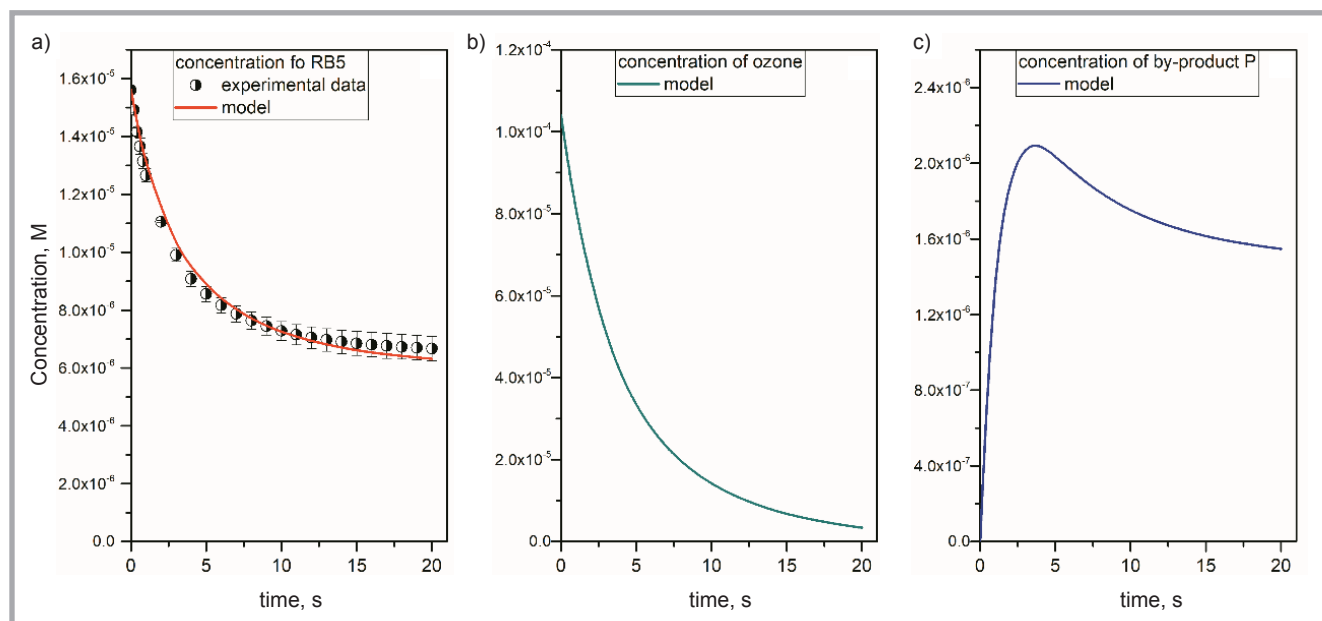

Figure 6. *Kinetics of the decolourisation of BR5 calculated from the model: a) decay of RB5, b) concentration of ozone, c) concentration of by-product P (initial concentrations of RB5 = 1.6 × 10⁻⁵ M, initial concentration of ozone = 1.04 × 10⁻⁴ M, pH = 1.88).*

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