

Application of Advanced Oxidation Technologies for Decolorization and Mineralization of Textile Wastewaters

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Abstract:

Reactive dyes are the most abundantly used in textile industry due to their high color fastness, wide color spectrum as well as low energy consumption. The presence of these dyes in effluent released into receiving waters has become a serious environmental problem not only related to their color but mainly because of the hazardous byproducts. An environmentally sustainable development policy in textile industry requires development of new technologies to reduce water consumption as well as negative environmental impact of discharged wastewater. Advanced oxidation processes (AOPs) are the most promising technology for decolorization and mineralization of wastewater contamination. This paper presents the results of ozonation, Fenton's oxidation and H₂O₂/UV treatment of simulated as well as industrial textile wastewater containing Reactive Black 5. The AOPs were carried out under varied process parameters such as: dye concentration, pH, oxidant and detergent doses and wide range concentration of NaCl. The decolorization was followed by absorbance while oxidation and mineralization progress by COD and TOC measurements respectively. The almost completely inhibition of decolorization in the presence of NaCl in concentration usually used in industry (60 – 80 g/L) was observed for Fenton reagent. The slight inhibition was observed for H₂O₂/UV system while for ozonation there was no influence of NaCl on the decolorization. The similar relationship of the influence of anionic detergent concentration was observed. The experiments indicated that ozonation is the best method from TOC and COD removal point of view. For the decolorization of real textile effluents two streams were used 1) containing C.I. Reactive Yellow 145, Red 195, Blue 221 and 2) Reactive Black 5. As a result of the treatment, almost complete decolorization of the wastewater was obtained. Considering both the experimental results and technological problems, it can be presumed that advanced oxidation with a application of ozone or hydrogen peroxide/UV are a very promising techniques for potential industrial implementation, however from economic point of view the more reasonable is the ozonation process.

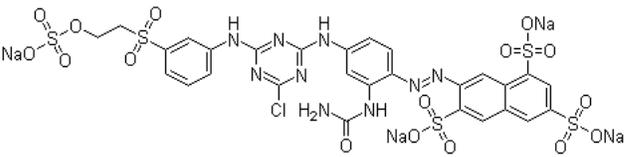
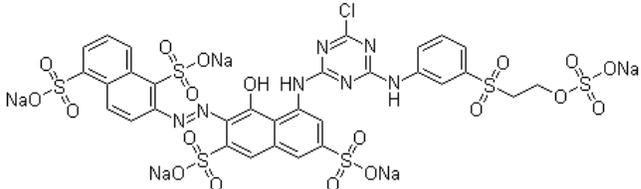
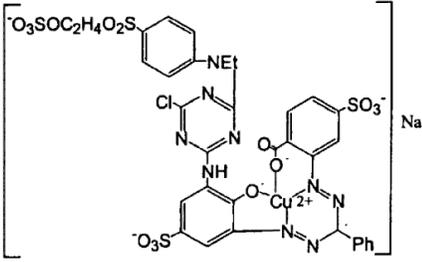
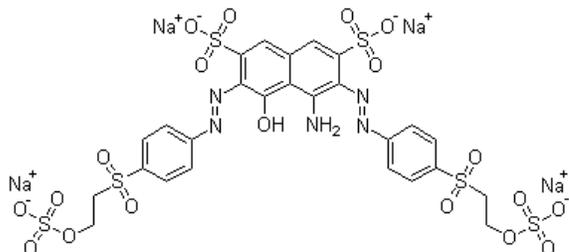
Introduction

Reactive dyes are the most frequently used in the textile industry in comparison to other, due to their exceptionally good properties – good cloth application and color fastness. Their usage is very wide. Reactive dyes are successfully used in dyeing processes of cellulose, wool and polyamide. Their usage in textile's printing operations is also popular. The annual production of reactive dyes amounts 140 000 tones [Constapel et al. (1)]. Reactive Black 5 is the most commonly used in dyeing processes among them. The use of reactive dyes in textile industry operations cause serious environmental pollution. In case of reactive dyeing process special cloth pretreatment is required, what inserts multitude of operations (washing, bleaching, rising, etc.). Moreover, the use of appropriate auxiliaries to the dyeing bath is necessary. 60 - 80 g/L NaCl or Na₂SO₄, the dyeing assistant, usually active

surface active agents (SAA) in amount from 0.5 to 2.0 g/L must be used and alkaline pH is also required (eg. NaOH in concentration of 1.5 g/L or higher must be used). The relatively low fixation of reactive dyes is additional problem causing pollution. Residues of dyes, detergents, organic and inorganic auxiliaries cause high color, pH and salinity of textile waste water. It is also characterized by a high COD and a disproportionately low BOD, which means that it is not very susceptible to biological degradation. The average sized dye-house, which works 24 h/day can generate daily between 2400 - 5200 m³ of wastewater. Therefore, it is important to develop effective textile wastewater treatment methods. Techniques that use high EOP (electrochemical oxidation potential) of hydroxyl radicals (2.8V) or ozone (2.07V) may be an effective treatment or pre-treatment of the textile wastewater. There are many literature reports concerning the treatment of dye solutions and textile wastewater by applying the AOP methods and ozone

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Table 1. Characteristic of tested dyestuff.

Name	Chemical structure	Characteristic
Synozol Yellow KHL (YKHL)		C.I. Reactive Yellow 145 CAS No. 93050-80-7 Molec. mass: 1026 g/mol λ_{\max} = 420 nm
Synozol Red K-3BS ₁₅₀ (RK3BS)		C.I. Reactive Red 195 CAS No. 93050-79-4 Molec. mass: 1136 g/mol λ_{\max} = 543 nm
Synozol Blue KBR (BKBR)		C.I. Reactive Blue 221 CAS No. 93051-41-3 Molec. mass: 890 g/mol λ_{\max} = 604 nm
Setazol Black DPT (BDPT) (RB5)*		C.I. Reactive Black 5 CAS No. 12225-25-1 Molec. mass: 991.8 g/mol λ_{\max} = 596 nm

* purified dye

[Al-Kdasi et al. (2)]. However, only few works are focused on the effects of salts or SAAs on dyes' degradation process [Malik and Saha (3) Ashraf et al. (4), Alaton Arslan et al. (5), Alnuaimi et al. (6), Riga et al. (7), Dong et al. (8)].

