Comparison between industrial and simulated textile wastewater treatment by AOPs – Biodegradability, toxicity and cost assessment

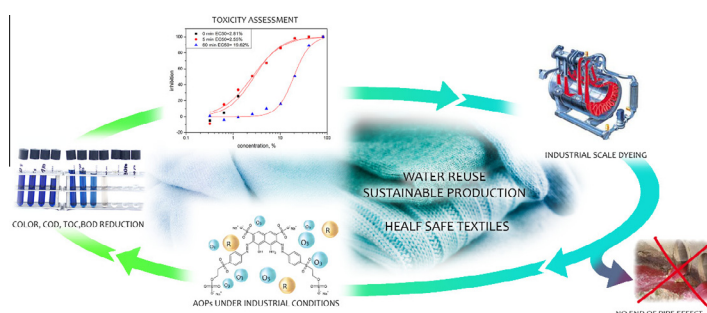Lucyna Bilińska [a,b,*], Marta Gmurek [a], Stanisław Ledakowicz [a]

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HIGHLIGHTS

- Application of AOPs for simulated and industrial wastewater were compared.
- No synergistic effect of O_3, UV and H_2O_2 acting together within AOPs was observed.
- The decomposition by ozone-based AOPs was not influenced by textile auxiliaries.
- Toxicity decrease, biodegradability, cost assessment are advantages of ozonation.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Despite the fact that there are many literature reports concerning textile wastewater treatment by advanced oxidation processes (AOPs), mostly they are not oriented on the industrial applications. The research focused on Reactive Black 5 (RB5) and its industrial form (Setazol Black DPT), which, despite being hazardous, is still one of the most commonly used dyestuffs in industrial practice. Several ozone-based AOPs (e.g., O_3, UV/O_3, O_3/H_2O_2, and $O_3/UV/H_2O_2$) and H_2O_2/UV processes have been compared in terms of their effectiveness in removing RB5 (purified and commercial form) from simulated and industrial textile wastewater. The color, COD, TOC and BOD reduction were considered. Almost completely color reduction was achieved for the simulated as well as industrial wastewater, but only in case of ozone-based AOPs. The H_2O_2/UV processes were found highly not effective for industrial application. For industrial wastewater the COD and TOC decrease were not very high (10% of COD and 20% of TOC) in contrast to simulated one (90% and 50%, respectively). However, the mineralization, biodegradability and Average Oxidation State (AOS) assessment indicated that the application of AOPs resulted in more oxidized by-products. The toxicity assessment based on *V. fischeri* bacteria proved extremely high toxicity of BR5 ($EC_{50} = 3.86 \pm 0.32$ mg/L). All of the tested ozone-based AOPs increased biodegradability and decreased toxicity, proving that oxidation should be performed before biological treatment. The cost analysis and the obtained results showed that O_3 and O_3/H_2O_2 (0.005 M) can be effectively used in the industry.

1. Introduction

The textile industry is one of the most significant sectors of the global economy, especially in countries such as China, India, Pakistan, Bangladesh and Malaysia. In 2014 in Poland, employment

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in this industry reached 114 thousand people, and the profit was near 3.85 billion euro (statistics for companies employing more than 9 employees, clothing and textile sector) [1].

Wastewater from the textile industry should be considered a serious environmental problem. Despite the use of high-tech equipment and modern technologies, the textile industry is among the highest water-consuming industries and produces a huge amount of wastewater. Water consumption and wastewater generation during the dyeing and finishing of textiles can reach 150–350 L per kg of product [2,3]. Residues of detergents, dyes and auxiliary agents present in discharge result in high pH, intensive color and salinity. Textile wastewater is often characterized by a low BOD_5/COD ratio, which can have an adverse effect on the biological treatment. The BOD_5/COD values are between 0.06 and 0.35 [4–7]. Considering that a BOD_5/COD ratio less than 0.4 indicates low biodegradability, the textile wastewater biodegradation is unsatisfactory. Advanced oxidation processes (AOPs) may be effective purification methods of textile industrial wastewater; due to the high oxidative potential of ozone and $\cdot$OH radicals generated by these methods, many organic substances can be decomposed [8].

