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A Kinetic Model of Decoloration of Water Solution of Anthraquinone Dye Initiated by Generality Hydroxyl Radicals

Abstract
A kinetic model of the decoloration process based on the example of a water solution of the anthraquinone dye Acid Blue 62 was proposed. The importance of decoloring water solutions for the textile industry is emphasised. The wastewater remaining after yarns and fabrics are dyed is generally too coloured for re-use in technological applications or in surface water circulation. A common schematic of the reactions initiated by a hydroxyl radical was proposed for decolouring solutions during an irradiation process in the presence of nitrous oxide, a photochemical process with hydrogen peroxide and induced by ozone. In each version of the model, a different method was considered for generating hydroxyl radicals (HO). On the basis of experimental data, the model parameters describing the decoloration process were estimated, and the experimental data were compared with theoretical calculations. A relatively good agreement of the comparison was obtained.

Keywords: *dye, advanced oxidation, decoloration model, hydroxyl radical.*

Introduction

Recently, much attention has been paid to the decomposition of various dyes in water solutions. The problem is of great importance, especially for the textile industry, where practically all fibres, yarns, and fabrics are dyed with different dying processes. We deal first of all with the processes of chemical oxidation resulting in the decoloration of coloured solutions which the majority of textile wastewater consists of. This follows from the fact that during the biological treatment of wastewater, most dyes are not decomposed, or the process of their decomposition is very slow. So, after the treatment, water is obtained which has the physicochemical parameters to permit its re-use in the technological cycle or enable its discharge into surface reservoirs. However, this water is often very intensely coloured. This is why there is so much interest in methods for wastewater decoloration.

One efficient and economically justified technique is undoubtedly chemical oxidation, in particular the advanced oxidation method. So far, there has been no complete and explicit definition of this process. In a common version of the advanced oxidation process, a predominant role is played by highly reactive hydroxyl radicals HO [1,2,3]. Hence, in all cases, the oxidation reactions should be the same. Particular versions of the process will differ only in the method of generating an oxidising agent, i.e. a hydroxyl radical (HO).

We selected anthraquinone dyes as the basic compound for our attempt to create a general kinetic model of decoloration, as these dyes are commonly used for dyeing yarn and fabrics in the textile industry, especially fabrics of cotton and cotton blends.

Anthraquinone dyes are characterised by their special resistance to external factors, including UV radiation [4,5]. Their decomposition under the influence of UV radiation is only several percent per hour. The application of different versions of advanced oxidation processes gives very good results in this case [6,7]. A highly reactive and not very selective hydroxyl radical is the main factor leading to the decomposition of various types of dyes, including anthraquinone [8,9,10]. Water solutions of Acid Blue and their decoloration were analysed by the impulse radiolysis method. We determined the rate constants of the primary reaction of the dye with hydroxyl radicals, hydrogen atoms and hydrated electrons [10], as well as of the stationary reaction [11]. Typical AOPs practically involving only hydroxyl radicals HO include oxidation in the UV/H_2O_2 system (simultaneous exposure to UV radiation and hydrogen peroxide) and irradiation process in the system saturated with nitrous oxide. Slightly more complicated is the process of ozonation, which can take place in two ways: directly by ozonolysis, or induced by hydroxyl radicals formed as a result of ozone decomposition in water.

Decomposition and decoloration of water solutions of Polan Blue E2R (Acid Blue 62) as results of the use of different versions of advanced oxidation processes have been described in our previous studies [12, 13,14].

An attempt was made to describe these processes by means of a mathematical model on the basis of spectrophotometric measurements. The necessary simplifications were made so the proposed model could be easily used in designing the technology for textile wastewater treatment. It was possible to describe the complex process of decoloration by a simple model using only a global approach.

In this paper, the mechanism of decoloration by irradiation proposed by Hashimoto et al. (1979) was adapted with some changes to a general description of the kinetics of a radical reaction in the presence of oxygen [15]. A modification of this model in reference to decoloration

by irradiation of water solutions of commercial dyes is discussed in [16]. Now, an attempt to extend the model onto other AOP versions is presented.