In this work an ability of ozonation, H_2O_2/UV process and Fenton's oxidation application for reactive dye solutions (RB5, YKHL, R3KBS, BKBR) and industrial textile wastewater treatment was tested. The initial concentration of the dye, pH and reagents doses as well as the effect of NaCl and SAA presence were considered. TOC and COD reduction was also determined and the best method of textile wastewater treatment was chosen.

Experimental

Materials

Reactive Black 5 (RB5) as purified reagent was obtained from Boruta-Zachem (Poland). Setazol Black DPT (industrial product based on RB5) was purchased

from Setas-Kiyma (Turkey) and it was present in wastewater samples. Synozol Yellow KHL (YKHL), Synozol Red K-3BS 150% (RK3BS), Synozol Blue KBR (BKBR) industrial dyestuffs were purchased from Kisco Co. (Turkey). Table 1 contains chemical structures and characteristic of these dyes. Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), NaCl, H_2SO_4 , were purchased from POCH (Poland) all as A.R.. NaOH A.R. was product of Stanlab (Poland). The buffer basis: Na_2HPO_4 and KH_2PO_4 were purchased from Chempur (Poland) as well as Na_2SO_4 and hydrogen peroxide solution (30%, w/w) all were A.R. Industrial dyeing assistant – Perigen LDR (SAA – naphthalenesulfonic acid and carboxylates' mixture) was obtained from Textilchemie Dr. Petry Co. (Germany).

Analytical Methods

Ozonation of the wastewater and dyes solutions was carried out in semibatch glass reactor with capacity of 1 dm³. The pH and temperature of tested

samples were measured by using Elmetron meter (Poland). Mixing was kept by using a magnetic stirrer (Wigo type ES 21). Ozone was produced by using Ozonok ozone generator (Poland). The maximal ozone production provide by this device was 65 mgO₃/L at a flow rate of 20 L/h (minimum flow) and the supply current 8.5 kV. The oxygen used to ozone production was supplied from a gas cylinder. Ozone concentration was measured with ozone meter's BMT type 963 Vent at the inlet and outlet of the reactor. During the ozonation process samples were collected and reaction progress was stopped by 0.01 M Na₂SO₃ addition.

The H₂O₂/UV study was conducted in a merry-go-round device with quartz test tubes (volume:10cm³, average optical path length: 0.85 cm) placed between two exposure panels (distance between the panels during the study was 30 cm). Each panel consisted of three low-pressure mercury lamps (G8T5 Hg USHIO), which emitted the light with main band at 253.7 nm (88.6%). During experiment test tubes were collected at appropriate intervals, and tubes with pure water ("blank") were inserted in their place, in order to ensure uniform irradiation of tested solutions.

Fenton oxidation experiment was carried out in batch reactor covered with aluminum foil to minimize the exposure of samples to light. Mixing speed was set at 200 rpm. The pH and temperature of tested solutions were measured by using Elmetron meter (Poland). Fenton reaction progress was stopped by pH change (phosphate buffer pH 12). The temperature for all experiments was kept at 23°C (± 0.5).

All tested samples collected at certain time intervals were measured by spectrophotometer (Helios Thermo). Calibration plots based on Lambert-Beer's law for each dye were used to determine the dye concentration of the samples. TOC (total organic carbon) was measured on HACH IL 550TOC-TN apparatus. COD (chemical oxygen demand) measurement was carried out using standard method with dichromate (VI), at HACH-LANGE apparatus (DR 3800) accordance with the procedure specified by the manufacturer.

Results and Discussion

Effect of the Initial Dye Concentration

Various decolorization rates for different initial concentrations of RB5 could be observed for the tested methods (Figure 1). In a case of H₂O₂/UV process, investigated initial concentrations of RB5 were: 50, 104, 125, 163, 214, 346 mg/L. The reaction solutions were irradiated with 6 UV lamps. The experiment was conducted in deionized water (Mill-Q) at pH 6.28. In Figure 1B was shown that degradation

RB5 during H₂O₂/UV process is strongly dependent on initial dye concentration. The degradation efficiency increases with increasing initial concentration of this dye. It rises to some limit RB5 concentration, and then it starts to decrease. This phenomenon occurs in a relatively narrow range of dye's concentrations. It can be explained by a fact that that increasing dye concentration increases the fraction of radiation absorbed by this compound, thus the amount of radiation absorbed by the hydrogen peroxide decreases. Moreover, high concentration of the dye makes access of the light to the deeper layers of the solution impossible because of the intensive color. The maximum concentration in the case of RB5's decolorization by H₂O₂/UV seems to be 125mg/L.

The initial dye concentration influence on decoloration rate presents differently to ozone and a Fenton's reagent treatment. In case of ozonation the initial concentrations of RB5 were in the range of 125 - 1000 mg/L. The dye was dissolved in distilled water. The reaction was conducted at pH 12 (phosphate buffer) to keep the radical mechanism. The highest decolorization rate was reported at RB5's initial concentration of 500 mg/L. It can be associated with a continuous supply of a certain concentration of O₃ in a time unit (a semi-continuous reactor). That allowed the oxidation of sufficiently large number of dye's molecules. A significant decrease in the rate could be observed for the initial dye concentration of 1000 mg/L, due to insufficient amount of the hydroxyl radicals in relation to the number of the dye molecules and the degradation products involved in oxidation process with •OH. Slowdown effect for ozone was not as significant as in case of H₂O₂/UV process (no UV radiation dependence).