There are several literature reports on the degradation of textile dyestuff in both simulated mixtures [9–22] and real industrial wastewater [7,23–26,14,27–29] using ozone-based AOPs. However, few of these reports reflect the impact of conditions characteristic for textile wastewater on the oxidation process [16–19]. Some authors studied the influence of auxiliary agents' presence in the reaction mixture on dye degradation using ozone-based AOPs. Muthukumar & Selvakumar [16] showed an inhibiting effect of various salts on the ozonation process, but Colindres et al. [17] noticed that salts (Na_2SO_4) and alkaline (NaOH, $CaCO_3$) conditions accelerated the ozonation. Bamperng et al. [18] indicated a negligible effect of NaCl on ozonation due only to differences in the solubility of ozone in various media. Bilinska et al. [19] showed that there is no visible effect of NaCl and surface active agents (SAA) on the ozonation process. Additionally, neither the mechanism of $\cdot$OH radicals' formation nor the possibility of a scavenging effect caused by textile wastewater conditions was discussed.

All of the works found in the literature that applied AOPs for real textile wastewater cleaning were related to global wastewater. Most of them were general wastewater taken from the textile plant, some were equalized wastewater streams taken from several random finishing operations [7,23–26,14,27–29]. In most cases, the authors tested only ozonation [7,23,24] or were focused on coupling ozonation with biological treatment [25,26,14,27]. Few publications focused on a comparison of several ozone-based AOPs used for real wastewater (Chung & Kim [28] – O_3/H_2O_2, O_3/UV, $O_3/H_2O_2/UV$; Azbar et al. [29] – O_3/H_2O_2, O_3/UV, $O_3/H_2O_2/UV$, H_2O_2/UV, Fenton and coagulation). Additionally, Konsowa et al. [20] claimed that their work concerned industrial wastewater, but the research was performed for a synthetic mixture – aqueous dye solutions. Similarly, Bamperng et al. [18] suggested treatment of dye wastewater, whereas synthetic mixtures were studied.

None of these studies were focused on the purification of the textile wastewater stream most polluted with dyestuff, which is the bath after dyeing operation. This textile wastewater stream is characterized by the most intensive color, the highest pH value and the highest concentration of salt. Only Colindres et al. [17], Arslan et al. [21] and Arslan Alaton et al. [22] used ozone-based AOPs to clean a mixture that simulated real wastewater after dying. However, they did not investigate this type of wastewater after a real industrial dyeing process. Moreover, Arslan Alaton et al. [22] diluted their simulated mixture 15 times before treatment. Than Arslan et al. [21] used a 40 times dilution of the simulated mixture, which does not reflect the conditions of real dyeing wastewater.

In this study, several ozone-based AOP methods (O_3, UV/O_3, O_3/H_2O_2, $O_3/UV/H_2O_2$) and an H_2O_2/UV process for simulated mixtures and industrial wastewater after dyeing with RB5 (purified and commercial form, respectively) were applied for the first time. All tests were conducted in similar, comparable research conditions. The color, COD, TOC, and BOD reduction were considered. A toxicity assessment and cost analysis for the AOPs were performed. The mechanism of hydroxyl radical formation in the alkaline reaction medium and the characteristics of the industrial wastewater after dyeing operation were also investigated.

2. Experimental

2.1. Materials

Reactive Black 5 (RB5) was obtained from Boruta-Zachem (Poland) as a purified reagent. The chemical structure and characteristics of this dye are presented in Fig. 1. The buffer components, NaOH (AR) and Na_2HPO_4 (AR), were purchased from Stanlab (Poland) and Chempur (Poland), respectively. Na_2SO_3 and hydrogen peroxide solution (30%, w/w) (both A.R. grade) were purchased from Chempur (Poland). Catalase was purchased from Sigma-Aldrich (USA). The substances present in industrial textile wastewater were Setazol Black DPT (industrial product based on RB5, Setas-Kiyma (Turkey)), industrial dyeing assistant – Perigen LDR (SAA – naphthalenesulfonic acid and carboxylates' mixture, Textilchemie Dr. Petry Co. (Germany)) as well as NaCl, NaOH, and Na_2CO_3 (technical products). The exact composition of the dye bath (given by the textile company) and the industrial wastewater indicators (wastewater after the specific dyeing process) are given in Table 1. The initial dye concentration of the dyeing bath was 5.68 g/L. Due to dye liquor exhaustion of the textile material, the final dye concentration in the wastewater was 730 mg/L. The wastewater was diluted to achieve 125 mg/L of industrial dye to compare the wastewater and purified dye aqueous solution.