A future practical aim of this study will be to formulate a model that would enable the selection of an oxidant dosage necessary to obtain a specific, desired decoloration degree for the solution. In the future, conditions of wastewater treatment should be adapted quickly to the variable quantitative and qualitative composition of the wastewater, in order to minimise costs and maximise the results. This task can only be fulfilled by developing relatively simple, universal and precise mathematical models and their swift computer analysis, instead of performing long and costly experiments and analyses.

■ Experimental Methods

As a model arrangement, the aqueous solutions of the anthraquinone dye Acid Blue 62, C.I. 62045 were selected. It was a pure substance synthesised and purified by repeated crystallisation at the Research Centre of the Boruta Chemical Plant in Zgierz, and is subsequently referred to as Alizarin Brilliant Sky Blue R (ABSBR). The chemical formula of the dye is shown in Figure 1.

The water solutions of the dyes were analysed by a spectrophotometric method. Measurements were made using a HP 8452A Hewlett Packard spectrophotometer in the wavelength range from 190 nm to 820 nm. For calculations of the decoloration process, a change in the absorbency in the visible spectrum range, where the maximum absorption appeared for a given dye was used. Figure 2 shows a spectrum of a dye solution, and Table 1 gives data on the maximum absorption, molar absorbency coefficient and the range of concentrations applied in the experiments.

Experimental procedure

Radiation method

The dye solutions of predetermined concentrations were placed in glass ampoules 10 cm^3 in volume, and gaseous N_2O was passed through the orifice until the air was removed and saturation with nitrous oxide was complete. The ampoules containing the dye solutions were tightly sealed, so as not to allow any oxygen from atmosphere to enter the solution.
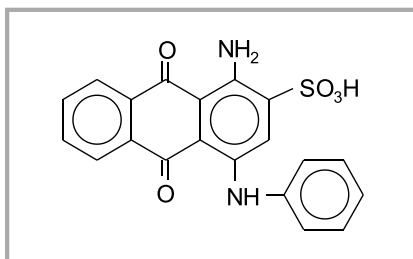

Figure 1. *Chemical formula of Alizarin Brilliant Sky Blue R.*

Next, they were irradiated at room temperature in a BK10000 cobalt bomb at the Institute of Applied Radiation Chemistry at Technical University of Łódź. After the irradiation, the solution was analysed by spectrophotometric methods.

It stands to reason that a process using N_2O will not have any practical significance, and no-one would perform such a process under industrial conditions. However, it creates a convenient means for generating pure hydroxyl radicals and investigating the reaction which proceeds by their influence.

During the irradiation of water, primary and secondary products of its radiolysis are formed, the most important of which are hydroxyl HO• and hydrogen H• radicals and hydrated electron e_{aq}^-.

To separate one product, the so-called 'scavengers', i.e. compounds removing undesirable products from the reaction medium, are used. In order to obtain only hydroxyl radicals in the solutions, nitrous oxide is used. The following reactions proceed in the irradiated solution:

$$e_{aq}^- + N_2O \xrightarrow{H_2O} HO^• + HO^- + N_2 \quad (1)$$

$$k = 9.1·10^9 \text{ dm}^3/\text{mol s}$$

$$N_2O + H^• \rightarrow N_2 + HO^• \quad (2)$$
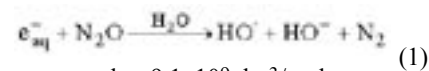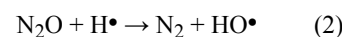
Photochemical reaction with the use of H_2O_2

1 dm^3 of dye solution at a predetermined concentration was placed in a glass reactor equipped with a UV lamp. The liquid in the reactor was mixed by means of argon in the form of fine bubbles and thermostabilised. At the onset of the process, hydrogen peroxide solution in the form of a 30% water solution was added in a single dose to the reaction mixture. 5 dm^3 samples for analysis were taken at planned time intervals and subjected to spectrophotometric analysis.