The Fenton's reaction was investigated for initial dye concentrations in the range of 50 to 2000 mg/L. The experiment was carried out in a batch reactor at pH 3 (H₂SO₄) by dissolving the reactants in distilled water. The highest decolorization rate was observed for RB5 initial concentration of 1000 mg/L at a mass ratio of the reactants equal 0.05 ([Fe(II)] = 5 mg/L). But not very high final color reduction was obtained at the same time. It may be induced by an extra coagulation phenomenon caused by Fe(II) and Fe(III) ions (which is indicated by experimental data points distribution on the Figure 1C - acceleration in the initial process phase and the subsequent slowdown). Precipitation and sludge production was observed also by other authors [Liu et al. (9)]. During Fenton oxidation the process slowdown was observed for initial RB5 concentrations higher than 1000 mg /L. Analyzing the decolorization process by Fenton reagent one can

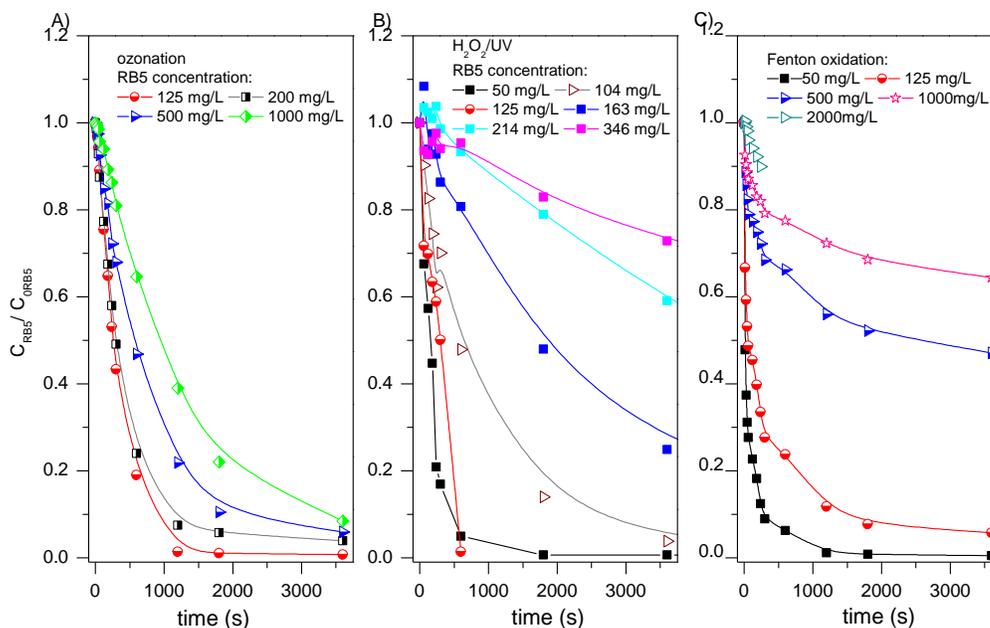


Figure 1. Effect of the initial dye concentration on the decolorization of RB5 solution by: A) ozonation ($[RB5]_0=125, 200, 500, 1000$ mg/L, $[O_3]_{in}=20$ mg/L, $Q_{in}=20$ L/h, $pH=12$), B) H_2O_2/UV process ($[RB5]_0=50, 104, 125, 214, 346$ mg/L, $[H_2O_2]_0=6.8 \times 10^3$ mg/L, $pH=6.28$) and C) Fenton's oxidation ($[RB5]_0=50, 125, 500, 1000, 2000$ mg/L, $[Fe(II)]=5$ mg/L, $[H_2O_2]_0=100$ mg/L, $pH=3$).

recognize two stages: the first one with very high decoloration rate and the second one proceeds with much slower variation. These observations support the hypothesis that Fenton process could be divided into two stages [Malik & Saha (3), Lucas & Peres (10)].

Effect of pH

RB5's decomposition by H_2O_2/UV process, ozonation and Fenton's reagent was examined in a wide pH range from 2 to 12. In case of H_2O_2/UV process and ozonation, the phosphate buffers were used to set pH value and during the Fenton's oxidation H_2SO_4 and NaOH were used. Figure 2 shows the effect of pH on RB5 decomposition. A strong pH dependence of the RB5 rate decomposition for all tested methods can be observed. The decay efficiency of the RB5 using H_2O_2/UV is almost the same for pH 5 and 7 and decreases with increasing pH value. This may be explained by the reaction of dissociation of hydrogen peroxide ($pK_a = 11.6$ [Muthukumar et al. (11)]). Ions formed during the reaction, react with hydrogen peroxide as well as with hydroxyl radicals. Thus this phenomenon of decreasing the rate of RB5 degradation with increasing pH can be seen. In the case of Fenton's reagent the highest RB5 decomposition rate was obtained at pH 3 to 4 (Figure 2). Decomposition of hydrogen peroxide is catalyzed by Fe(II) ions in that pH values most efficiently, which is consistent with the results obtained by other authors [Liu et al. (9), Behnajady et al. (12)]. At higher pH values

partial precipitation of iron ions to hydroxide is much more probable. It can be the reason of reduction efficiency in dye decolorization's by Fenton's reagent. The highest RB5 decomposition rate using ozone was observed at pH 12. Ozone decomposing in alkaline pH generates $\cdot OH$ radicals. Ozonation rate is greater in alkaline pH because $\cdot OH$ radicals' (2.8V) redox potential is higher than ozone's (2.07V), which was confirmed in other studies as well [Muthukumar et al. (11), Sarayu et al. (13)]. Ozonation was carried out also for reaction mixture without buffer. In these case decrease of pH value from 5.8 to 3 was observed. These phenomenon can be caused by acidic degradation products appearance.