2.2. Analytical methods

Ozonation of the industrial textile wastewater and dye solutions was performed in a semibatch glass reactor (heterogeneous gas–liquid system) that had a capacity of 1 dm^3 and was equipped with a porous plate to deliver ozone gas into the reaction solution. Mixing was performed with a magnetic stirrer (Wigo type ES 21).
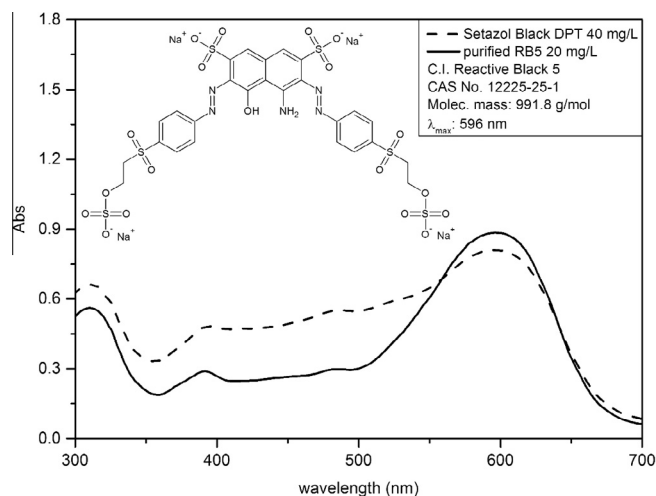

Fig. 1. Chemical structure and UV–vis spectrum of Reactive Black 5 (RB5).

Table 1
Dyeing bath composition A), dyeing process conditions B), industrial wastewater characteristics C).

A) Dyeing bath content	
Setazol Black DPT (industrial RB5)	5.68 g/L
Perigen LDR (SAA)	0.76 g/L
NaCl	65 g/L
Na$_2$CO$_3$	1.4 g/L
NaOH 50% (a.s.)	1.95 g/L
B) Dyeing process conditions	
Batch type	95% Viscose, 5% Elastane
Weight	580 kg
Dyeing ratio	1:13.2
Bath volume	7 656 L
Machine type	Thies TRD
C) Industrial wastewater indicators	
pH	11.23
Conductivity	78.41 mS/cm
COD	2677 mgO$_2$/L
TOC	290 mg/L
Approx. conc. of the dye	730 mg/L

Ozone was produced by an Ozonek Ozone Generator (Poland). The oxygen used for ozone production was supplied from a compressed gas cylinder (O$_2$ purity 99.5%). The ozone concentration was measured at the inlet and outlet of the reactor using a BMT 963 Vent ozone analyzer. For the UV/O$_3$ and O$_3$/UV/H$_2$O$_2$ processes, a UVC low-pressure mercury lamp (Herraus 15 W) was added to the experimental set-up. The lamp was placed inside quartz tube and immersed inside the thermostated reactor. For the O$_3$/H$_2$O$_2$ and O$_3$/UV/H$_2$O$_2$ processes, hydrogen peroxide was added to the reaction mixture before the ozone was applied. The reaction progress for all ozone-based AOPs was stopped by the addition of 0.01 M Na$_2$SO$_3$ to the collected samples.

The H$_2$O$_2$/UV process was conducted in a merry-go-round device with quartz test tubes placed between two exposure panels with UV lamps. The details are presented elsewhere [19].

All samples collected at specified time intervals were measured by a spectrophotometer (Helios Thermo). A calibration plot based on Lambert-Beer's law, (Eq. (1)), was used to determine the concentration of the samples.

$$A = \varepsilon \cdot l \cdot c \tag{1}$$

where: A – absorbance, ε – molar absorption coefficient (L mol^{-1} cm^{-1}), l – the length of the light path (cm), c – concentration of the sample (mol L^{-1}).

