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Efficiency of Reactive Orange 16 Dye Removal by Ozonation

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1. Introduction

The removal of wastewaters color constitutes a significant element in the treatment process. Most of the organic dyes produced exhibit a considerable resistance to biochemical oxidation. The presence of dyes in wastewaters poses difficulties not only in biological treatment plants but also in natural environment, once wastewaters are discharged to natural receivers.

Even negligible amounts of dyes that will penetrate to the receivers are highly noticeable and exert a negative effect on aquatic habitat. They impair penetration of sun rays, thus reducing the reaction of photosynthesis. In addition, some dyes are toxic and carcinogenic [9]. Investigations have demonstrated that discharge of dye-containing wastewaters to municipal treatment plants operating with a conventional treatment system proved inefficient, and that application of only chemical or biological treatment did not yield satisfactory results in the removal of dye and reduction of inorganic matter [2, 3, 4]. Synthetic dyes include several structural varieties of dyes such as acidic, reactive, basic, azo, diazo, antraquinone based and metal complex dyes. Due to the inhibitory nature of many compounds towards biological oxidation, the need for pretreatment by advanced oxidation process (AOP) has become essential [6]. One of the AOP processes is ozonation which has a wide array of applications and is environment-friendly [8]. Apart from discoloration, it is also used for: removal of bacteria and viruses, oxidation of dissolved iron and manganese, removal of flavor and odor, oxidation of organic and inorganic substances, and removal of turbidity. The process of ozonation is based on reactions with the share of hydroxyl radicals $OH^{\bullet}$. Those radicals are the strongest oxidants that may be used for treatment of water and sewage (their oxidative potential reaches 2.08 V). They are generated, e.g., during ozone degradation in aquatic environment in radical chain reactions, and also during photolysis of hydrogen peroxide, chlorine in the aquatic environments, an aqueous solution of Fe (III), during Fenton's reactions or under the influence of ionizing radiation. Hydroxyl radicals are poorly selective and react with most of dissolved organic compounds and a number of inorganic ones, at a high reaction rate constant.

The decolourisating action of ozone against dyes occurring in an aqueous solution in based on a reaction with binding unsaturated dyes, which leads to the generation of ozonides that undergo rapid hydrolysis, thus causing molecules disintegration. Ozone readily reacts with carboxyl and azo groups, whereas more slowly with the nitro group. Decolourisation of wastewaters by means of O_3 is determined by: its dose, solution temperature, reaction time and solution pH. The ozonation, aimed at dye removal from an aqueous solution, is a short-term (thus less expensive) and highly effective process. Ozonation of colored dyes is a promising process, since it is safer than hydrogen peroxide or other agents, and does not evoke the formation of chemical deposit. Yet, of key significance is the fact that ozone generally produces nontoxic end products which are converted to CO_2 and H_2O depending on the conditions [6].

The paper reports on an experiment aimed at removing a reactive dye Orange 16 from aqueous solutions with the use of ozone. The study involved the determination of the effect of dye concentration in a solution and ozone dose on the effectiveness of the ozonation process. In addition, reaction rate constants were determined for various dye concentrations in the solution and different ozone doses.

2. Materials and Methods

2.1 Characteristics and preparation procedure of the dyes examined

Dye used in the study originates from the class of reactive dyes. Analyses were carried out for the dye – Reactive Orange 16 from the group of vinylsulfone dyes. Molecular formula of the dye was presented in table 1.

Solutions of the reactive dye were prepared by weighing 1 g of the dye powder. Next the dye was quantitatively transferred into a measuring flask (with a capacity of 1 l) which was then filled up with distilled water at pH 7.0. The stock solution was then used to prepare working solutions. Dye concentration in the working solutions was 50, 100 and 200 $mg \cdot dm^{-3}$.

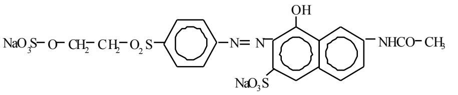
2.2 Experimental stand

Experiments were carried out in a reactor with a volume of 1 dm^3, containing a dye solution in an appropriate concentration (50, 100 or 200 $mg \cdot dm^{-3}$). Ozone was supplied to the reactor at five doses, i.e. 8 16, 24, 32 and 40 g $O_3 \cdot m^{-3}$. Fifteen experimental series were carried out. Several samples were taken at regular time intervals (5 min). In each of the experimental series, analyses were conducted until dye concentration in the reactor stabilized.