Effect of Reagents Dosages

The pseudo-first order constants vs oxidative doses have been presented to showed the effects of reagents dosages in Fig 3. To determine the effect of O_3 dose on the RB5 solution's decolorization the ozonation process was carried out in the O_3 concentration range of 5 to 42.3 mg/L. Additionally, different values of flow gas rate was used ($Q_{in} = 20, 30$ and 40 L/h). The reaction was conducted at pH 12 (phosphate buffer) and RB5 initial concentration was set at 125 mg/L. A strong dependence of the decomposition pseudo-first order constants on the gas flow rate was observed (Figure 3A). This suggests that in the reactor used in the experiment, the mass transfer limitation is significant. Simultaneously, an increase of RB5

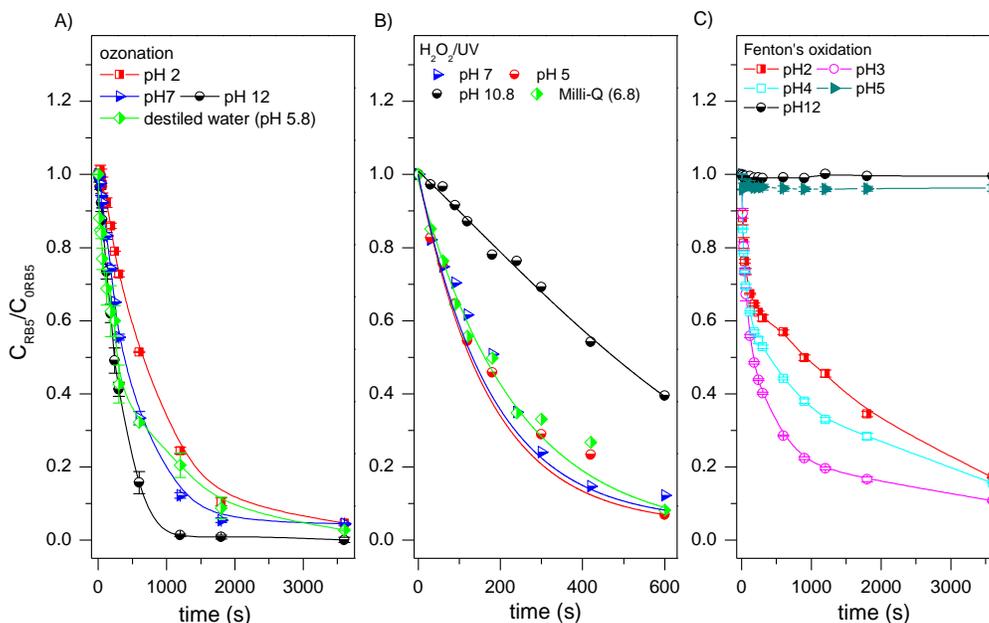


Figure 2. Effect of pH on the decolorization of RB5 solution by: A) ozonation ($[RB5]_0=125$ mg/L, $[O_3]_{in}=20$ mg/L, $Q_{in}=20$ L/h, pH=12), B) H_2O_2/UV process ($[RB5]_0=125$ mg/L, $[H_2O_2]_0=6.8 \times 10^3$ mg/L, pH=6.28) and C) Fenton's oxidation ($[RB5]_0=125$ mg/L, $[Fe(II)]_0=5$ mg/L, $[H_2O_2]_0=25$ mg/L, pH=3).

degradation pseudo-first order constants was achieved with increasing doses of O_3 . For higher concentrations of O_3 more of its molecules may have been absorbed in the liquid phase and react with the dye.

Additionally, in Figure 4 ozonation efficiency for O_3 concentration range of 5 to 42.3 g /Nm³, flow gas rate $Q_{in} = 40$ L/h, pH 12 and RB5 initial concentration 125 mg/L was shown. Figure 4B shows that an increasing O_3 fed to the reactor causes faster saturation of the reaction mixture. The efficiency of the ozonation process shows (Figure 4A) that the highest consumption of the ozone can be observed at the beginning of the RB5 decomposition and that with increasing O_3 initial concentration more rapid RB5 decomposition can be observed. Moreover, it should also be noted that the reaction solution becomes saturated with ozone only when the RB5 is almost completely removed from the reaction solution. Figure 4C shows that increasing O_3 concentration at the reactor inlet results in an decrease of $C_{RB5}^{removed}/CO_3^{applied}$ ratio. It can be seen that in order to reach the higher $C_{RB5}^{removed}/CO_3^{applied}$ ratio it is not necessary to apply higher O_3 concentration, because the applied dose of ozone is already in excess.

In case of H_2O_2/UV process tested RB5's solutions contained from 0.34×10^3 to 12×10^3 mg/L of hydrogen peroxide. 125 mg/L RB5 concentration was dissolved in Milli-Q water (pH 6.28). The results obtained during the irradiation of tested solutions are illustrated on Figure 3B. RB5 decomposition pseudo-first order constants increases with increasing hydrogen peroxide

concentration up to a point and then begins to decrease (due to scavenging effect). This decrease is caused by the hydrogen peroxide reaction with hydroxyl radicals. The optimum concentration of hydrogen peroxide for H_2O_2/UV process is equal 6.80×10^3 mg/L.