Due to the lack of measuring series for highly differentiated values of light intensity 'I', it was impossible to determine the exponent 'n', and so as in the case of the irradiation processes, its value

Table 1. *Maximum absorption, molar absorbency coefficient and the range of concentrations applied in the experiments with Acid Blue 62 decoloration; *The pH value changed during our experiments within ± 0.1.*

Dye	Maximum absorption, nm	Molar absorbency coefficient, dm^3/mol mm	Range of tested concentrations, mg/dm^3	pH
Acid Blue 62	620	806	30 - 100	5.0*

Figure 2. *The spectrum of Acid Blue 62 in water solution.*

was assumed to be 1. The intensity of light absorbed by the solution was determined from actinometric measurements. In experimental conditions, this value was 1.99 W/dm^3. The efficiency of hydroxyl radical formation $\Phi = 4.25 \cdot 10^{-6}$ mol($\bullet$OH)/J, was also calculated on the basis of data presented elsewhere [16].
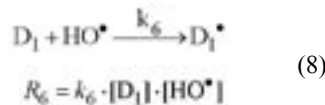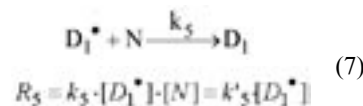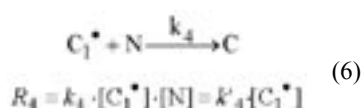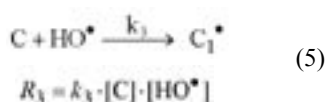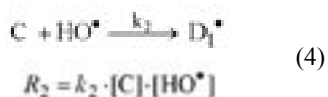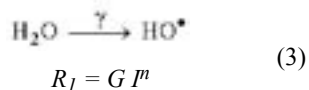
Ozonation

1 dm^3 of dye solution at a predetermined concentration was placed in a glass reactor. Gas (a mixture of oxygen and ozone) was supplied to the solution in the form of fine bubbles at a determined rate. Ozone was generated by a generator, and its concentration in the gas was controlled and measured at the inlet and outlet from the reactor by means of meters. In the experiments, the gas flow rate at the reactor inlet was constant at 20 dm^3/h, the ozone concentration at the reactor inlet was 6, 16, 20 and 35 mg O$_3$/dm^3 and remained constant in every experiment. 5 dm^3 samples for analysis were taken at planned time intervals and subjected to spectrophotometric analysis.

The gamma radiation dosage was measured by Fricke's dosimeter, and UV radiation actinometry by means of an uranyl-oxalate actinometer. The concentration of hydrogen peroxide was determined by titration.

The kinetic parameters were identified using the Marquardt method.

Irradiation process

According to the schematic following the model of Hashimoto [15], the rates of individual reactions leading to dye decomposition are given by the following equations:

$$ H_2O \xrightarrow{\gamma} HO^\bullet $$
$$ R_1 = G\,I^n \tag{3} $$

$$ C + HO^\bullet \xrightarrow{k_1} D_1^\bullet $$
$$ R_2 = k_2 \cdot [C] \cdot [HO^\bullet] \tag{4} $$

$$ C + HO^\bullet \xrightarrow{k_1} C_1^\bullet $$
$$ R_3 = k_3 \cdot [C] \cdot [HO^\bullet] \tag{5} $$

$$ C_1^\bullet + N \xrightarrow{k_4} C $$
$$ R_4 = k_4 \cdot [C_1^\bullet] \cdot [N] = k'_4 [C_1^\bullet] \tag{6} $$

$$ D_1^\bullet + N \xrightarrow{k_5} D_1 $$
$$ R_5 = k_5 \cdot [D_1^\bullet] \cdot [N] = k'_5 [D_1^\bullet] \tag{7} $$

$$ D_1 + HO^\bullet \xrightarrow{k_6} D_1^\bullet $$
$$ R_6 = k_6 \cdot [D_1] \cdot [HO^\bullet] \tag{8} $$

where:
HO$^\bullet$ – the hydroxyl radical;
C – the dye molecule;
$D_1^\bullet$, $C_1^\bullet$ – the radical products of hydroxyl radical reaction with a dye (colourless and coloured, respectively);
D_1, C_1 – the products of the reaction (colourless and coloured, respectively);
N – the inert molecule;
$k_1, k_2,..., k_6$ – the reaction rate constants;
$R_1, R_2, ..., R_6$ – the reaction rate;
G – the specific rate of hydroxyl radical formation mol/dm^{3}Gy, resulting from the irradiation yield of HO$^\bullet$ radicals formation;
I – the dose rate, Gy/s.