The efficiency of the process was calculated by monitoring the decolourisation. Dye concentration was measured spectrophotometrically using a UV-VIS Spectrophotometer SP 3000 apparatus.

Dye Reactive Orange 16 was assigned a visual wavelength λ (tab. 1) at which absorbance was measured in order to plot a standardization curve and compute a conversion coefficient.

Table 1. Type of the dye examined
Tabela 1. Rodzaj badanych barwników

Commercial Name	CI	Reactive group	λ	Structural formula
Brilliant Orange3R	Reactive Orange16	Vinyl-sulfone	490	

Ozone was produced by means of an OZOMATIC LAB 802 generator (WADECO, Poznań, Poland), using pure oxygen. At an overpressure of 0.5 bar, gas flow rate of 100 $g \cdot Nm^{-3}$, and temperature of 20°C, the production of ozone reaches 4g/h. The maximum potential ozone concentration accounts for 250 $g \cdot Nm^{-3}$.

3. Results and discussion

Time curves obtained in the 15 experimental series and depicting changes in the concentration of Orange 16 during ozonation in time were presented in Figures 1-3. The obtained experimental results enabled determining reaction rate constants *k*.

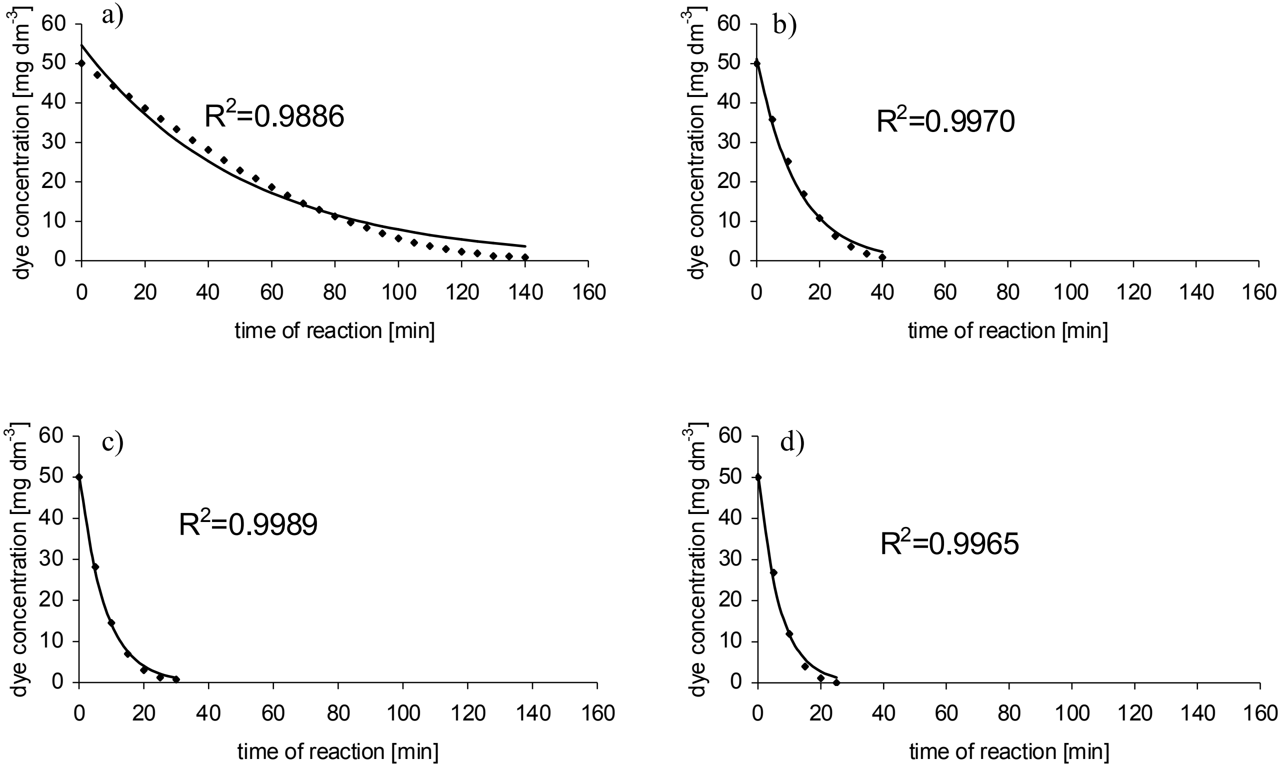


Fig. 1. Color removal during ozonation versus ozone concentration and time of reaction. a) 16 g $O_3\cdot m^{-3}$, b) 24 g $O_3\cdot m^{-3}$, c) 32 g $O_3\cdot m^{-3}$ and d) 40 g $O_3\cdot m^{-3}$. Initial dye concentration was 50 mg$\cdot$dm^{-3}

Rys. 1. Usuwanie barwy w procesie ozonowania w zależności od stężenia ozonu i czasu reakcji; a) 16 g $O_3\cdot m^{-3}$, b) 24 g $O_3\cdot m^{-3}$, c) 32 g $O_3\cdot m^{-3}$ i d) 40 g $O_3\cdot m^{-3}$. Stężenie początkowe barwnika 50 mg$\cdot$dm^{-3}

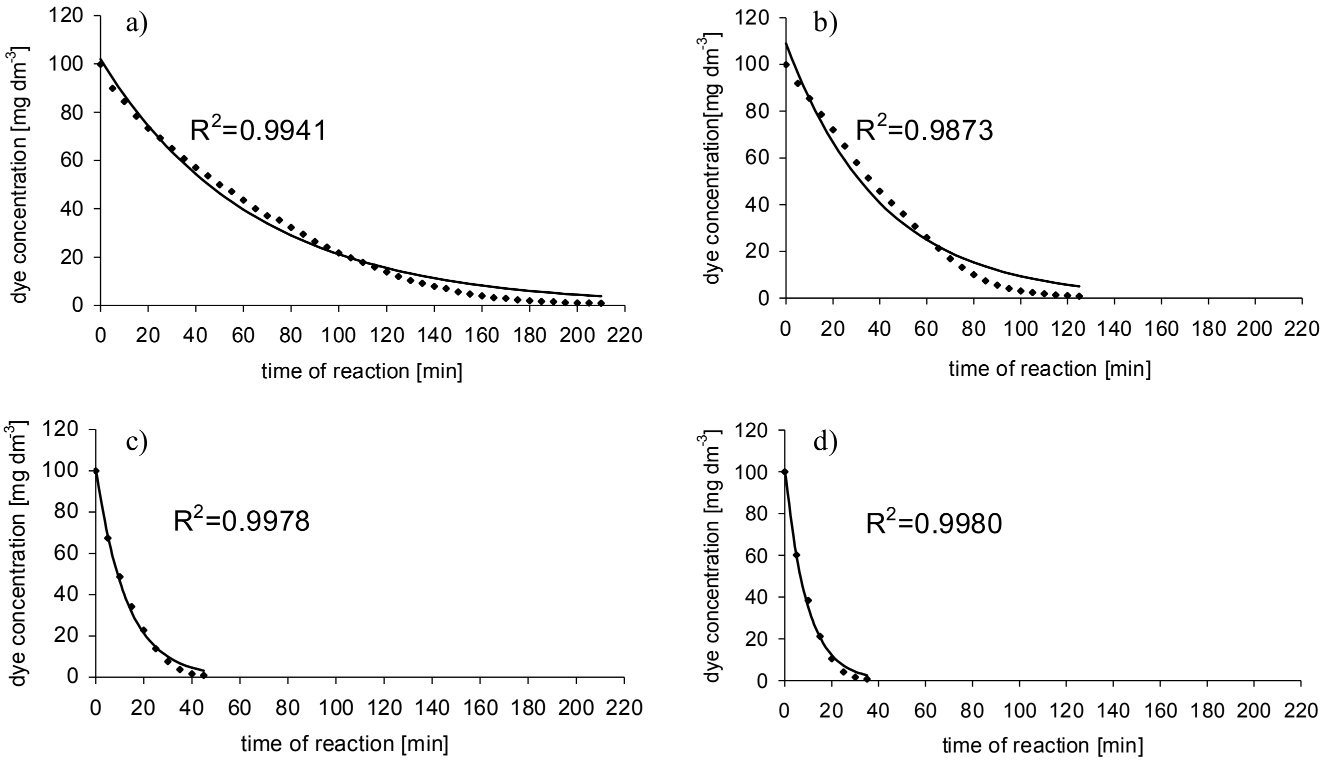


Fig. 2. Color removal during ozonation versus ozone concentrationn and time of reaction. a) 16 g O_3·m^{-3}, b) 24 g O_3·m^{-3}, c) 32 g O_3·m^{-3} and d) 40 g O_3·m^{-3}. Initial dye concentration was 100 mg·dm^{-3}