For RB5 solution discoloration with Fenton reagent experiments were carried out at a constant Fe(II) ions concentration of 5 mg/L ($FeSO_4 \cdot 7H_2O$ was used), and a variable amounts of H_2O_2 from 25 to 500 mg/L (30% H_2O_2 - reagent). Reagents ratio examined in the experiment were: 5:25, 5:50, 5:100 and 5:500 for $[Fe(II)]:[H_2O_2]$, respectively. Very high RB5 initial decomposition pseudo-first order constants values were observed even when low concentration of hydrogen peroxide was used (Figure 3C). Therefore, it is reasonable to use lower concentrations of the reactants at a ratio of 1:5. No scavenging effect by increasing H_2O_2 concentration was noted even up to 500 mg/L. Fenton reaction's slowdown effected by the reaction of hydrogen peroxide with hydroxyl radicals, as in the H_2O_2/UV process, was not observed as well as in the Bahmani et al. work [Bahmani et al. (14)]. Although this phenomenon occurred in others works [Hsueh et al. (15)]. Moreover, the obtained values of pseudo-first order decolorization rate constants for the Fenton's reaction were higher than that obtained for the H_2O_2/UV process and O_3 oxidation. That might be caused by an extra ferrous ions' coagulation phenomenon already mentioned in section 3.1. Moreover, the two stages of Fenton's reaction could be clearly observed. The first - very fast

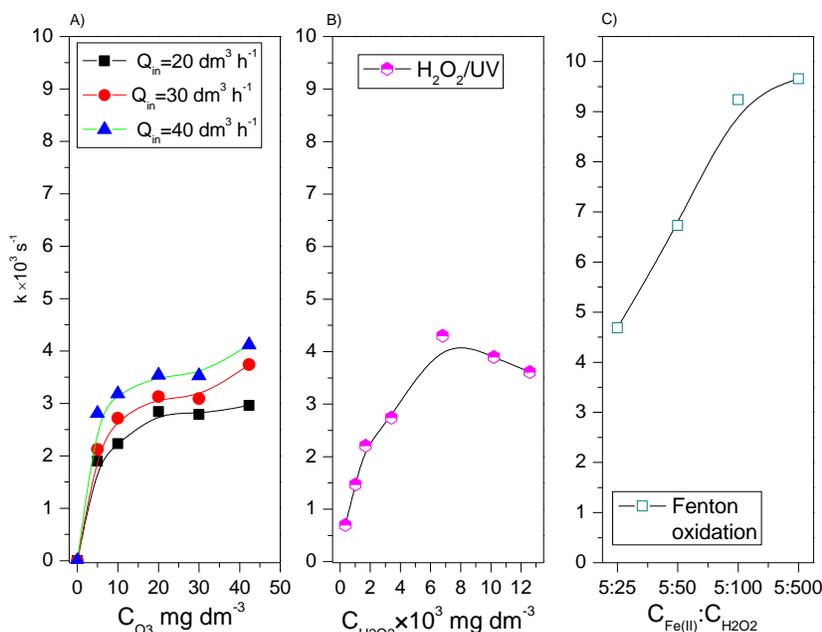


Figure 3. Effect of reagents dosages on the decolorization rate of RB5 solution by: A) ozonation ($[RB5]_0=125 \text{ mg/L}$, $[O_3]_{in}=20 \text{ mg/L}$, $Q_{in}=20, 30, 40 \text{ L/h}$, $\text{pH}=12$), B) H_2O_2/UV process ($[RB5]_0=125 \text{ mg/L}$, $[H_2O_2]_0=0.34 \times 10^3, 1.02 \times 10^3, 1.70 \times 10^3, 3.40 \times 10^3, 6.80 \times 10^3, 10.20 \times 10^3, 12.59 \times 10^3 \text{ mg/L}$, $\text{pH}=6.28$) and C) Fenton's oxidation ($[RB5]_0=125 \text{ mg/L}$, $Fe(II)=5 \text{ mg/L}$, $[H_2O_2]_0=25, 50, 100, 250 \text{ mg/L}$, $\text{pH}=3$).

might be caused by combined effects of flocculation with iron compounds and oxidation with the hydroxyl radical. The second - much slower stage, when Fe (II) ion concentration could be not sufficient to produce significant number of hydroxyl radicals and other oxidants like $O_2^{\bullet-}$ or 1O_2 could appear then. This hypothesis suggests that Fenton oxidation reaction mechanism is much more complicated than in case of H_2O_2/UV process or ozonation and requires further research.

NaCl Influence

Effect of NaCl on the RB5's ozonation process was tested at the O_3 concentration of 20 mg/L , and the gas flow rate $Q_{in} = 20 \text{ L/h}$. RB5 was dissolved in distilled water to achieve 125 mg/L and a pH was adjusted to 12 with phosphate buffer. NaCl concentration was examined in the range of 0 to 65 g/L . The lack of NaCl effect of on the ozonation process (Figure 5A) was noted. No NaCl effect on the ozonation was also found at initial pH approx. 6 (RB5 solution without buffer). Results have not been included in the work.

RB5 decomposition during H_2O_2/UV process using various concentrations of NaCl in Milli-Q water ($\text{pH} 6.28$) was tested. RB5 125 mg/L solution with the addition of $6.8 \times 10^3 \text{ mg/L}$ H_2O_2 was used. The effect of NaCl concentration from 0 to 80 g/L was studied. The solutions were irradiated with 6 lamps. The results of the reaction are shown in Figure 5B. The

experiment demonstrate that there is visible effect of NaCl on the H_2O_2/UV process. It was noted that with increasing concentration of chloride ions the stronger inhibition of the RB5 degradation takes place. However, for each tested NaCl concentration, almost complete color reduction of RB5 after 90 minutes was achieved. The inhibition in this case can be explained by the formation of chloride ion-radicals $Cl^{\bullet-}$, which reactivity is much lower than hydroxyl radicals or dye aggregation caused by NaCl [Dong et al. (8)].

In Fenton oxidation a solution of RB5 (125 mg/L) at pH 3 (adjusted by H_2SO_4) was examined. The NaCl concentration range used in this study was changed from 0 to 80 g/L . The reagents ratio $[Fe(II)]:[H_2O_2]$ was set at 0.05 ($[Fe(II)] = 5 \text{ mg/L}$, and $[H_2O_2] = 100 \text{ mg/L}$). The results are shown in Figure 5C. A strong dependence of the decomposition rate of the RB5 on NaCl concentration was observed. The process inhibition is very significant. Decolorization efficiency of the RB5 solutions containing more than 5 g/L NaCl was never greater than 20% after 60 min. The conclusion is that chloride ion-radicals formation or dye aggregation takes place. In addition, formation of a precipitate was observed in the reaction mixtures containing NaCl (not shown in the work). Thus precipitation of iron ions can also influence the process. These observations were also presented by other authors [Ashraf et al. (4), Alnuaimi et al. (6), Riga et al. (7)].