According to the schematic of the reaction presented above (Equations 3-8), the rate of dye decay is given by the equation:

$$ \frac{d[C]}{dt} = -R_2 - R_3 + R_4 \tag{9} $$

The formation rate of a coloured radical product is given by the formula:

$$ \frac{d[C_1^\bullet]}{dt} = R_3 - R_4 \tag{10} $$

Upon substitution of the reaction rate equations, we obtain:

$$ \frac{d[C]}{dt} = -k_2 \cdot [C] \cdot [HO^\bullet] + $$
$$ - k_3 \cdot [C] \cdot [HO^\bullet] + k'_4 [C_1^\bullet] \tag{11} $$

$$ \frac{d[C_1^\bullet]}{dt} = k_3 \cdot [C] \cdot [HO^\bullet] - k'_4 \cdot [C_1^\bullet] \tag{12} $$

Assuming a steady state in relation to the concentration of $C_1^\bullet$ radicals, we have:

$$ k_3 \cdot [C] \cdot [HO^\bullet] - k'_4 \cdot [C_1^\bullet] = 0 \tag{13} $$

Substituting equation (13) into equation (11), we obtain

$$ \frac{d[C]}{dt} = -k_2 \cdot [C] \cdot [HO^\bullet] \tag{14} $$

The dependence of absorbency on concentration is given by the formula:

$$ [C] = \frac{A}{\varepsilon \cdot l} \tag{15} $$

where:
A – absorbency;
ε – dye extinction coefficient, dm^3/mol mm;
l – cuvette thickness, mm.

The total rate of absorbency decay is expressed by the formula:

$$ \frac{dA}{dt} = -k_2 \cdot A \cdot [HO^\bullet] \tag{16} $$

The rate of hydroxyl radical decay is described by the formula:

$$ \frac{d[HO^\bullet]}{dt} = R_1 - R_2 - R_3 - R_6 \tag{17} $$

and further by substituting (3), (4), (5), and (8) we obtain (18).

$$ \frac{d[HO^\bullet]}{dt} = G \cdot I^n - k_2 \cdot [C] \cdot [HO^\bullet] + $$
$$ - k_3 \cdot [C] \cdot [HO^\bullet] - k_6 \cdot [D_1] \cdot [HO^\bullet] \tag{18} $$

Since the concentration of HO$^\bullet$ hydroxyl radicals is very small and constant during the decoloration process, a steady state can be assumed, and so we have:

$$ \frac{d[OH^\bullet]}{dt} = 0 \tag{19} $$

After equating equation (18) to zero, we obtain an equation from which the concentration of hydroxyl radicals [HO$^\bullet$] can be obtained:

$$ [HO^\bullet] = \frac{G \cdot I^n}{(k_2 + k_3) \cdot [C] + k_6 \cdot [D_1]} \tag{20} $$

Substituting equation (18) for formula (12), we have

$$ -\frac{d[C]}{dt} = \frac{k_2 \cdot [C] \cdot G \cdot I^n}{(k_2 + k_3) \cdot [C] + k_6 \cdot [D_1]} \tag{21} $$

assuming that

$$ [D_1] = [C]_0 - [C] \tag{22} $$

where $[C]_0$ – initial dye concentration

$$ -\frac{d[C]}{dt} = \frac{\frac{k_2}{k_6} \cdot [C] \cdot G \cdot I^n}{\left(\frac{k_2 + k_3}{k_6} - 1\right) \cdot [C] + [C]_0} \tag{23} $$

Introducing the notation

$$ P_1 = \frac{k_2}{k_6} \cdot G \quad \text{and} \quad P_2 = \frac{k_2 + k_3}{k_6} - 1 \tag{24} $$

we obtain the final formula for the dye decomposition rate:

$$ -\frac{d[C]}{dt} = \frac{P_1 \cdot [C] \cdot I^n}{P_2 \cdot [C] + [C]_0} \tag{25} $$

Taking equation (15) we can derive a formula for the decoloration rate of the solution.