Rys. 2. Usuwanie barwy w procesie ozonowania w zależności od stężenia ozonu i czasu reakcji; a) 16 g O_3·m^{-3}, b) 24 g O_3·m^{-3}, c) 32 g O_3·m^{-3} i d) 40 g O_3·m^{-3}. Stężenie początkowe barwnika 100 mg·dm^{-3}

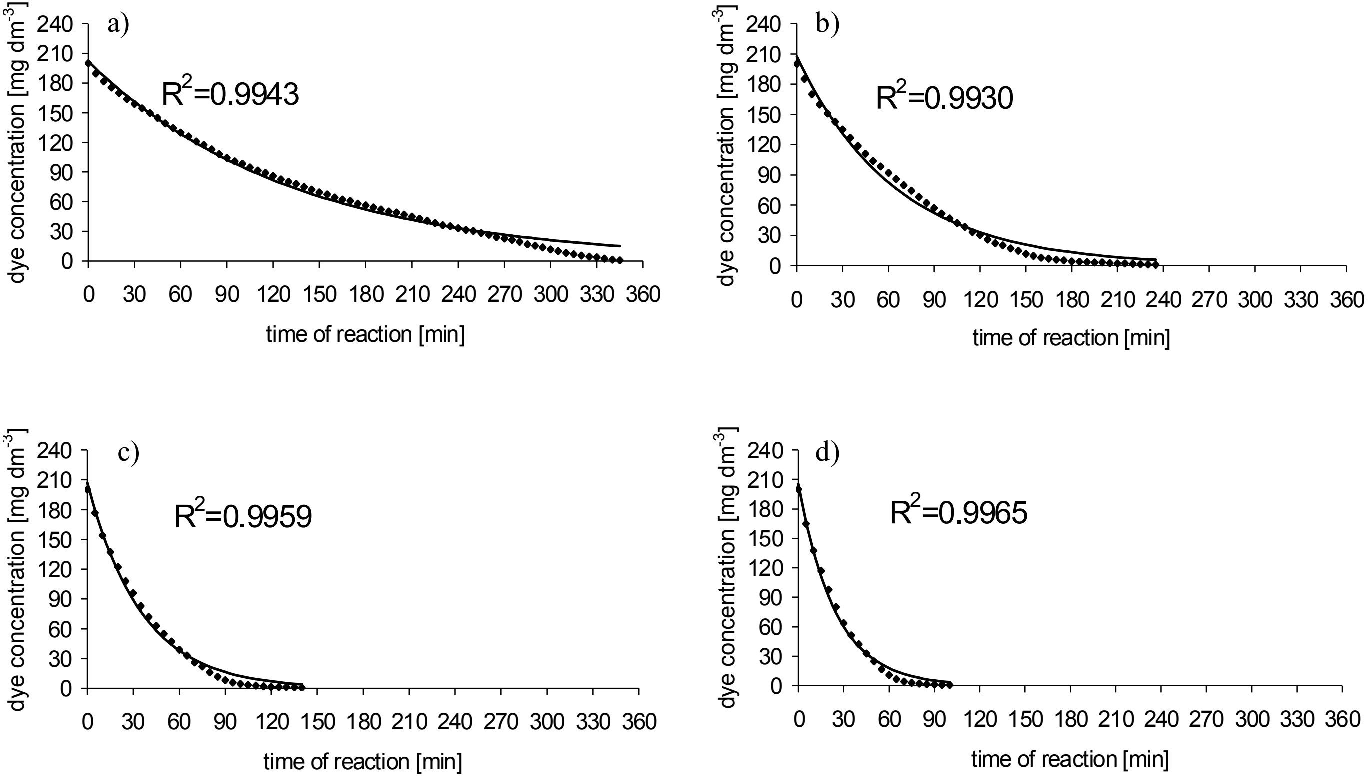


Fig. 3. Color removal during ozonation versus ozon concentration and time of reaction. a) 16 g $O_3 \cdot m^{-3}$, b) 24 g $O_3 \cdot m^{-3}$, c) 32 g $O_3 \cdot m^{-3}$ and d) 40 g $O_3 \cdot m^{-3}$. Initial dye concentration was 200 $mg \cdot dm^{-3}$