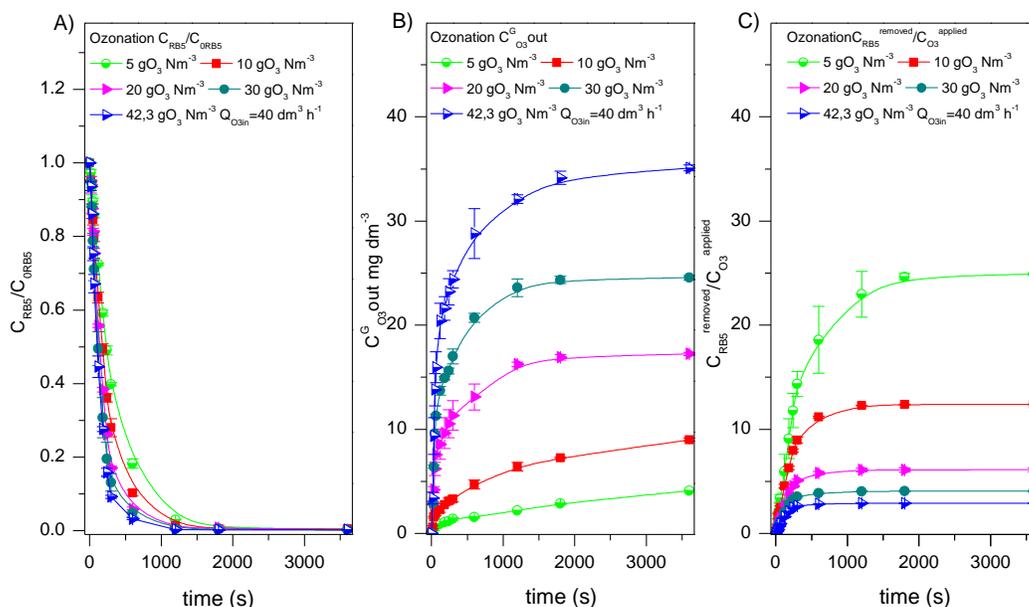


Figure 4. Effect of the ozone dosage on A) ozonation efficiency, B) ozone concentration on reactor outlet, C) $C_{RB5}^{removed}/C_{O3}^{applied}$ ratio; $[RB5]_0=125$ mg/L, $[O_3]_{in}= 5$ mg/L, 10 mg/L, 20 mg/L, 30 mg/L, 42.3 mg/L $Q_{in}= 40$ L/h, pH=12).

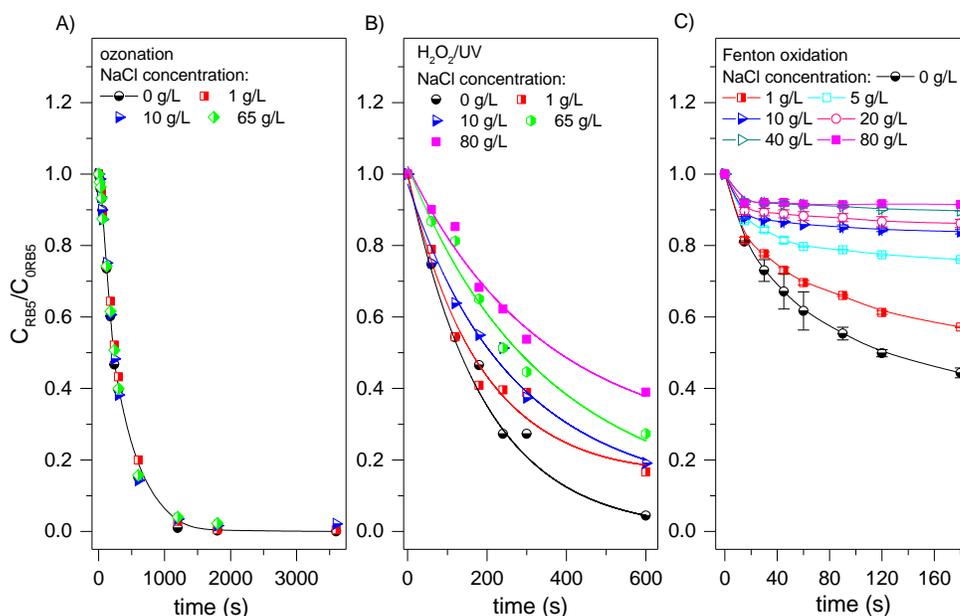


Figure 5. NaCl influence effect on the decolorization of RB5 solution by: A) ozonation ($[RB5]_0=125$ mg/L, $[O_3]_{in}=20$ mg/L, $Q_{in}= 20$ L/h, pH=12) , B) H_2O_2/UV process ($[RB5]_0=125$ mg/L, $[H_2O_2]_0= 6.80 \times 10^3$ mg/L, pH=6.28) and C) Fenton's oxidation ($[RB5]_0=200$ mg/L, $[Fe(II)]= 5$ mg/L, $[H_2O_2]_0= 100$ mg/L, pH=3).

Surface Active Agent Influence

The ozonation process of the RB5 in the presence of Perigen LDR (surfactant commonly used in dyehouses as dyeing assistant) was performed with a dye solution with a concentration of 125 mg/L. The dye was dissolved in distilled water. pH equal 12 was obtained by using a phosphate buffer. The O_3 concentration used in the experiment was equal 20 mg/L, and the gas flow rate was fixed at 20 L/h. The tested Perigen LDR's concentration range varied from

0 g/L to 1 g/L. The results obtained in the experiment are shown in Figure 6A. There was no effect of surfactant presence on the RB5 decomposition by ozonation.