Provided A = ε l [C], and introducing the notion of a decoloration degree

$$\alpha = \frac{A_0 - A}{A_0} = \frac{[C]_0 - [C]}{[C]_0} \quad (26)$$

i.e.

$$[C] = [C]_0 (1 - \alpha)$$

substituting for Equation (25), we have

$$-\frac{d\{[C]_0(1-\alpha)\}}{dt} = \\ = \frac{P_1 \cdot [C]_0 (1-\alpha) \cdot I^n}{P_2 \cdot [C]_0(1-\alpha) + [C]_0} = \\ = \frac{P_1 \cdot (1-\alpha) \cdot I^n}{P_2 \cdot (1-\alpha) + 1} \quad (27)$$

While the radiation dose (*E* in Gy) and the time of reaction (*t* in s) are mutually inter-related by a linear dependency (*E = p t*), where *p* is the proportionality factor, we can introduce *E* for *t*, and obtain (28):

$$\frac{d\alpha}{dE} = \frac{P_1 \cdot (1-\alpha) \cdot I^{n-1}}{[C]_0 \cdot \{P_2 \cdot (1-\alpha) + 1\}} \quad (28)$$

It was assumed in the model that *n* = 1, i.e. the reaction rate in reference to the total dose E does not depend on the dose rate *I*. The irradiation yield of hydroxyl radical formation in the presence of N_2O was assumed to be $G(OH) = 5.4$. Hence the specific hydroxyl radical formation rate is $G = 5.596 \cdot 10^{-7} \, mol/dm^3Gy$.

The kinetic parameters of equation (26) were identified by Marquardt's method. The results are given in Table 2.

Based on the values obtained for P_1 and P_2 and assuming $k_2 = 1 \cdot 10^{10} \, dm^3/(mol \cdot s)$ [10], which was determined by the pulse radiolysis method for the reaction of Acid Blue 62 with hydroxyl radicals, the constants $k_3 = 4.97 \cdot 10^{10}$ and $k_6 = 2.55 \cdot 10^{10}$ can be estimated. Figure 3 shows a comparison of the experimental data and the calculated curves.

Simultaneous action of hydrogen peroxide and UV radiation

As a result of the UV irradiation of the water solutions of hydrogen peroxide, it is decomposed into hydroxyl radicals. This is the most direct way of forming them. To form two hydroxyl radicals, one quantum of absorbed radiation at the wavelength of 254 nm is sufficient.

Table 2. Parameters of the models of decoloration by irradiation, ozonation, and combined action of hydrogen peroxide and UV radiation.

Process	Exponents of reaction compounds	P_1	P_2	Reaction rate constants k
Irradiation	-	$2.19 \cdot 10^{-7}$	1.35	-
combined action of: H_2O_2 +UV	n = 0.4 m = 0.4	$3.57 \cdot 10^{-7}$	1.35	$k_{10} = 1.0 \cdot 10^{-13}$
ozonation: O_3	w = 0.53 z = 0	$3.14 \cdot 10^{-4}$	1.35	$k_9 = 2.16 \cdot 10^{-4}$
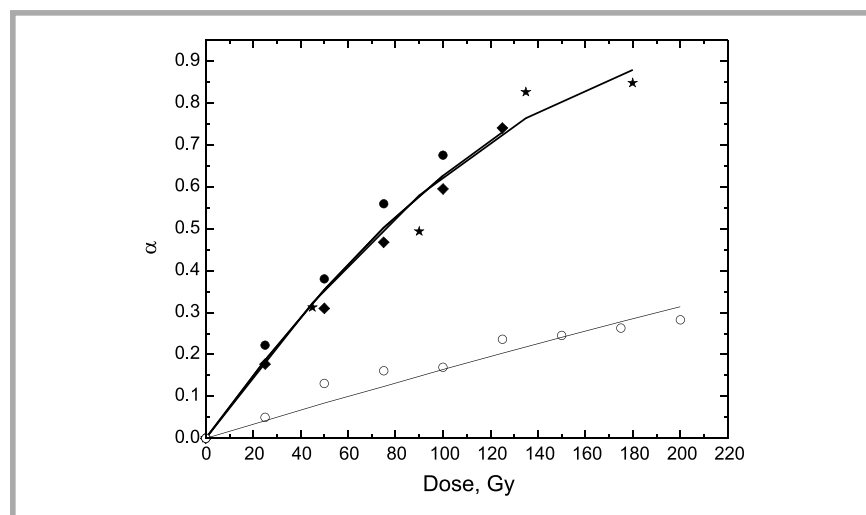
Figure 3. Dependence of decoloration degree α on radiation dose γ. Correlation coefficient of the model curve R = 0.9740; Experimental data: • - $1.2\times10^{-5}mol/dm^3$; 69 kRad/h; ♦ - $1.2\times10^{-5}mol/dm^3$; 600 kRad/h; ★ - $1.2\times10^{-5}mol/dm^3$; 3 kRad/h; o - $1.2\times10^{-5}mol/dm^3$; 69 kRad/h; — - model curve.