Rys. 3. Usuwanie barwy w procesie ozonowania w zależności od stężenia ozonu i czasu reakcji; a) 16 g $O_3 \cdot m^{-3}$, b) 24 g $O_3 \cdot m^{-3}$, c) 32 g $O_3 \cdot m^{-3}$ i d) 40 g $O_3 \cdot m^{-3}$. Stężenie początkowe barwnika 200 $mg \cdot dm^{-3}$

In the description of experimental data obtained for changes of dye concentration C in time t, a good fit was demonstrated by the first-order kinetic model described by the following equation:

$$r = \frac{dC}{dt} = -k \cdot C \tag{1}$$

where k (min^{-1}) represents the first order rate constant and C ($\text{mg}\cdot\text{dm}^{-3}$) is dye concentration in each instant. Integration of eq. (1) , considering $C = C_0$ when $t = 0$, leads to:

$$\ln\frac{C}{C_0} = -k \cdot t \tag{2}$$

or

$$C = C_0 \cdot e^{-kt} \tag{3}$$

Table 2 collates reaction rate constants determined with the method of non-linear regression. The study demonstrated that for the dye concentrations and ozone doses applied the reaction rate constants ranged from 0.00752 to 0.1456 min^{-1} and depended on both the quantity of ozone delivered and concentration of the dye.

Table 2. First order rate constants of decolourisation by ozonation at different concentrations of dye and ozone

Tabela 2. Stałe szybkości reakcji I-rzędu usuwania barwy w procesie ozonowania przy różnym stężeniu barwnika i dawce ozonu

dye concentration ($\text{mg}\cdot\text{dm}^{-3}$)	kinetics constants k [min^{-1}]				
	8 g $O_3\cdot m^{-3}$	16 g $O_3\cdot m^{-3}$	24 g $O_3\cdot m^{-3}$	32 g $O_3\cdot m^{-3}$	40 g $O_3\cdot m^{-3}$
50	0	0.01929	0.07755	0.12653	0.14563
100	0	0.01571	0.02457	0.07730	0.10551
200	0	0.00752	0.01537	0.02816	0.04082

At the lowest examined dose of ozone, i.e. 8 g $O_3\cdot m^{-3}$, no decrease in dye concentration was observed at any of its concentrations analyzed. For each of the three concentrations of Reactive Orange 16 an analogous dependency was observed of an increase in rate constant along with an increasing dose of ozone supplied. The strongest effect of ozone dose on the reaction rate constant was reported at the lowest analyzed concentration of the dye – 50 mg·dm^{-3}. Increasing ozone dose from 8 to 40 g O_3·m^{-3} caused an over 7.5-fold increase in the reaction rate constant. At Reactive Orange 16 concentration of 200 mg·dm^{-3}, the same increase of ozone supplied was accompanied by a 5.43-fold increase in the reaction rate constant.

At a stable dose of ozone, an increase in dye concentration in the solution resulted in a decrease of the constant *k*. That tendency was the most noticeable at an ozone dose of 24 g O_3·m^{-3}, at which the reaction rate constant decreased by over 5 times. Analogous tendency was reported by SARIOGLU et al. [7], who investigated the removal of C.I. Basic Red 46 in a methanogenic anaerobic culture. First-order kinetic constants presented in the reported study were observed to decrease along with an increase in the initial dye concentration in the solution from 0.469 to 0.0255 h^{-1} at a change of C_0 concentration from 50 to 1000 mg·dm^{-3}. Also in the study by DONG et al. [1] the reaction rate constants – 0.3082 min^{-1}, 0.1373 min^{-1}, 0.0622 min^{-1}, 0.0209 min^{-1} determined for different initial concentrations of Reactive Brilliant Blue KN-R - 10, 30, 50 and 100 mg·dm^{-3}, demonstrated a downward tendency along with an increase in the initial concentration of the dye.