During RB5 degradation with the H_2O_2/UV method various concentrations of surfactant - Perigen LDR (0.11, 0.3, 0.76, 1.0 g/L) diluted in Milli-Q water (pH 6.28) were used. RB5 solutions were studied at the dye concentration of 125 mg/L and H_2O_2 concentration was 6.8×10^3 mg/L. Samples were irradiated with 6

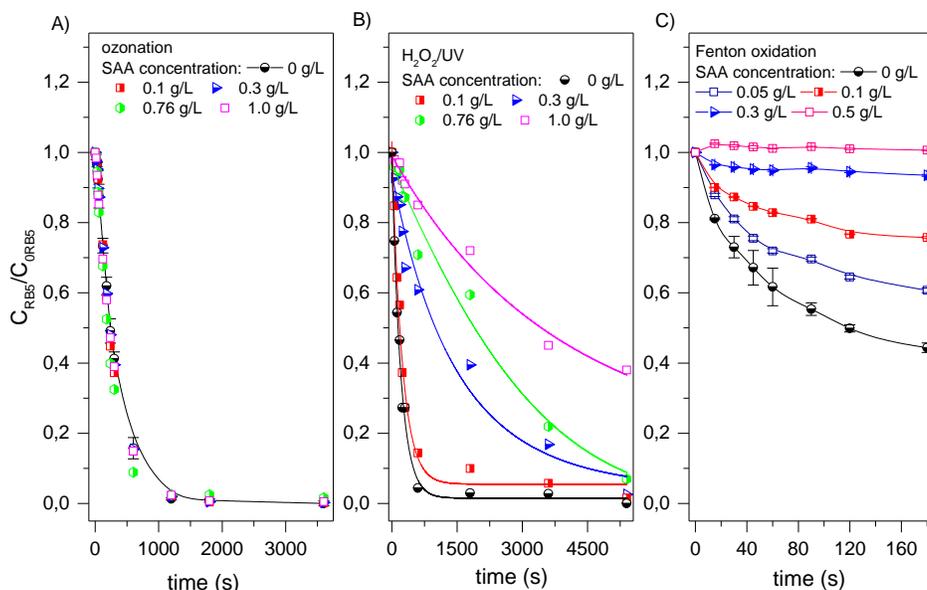


Figure 6. Surface-active agent influence on the decolorization of RB5 solution by ozonation ($[RB5]_0=125$ mg/L, $[O_3]_{in}=20$ mg/L, $Q_{in}=20$ L/h, pH=12), H_2O_2/UV process ($[RB5]_0=125$ mg/L, $[H_2O_2]_0=6.80 \times 10^3$ mg/L, pH=6.28) and Fenton's oxidation ($[RB5]_0=200$ mg/L, $[Fe(II)]=5$ mg/L, $[H_2O_2]_0=100$ mg/L, pH=3).

lamps. The results of the test are shown on Figure 6B. The SAA effect on H_2O_2/UV process was significant. RB5 degradation rate decreases with increasing concentration of surfactant.

The similar effect was observed during the decomposition of RB5 solutions with Fenton reagent (Figure 6C). In this case, the tested dye concentration was 125 mg/L. pH value was adjusted to a 3 with H_2SO_4 . The reagents ratio was set at 0.05 ($[Fe(II)]=5$ mg/L, and $[H_2O_2]=100$ mg/L). For concentrations of surfactant equal and greater than 0.3 g/L almost no progress in Fenton reaction was observed.

Color, TOC and COD Removal

Two treatment methods were employed for further tests: ozonation and H_2O_2/UV process. Fenton's reagent experiments was abandoned because of the high inhibitory effect of NaCl and SAA on it (NaCl and SAA are commonly used in the industry). Color, TOC and COD removal was examined for purified RB5 dye as well as for commercial industrial dyes: Synozol Yellow KHL (YKHL), Synozol Red K-3BS 150% (RK3BS), Synozol Blue KBR (BKBR). Decolorization of dyes: RB5, YKHL, RK3BS, BKBR was carried out in aqueous solutions for each dye individually. The study was conducted under the same conditions for each tested dye.

In case of degradation with H_2O_2/UV , the dye initial concentration of 125 mg/L, and hydrogen peroxide concentration of 6.8×10^3 mg/L was used. The solutions were prepared in Milli-Q water (pH 6.28). While, in case of ozone treatment solutions with

initial concentration of 125 mg/L were prepared by dissolving tested dyes in distilled water. The pH was set at 12 using phosphate buffer. In that examination of the ozonation, an O_3 concentration of 42.3 mg O_3/L , and the gas flow rate $Q_{in}=40$ L/h was used. Both studies were carried out during 600 s. Figure 7 shows results of ozonation A) and H_2O_2/UV degradation B). All tested dyes revealed similar characteristics of the decomposition process (similar decay curves could be observed - not shown in the work). For all tested dyes very high degree of discoloration was achieved. More than 90% of color reduction after 10 min could be noted (in both cases). For RK3BS and BKBR very similar process efficiency were obtained as well as for RB5. Slightly lower decolorization efficiency was obtained for YKHL (for ozone lower efficiency also for RK3BS was recorded). The analysis of TOC and COD shows that mineralization process of BKBR is the biggest (in both cases - ozone and H_2O_2/UV). Generally, mineralization of tested dyes due to ozone are greater than those due to H_2O_2/UV . (Although the TOC assessment in case of ozonation was troublesome because of a short time of analysis - significant effects of mineralization were evident after 20 min. - not shown in the work).