In the proposed version of the model, we assumed that the reaction rate of hydroxyl radical formation depended linearly on light intensity. The reaction of immediate oxidation with H_2O_2 was not taken into account, because this process had a negligible yield in these conditions. Since the concentration of hydrogen peroxide is in excess in relation to the dye concentration, it was assumed to be constant during the whole process.

$$H_2O_2 + h\nu \xrightarrow{k_7} 2 \, OH^\bullet \\ R_7 = k_7 \cdot [H_2O_2]^n \cdot \Phi \cdot I'^n \quad (29)$$
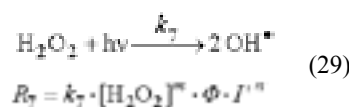
where: '*n*' and '*m*' are the exponents,
Φ – the specific yield of hydroxyl radical formation resulting from the quantum yield of HO• radical formation,
I' – the intensity of radiation absorbed in the solution, W/dm^3.

The subsequent reactions of hydroxyl radicals are identical to those in the model of the irradiation process. Proceeding in the same way when deriving a formula

for the decoloration process rate, we obtain the following equation:

$$[HO^\bullet] = \frac{k_7 \cdot [H_2O_2]^n \cdot \Phi \cdot I'^n}{(k_2 + k_3) \cdot [C] + k_6 \cdot [D_1]} \quad (30)$$

Because in addition to the oxidation by means of hydroxyl radicals, a process of immediate oxidation may occur, the total rate of dye decomposition should be expressed by formula (31).

$$-\frac{d[C]}{dt} = \frac{\frac{k_2 k_3}{k_6} \cdot [H_2O_2]^n \cdot [C] \cdot \Phi \cdot I'^n}{\left(\frac{k_2 + k_3}{k_6} - 1\right) \cdot [C] + [C]_0} \\ + k_{10}[C][H_2O_2]^m \quad (31)$$

Assuming that:

$$P_1 = \frac{k_2 \cdot k_7 \cdot \Phi \cdot I'^n}{k_6}$$

and

$$P_2 = \frac{k_2 + k_3}{k_6} - 1 \quad (32)$$

we obtain equation (33).

$$-\frac{d[C]}{dt} = \frac{P''_1 [C][H_2O_2]^n}{P_2 \cdot [C] + [C]_0} + k_{10}[C][H_2O_2]^k \quad (33)$$

Substituting decoloration degree α, we finally obtain the formula for the decoloration rate, in the shape of equation (34)

$$\frac{d\alpha}{dt} = \frac{P'_1 \cdot (1-\alpha) \cdot [H_2O_2]^n}{[C]_0 \cdot \{P_2 \cdot (1-\alpha) + 1\}} + k_{10} \cdot [C]_0 \cdot [H_2O_2]^k \cdot (1-\alpha) \quad (34)$$

Parameter P_2 includes the reaction rate constants which, according to the model assumptions, do not depend on the process of generating hydroxyl radicals, so in both cases, i.e. decoloration in the irradiation process or in the UV/H_2O_2 system, this parameter should be constant. Therefore, when identifying parameters of the oxidation model by means of UV/H_2O_2, we assumed that value of parameter P_2 was equal to the value calculated in the model for γ radiation, when only hydroxyl radicals are present.
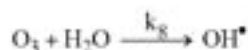
The model parameters are given in Table 2. As has already been mentioned, the value of P_2 was assumed to be the same as for the process of irradiation. From P'_1 one can estimate the value of constant $k_7 = 0.11$, which however can be burdened with a significant error. This may result from an imprecise determination of the light quantity absorbed. In the solution there is a variable amount of hydrogen peroxide, dye and products of decomposition. In addition, the value of Φ that results from the photolysis of

hydrogen peroxide in the experimental conditions may diverge significantly from the assumed value. Figure 4 shows a comparison of the experimental data and calculated curves.