A different tendency was observed in the analysis of the rate of Reactive Orange 16 removal in the ozonation process (tab. 3).

Table 3. Rate of decolourisation by ozonation at different concentrations of dye and ozone

Tabela 3. Szybkość usuwania barwy w procesie ozonowania przy różnym stężeniu barwnika i ozonu

dye concentration (mg·dm^{-3})	Reaction rate *r* [mg· dm^{-3}·min^{-1}]				
	8 g O_3·m^{-3}	16 g O_3·m^{-3}	24 g O_3·m^{-3}	32 g O_3·m^{-3}	40 g O_3·m^{-3}
50	0	0.9	3.88	6.33	7.28
100	0	1.57	2.46	7.73	10.55
200	0	1.50	3.07	5.63	8.16

There was no such a considerable decrease, as in the case of constants, in the effect of dye concentration in the solution on the rate of reaction. Increasing the dose of ozone evoked from 7.55-fold (for C_0 concentration of

50 mg·dm^{-3}) to 5.43-fold (for C_0 concentration of 200 mg·dm^{-3}) increase in the rate of reaction.

4. Conclusions

1. Ozonation may be applied as a highly efficient and independent decolourisation process of wastewaters examined.
2. In the ozonation process, dye concentration in the solution affected the determined reaction rate constants, whereas the rate of discolouration reaction was not as strongly dependent on dye content of the solution.
3. Ozone dose affected both the reaction rate constant and the rate of dye removal.

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Efektywność usuwania barwnika reaktywnego Orange 16 w procesie ozonowania

Streszczenie

Mechanizm odbarwiania roztworów wodnych przez ozonu polega na wiązania nienasyconych barwników, która prowadzi do tworzenia ozonidów ulegających gwałtownej hydrolizie, powodującej rozpad cząsteczek. Ozon chętnie reaguje z grupami karboksylowymi i azowymi, a wolniej z grupami nitrowymi. Odbarwianie ścieków przy zastosowaniu ozonu jest określone przez: jego dawkę, temperaturę roztworu, czas reakcji i pH roztworu. Ozonowanie mające na celu usunięcie barwników z wody, jest krótkim (tańszym) i wysoce efektywnym procesem. Ozonowanie barwników jest obiecującym procesem, ponieważ ozon jest bezpieczniejszy niż nadtlenek wodoru lub inne odczynniki oraz ozon nie wywołuje powstawania osadów chemicznych. Kluczowym faktem jest to, że końcowe produkty ozonowania nie są toksyczne i są konwertowane do CO_2 i H_2O w zależności od warunków [6].

W artykule przedstawiono badania mające na celu usunięcie barwnika reaktywnego Orange 16 z roztworu wodnego przy zastosowaniu ozonu. Badania obejmowały określenie wpływu stężenia barwnika w roztworze oraz dawki ozonu na skuteczności procesu ozonowania. Ponadto wyznaczono stałe szybkości reakcji dla różnych stężeń barwnika w roztworze i różnych dawkach ozonu.

Badania prowadzono w reaktorze o objętości 1 dm^3, zawierającego roztwór barwnika w odpowiednim stężeniu (50, 100 lub 200 $mg\cdot dm^{-3}$). Ozon był dostarczany do reaktora w pięciu dawkach: 8, 16, 24, 32 i 40 $g\ O_3\cdot m^{-3}$. Przeprowadzono piętnaście serii badań. Kilka próbek było pobieranych w regularnych odstępach czasu (5 min). W każdej z serii badań, analizy prowadzono do momentu ustabilizowania się stężenia barwnika.

Sprawności procesu określono przez monitorowanie odbarwiania. Stężenie barwnika mierzono spektrofotometrycznie używając spektrofotometru UV-VIS SP 3000.

Badania wykazały, że zarówno dawka doprowadzonego ozonu jak i stężenie barwnika w roztworze wpływały na szybkość procesu usuwania barwy. Wzrost dawki ozonu powodował wzrost stałej szybkości reakcji dla każdego testowanego stężenia barwnika. Przy stałej dawce ozonu stałe szybkości reakcji obniżały się wraz ze wzrostem stężenia barwnika w roztworze.