Industrial Textile Wastewater Treatment

Real textile wastewater was taken from the Textile Company "Bilinski" (Poland). Wastewater samples after dyeing of cellulosic cloth (bath after dyeing) were tested. This wastewater stream is characterized by the highest: color, salinity and pH value of all

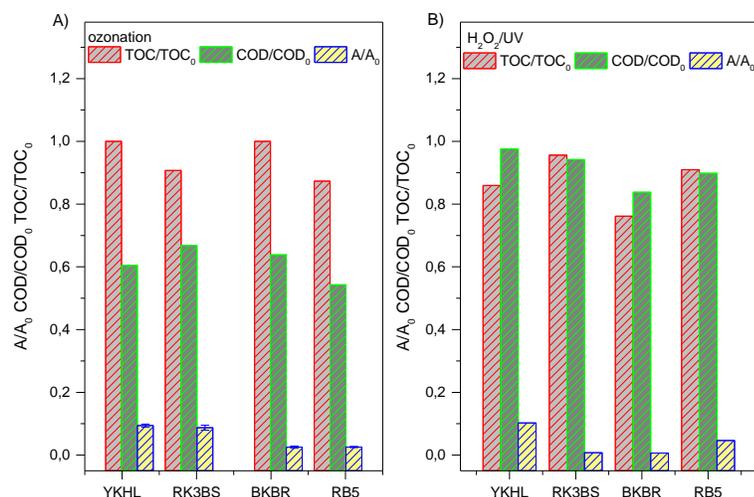


Figure 7. Color, TOC and COD removal for the decolorization of RB5, YKHL, RK3BS, BKBR solutions by: A) ozonation ($[\text{dye}]_0=125$ mg/L, $[\text{O}_3]_{\text{in}}=42.3$ mg/L, $Q_{\text{in}}=40$ L/h, pH=12) and B) $\text{H}_2\text{O}_2/\text{UV}$ process ($[\text{dye}]_0=125$ mg/L, $[\text{H}_2\text{O}_2]_0=6.80 \times 10^3$ mg/L, pH=6.28).

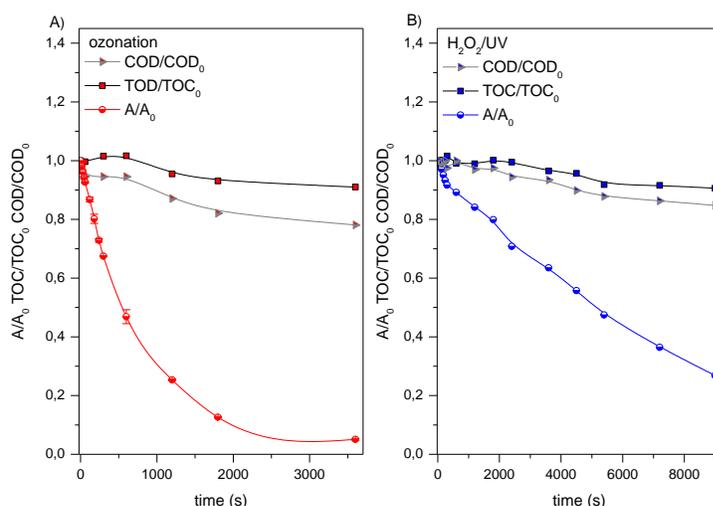


Figure 8. Color, TOC and COD removal for real textile wastewater treatment by ozonation ($[\text{O}_3]_{\text{in}}=42.3$ mg/L, $Q_{\text{in}}=40$ L/h, pH natural) and $\text{H}_2\text{O}_2/\text{UV}$ process ($[\text{H}_2\text{O}_2]_0=6.80 \times 10^3$ mg/L, pH natural).

wastewater generated by dyehouse. Examined wastewater contained: Perigen LDR approx. 0.76 g/L, NaCl 65 g/L, Setazol Black DPT (industrial RB5) approx. 5.68 g/L, Na_2CO_3 1.4 g/L, NaOH (50% a.s.) 1.95 g/L, and was characterized by: COD equal 3940 mgO₂/L, TC equal 1033 mg/L, TOC equal 434.8 mg/L, pH 11.5 and conductivity equal 61597 $\mu\text{S}/\text{cm}$. The wastewater decomposition by $\text{H}_2\text{O}_2/\text{UV}$ experiments were carried out using hydrogen peroxide ($[\text{H}_2\text{O}_2]=6.8 \times 10^3$ mg/L) and 6 UV lamps. During the ozone treatment, the O_3 concentration of 42.3 mg/L, and the gas flow rate $Q_{\text{in}}=40$ L/h were used. Both studies were carried out in the natural pH of the effluent (pH 11.5). Experimental results was shown in Figure 8. Approximately 50% color reduction after 75 min of $\text{H}_2\text{O}_2/\text{UV}$ wastewater treatment was achieved. Complete color reduction of treated wastewater did not occur even after time 150

min. Analysis of the TOC and COD reduction during the $\text{H}_2\text{O}_2/\text{UV}$ process revealed only a slight mineralization of the tested wastewater (only approx. 10% reduction in TOC and COD was observed – Figure 8B). Ozone treatment results are presented in Figure 8A. During wastewater treatment with ozone almost complete color decay at time 60 min was observed. TOC and COD reduction achieved by ozonation was twice higher than that achieved by $\text{H}_2\text{O}_2/\text{UV}$ wastewater treatment and amounted over 20%.

Conclusions

On the basis of results obtained the ozonation process can be proposed as the most effective decolorization method for highly loaded textile wastewater. This treatment method is efficient even in case of solutions (or wastewater) with a high concentration

of colored substances. While the phenomenon of inhibiting the UV rays access into the solution and light absorption by the dye molecules can be observed during H₂O₂/UV process (resulting in lower decolorization efficiency). Ozone treatment is particularly suitable for textile wastewater as textile wastewater is usually alkaline. Inhibitory effect on ozonation caused by textile auxiliaries agents was not observed. Moreover, the best color reduction and the highest mineralization degree was found for ozone treatment. However, TOC and COD reduction in case of the tested method was not sufficient to meet the regulation limits. To reach higher mineralization degree it seems reasonable to combine AOP method with biological treatment.

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