Ozone-induced decoloration

In the case of ozone-induced decoloration, two separate mechanisms should be considered: one proceeding towards an immediate ozonation, and the other by hydroxyl radicals that are formed in the reaction of ozone with water and oxygen, which is always present in the reaction medium [2]. The contribution of the particular mechanisms in the entire process depends on many factors, the most important being the pH of the solution. References to the reaction of anthraquinone dyes with ozone are very scarce in literature.

The mechanism of decoloration by means of ozone is launched by two general reactions. In fact, these processes are described by a very complex sequence of reactions.

$$O_3 + H_2O \xrightarrow{k_8} OH^\bullet$$
$$R_8 = k_8 \cdot [O_3]^w \cdot [H_2O] = k'_8 [O_3]^w \quad (35)$$
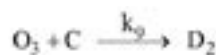
$$O_3 + C \xrightarrow{k_9} D_2$$
$$R_9 = k_9 \cdot [O_3]^z \cdot [C] \quad (36)$$

Assuming that further decoloration will proceed according to equations (4) to (8), the oxidation rate can be written in the following form

$$-\frac{d[C]}{dt} = \frac{\frac{k_2 k'_8}{k_6} \cdot [O_3]^w \cdot [C]}{\left(\frac{k_2+k_3}{k_6} - 1\right) \cdot [C] + [C]_0} + k_9[C][O_3]^z \quad (37)$$

Assuming:

$$P''_1 = \frac{k_2 \cdot k'_8}{k_6} \quad \text{and} \quad P_2 = \frac{k_2+k_3}{k_6} - 1 \quad (38)$$

we have:

$$-\frac{d[C]}{dt} = \frac{P''_1 [C][O_3]^w}{P_2 \cdot [C] + [C_0]} + k_9[C][O_3]^z \quad (39)$$

Introducing the decoloration degree α, we obtain the final formula for the decoloration rate:

$$\frac{d\alpha}{dt} = \frac{P''_1 \cdot (1-\alpha) \cdot [O_3]^w}{[C]_0 \cdot \{P_2 \cdot (1-\alpha) + 1\}} + k_9 \cdot [C]_0 \cdot (1-\alpha) \cdot [O_3]^z \quad (40)$$

Parameter P_2 includes reaction rate constants which, according to the model assumptions, do not depend on the process of generating hydroxyl radicals, so it should also have the same value in this case as in the two other versions of the process.

The value of parameter P''_1 depends on the constant k'_8. This is a constant that describes not a single reaction but approximates a complicated mechanism of hydroxyl radical formation from ozone in water. So, this will not be a typical reaction rate constant, but a value dependent on many factors which are both chemical (e.g. pH) and typical of a process (mass
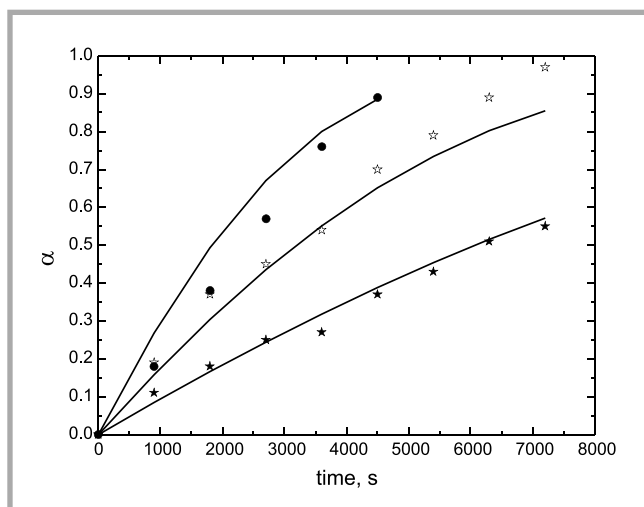
Figure 4. *Dependence of decoloration degree α on time. Correlation coefficient of the model curve R = 0.9654. H_2O_2 concentration was ★ - 9.8 10⁻³, ☆ - 4.9 10⁻², ● - 0.19 mol/dm³; — - model curve.*
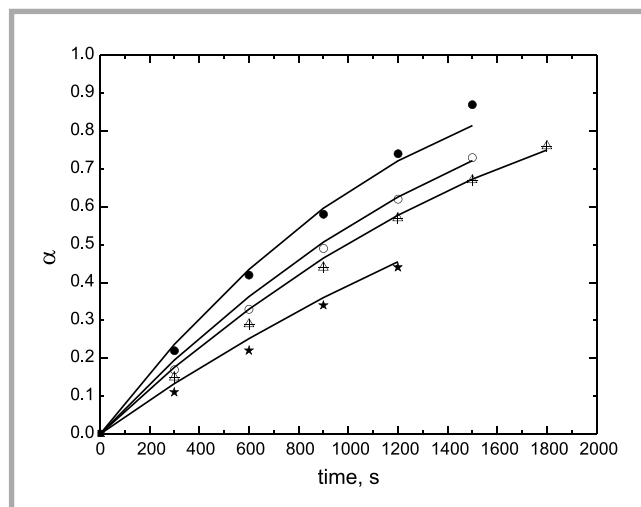
Figure 5. *Dependence of decoloration degree α on time for ozonation process. Correlation coefficient of the model curve R = 0.9933; O_3 concentration was ★ - 6, ○ - 16, △ - 20, ● - 35 mg/dm³; — model curve.*

transfer coefficients, etc.). Thus, it will be a characteristic of the given reaction conditions, and it is impossible at the present stage to propose a simple relation with typical values. Similar comments apply to the constant k_9. On the basis of P''_1, the value of the constant k'_8 can be estimated as $8.0 \cdot 10^{-4}$. The determined value of the exponent $z = 0$ means that the direct reaction of dye ozonation in experimental conditions did not depend on ozone concentration. The values of the parameters identified are presented in Table 2. Figure 5 shows a comparison of the experimental data and calculated curves.

■ Summary

The proposed kinetic model for decolouring water solutions of the selected dye by a hydroxyl radical offers a good approximation of the experimental data. The rate of decoloration of anthraquinone dye solution does not depend on the dose rate of γ radiation. In the case of the oxidation with UV/H_2O_2, tests were performed for only one value of UV light intensity. It was found that the calculated parameters of the model describing the process of radiolysis had values similar to those calculated for the process of oxidation with the use of UV/H_2O_2.

Modern science and technology take advantage of various types of simulation, mathematical models and calculations. This is served by more advanced software and better and faster computers. We can observe a transition from long, arduous and often expensive experiments to fast calculations. In many cases, we accept lower accuracy and the necessity to generalise numerous phenomena at the cost of obtaining a quick result and the possibility of its multiple verification in changing conditions. In many cases, the compatibility of the result with reality is sufficient to make important technological decisions.

This paper is an attempt to propose a uniform and universal model for the water solution decoloration induced by the advanced oxidation processes. The great variety of dyes applied in industry, and especially in the textile industry, is a serious problem in developing a uniform and general model. However, further studies should be carried out to achieve a better description of reality.

At the present stage, a model of decoloration for the selected Acid Blue 62 anthraquinone dye induced by hydroxyl radicals generated in the irradiation process, the photochemical process in the presence of hydrogen peroxide, and during ozonation, has been proposed. In the latter case. an immediate oxidation reaction was also involved.

An attempt is made in the model to use typical equations of chemical kinetics in the formulation of a simple decoloration model. The results obtained confirm the possibility of acquiring quite good agreement with the experimental data, despite many assumptions and approximations. The irradiation process in the presence of nitrous oxide, where the only reagents are hydroxyl radicals, formed a basis for verifying the process of decoloration in the H_2O_2/UV system. The results confirmed the predominant role of hydroxyl radicals in this case also. No immediate oxidation with hydrogen peroxide occurred in the experimental conditions.

■ Conclusions

■ A detailed analysis of the ozonation process requires a large number of experiments in changing conditions, mainly at different pHs of the solution. This will enable a precise determination of the contribution of an immediate reaction as well as that induced by hydroxyl radicals. In more advanced models, hydrodynamic parameters should be taken into account.
■ This study will be a starting point for the further improvement of the decoloration model and its extension to other versions of the advanced oxidation process such as a combined action of ozone and hydrogen peroxide, as well as ozone & hydrogen peroxide and UV radiation.
■ It is also necessary to verify the model's suitability for other groups of dyes, e.g. azo dyes, and the transition from pure chemical compounds to commercial preparations containing the different admixtures that are applied in industry.

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