The pH and temperature of the samples were measured using an Elmetron meter (Poland). The total organic carbon (TOC) was measured using a HACH IL 550TOC-TN apparatus. Chemical oxygen demand (COD) and biochemical oxygen demand (BOD) measurements were obtained using the HACH-LANGE apparatus (DR 3800) according to standard methods given by the producer. The COD analysis was done with the dichromate (VI) LCK 514 and 314 tests. The BOD was determinate using low-volume LCK 555 test, which is based on dilution method and the pyrocatechol derivative, which gives red color in the presence of Fe^{2+}, was the spectrophotometric factor in it. Before the BOD measurement a catalase addition was used to remove the residual H$_2$O$_2$. The acute toxicity bioassay was conducted using a Microtox Model 500 analyzer (Modern Water, USA) with the marine bacterium *Vibrio fischeri* as a bioluminescent indicator. The Microtox® 81.9% Screening Test and the 81.9% Basic Test protocols were used for the toxicity assessment of the samples [30,31]. The pH of the samples was adjusted to 7, and catalase was used to remove residual H$_2$O$_2$ from the reaction solution.

Calculations were performed using the Origin 9.1 version Pro software. Each experiment was repeated three times.

3. Results and discussion

3.1. H$_2$O$_2$ impact on the ·OH radicals formation mechanism

Hydroxyl radical formation is the main characteristic of the oxidation processes discussed in this work. Therefore, the impact of hydrogen peroxide addition to the mechanism of hydroxyl radical formation was studied for the wastewater treatment process in which a combination of ozone, H$_2$O$_2$ and UV radiation was used.

The impact of the hydrogen peroxide concentration on the RB5 decomposition rate was studied for the O$_3$/H$_2$O$_2$ and O$_3$/UV/H$_2$O$_2$ processes in the H$_2$O$_2$ concentration range of 0–0.1 M (the reaction rate constant had been changing significantly in this H$_2$O$_2$ concentration range Fig. 2). The experiment was conducted at pH 12 (which corresponds to the pH of the textile reactive dyeing discharge), as provided by the phosphate buffer. The O$_3$ concentration of the inlet gas mixture was 42.3 g/Nm^3, and the gas flow rate was set at Q$_{in}$ = 40 L/h (1.69 gO$_3$/L). RB5 was dissolved in distilled water at 125 mg/L.

In this study, pseudo-first-order constants were calculated to describe the RB5 decomposition in the presence of different H$_2$O$_2$ concentrations. The overall reaction process, for AOPs combining UV, H$_2$O$_2$ and ozone, consisted of three contributions: direct photolysis by UV, direct oxidation by ozone and oxidation by hydroxyl radical ·OH. Because the investigation was conducted in alkaline solution (pH = 12), the main pathway of the degradation should be followed by a reaction of RB5 with the hydroxyl radical [8]. However, based on the experiments with ·OH radicals scavengers the possible direct oxidation via O$_3$ at this pH cannot be excluded (Fig. A1 in Supplementary Materials). The occurrence of direct photolysis is neglected (Fig. A2 in Supplementary Materials). Therefore, as calculated using Eq. (2), the k$_{app}$ constant is the general constant of RB5 decay.

$$ln\frac{C}{C_0} = k_{app} \cdot t \tag{2}$$

The pseudo-first-order constant of the RB5 decomposition show a strong dependence on the hydrogen peroxide concentration for O$_3$/H$_2$O$_2$ (Fig. 2A) and for the O$_3$/UV/H$_2$O$_2$ process (Fig. 2B). In both cases, with an increasing H$_2$O$_2$ concentration, a decrease in the pseudo-first-order constant was noted. Based on the studies performed by Azbar et al. [29] and Chung and Kim [28], a synergic effect should occur; however, this effect was not observed in our investigation. This phenomenon can be explained by the scavenging effect of hydroxyl radicals by hydrogen peroxide, as shown in reactions (3) and (4).

$$\cdot OH + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \tag{3}$$

$$\cdot OH + HO_2^{\cdot} \rightarrow H_2O + O_2 \tag{4}$$

The scavenging effect was further enhanced in the alkaline reaction medium. In this medium, a significant part of ozone decomposed with ·OH radicals (a smaller share of the direct ozone reaction), which could then be scavenged. Furthermore, in the alkaline reaction medium, hydrogen peroxide was present in the dissociated form (pKa = 11.6) [32], as it was in reaction (5), which promoted the ·OH scavenging in accordance with reaction (6).

$$H_2O_2 + H_2O \rightarrow H_3O^+ + HO_2^- \tag{5}$$

$$\cdot OH + HO_2^- \rightarrow H_2O + O_2^{\cdot -} \tag{6}$$

The slowdown effect was slightly smaller for the O$_3$/UV/H$_2$O$_2$ process because part of the hydrogen peroxide was converted directly into ·OH radicals via UV irradiation, as shown in Fig. 2B.
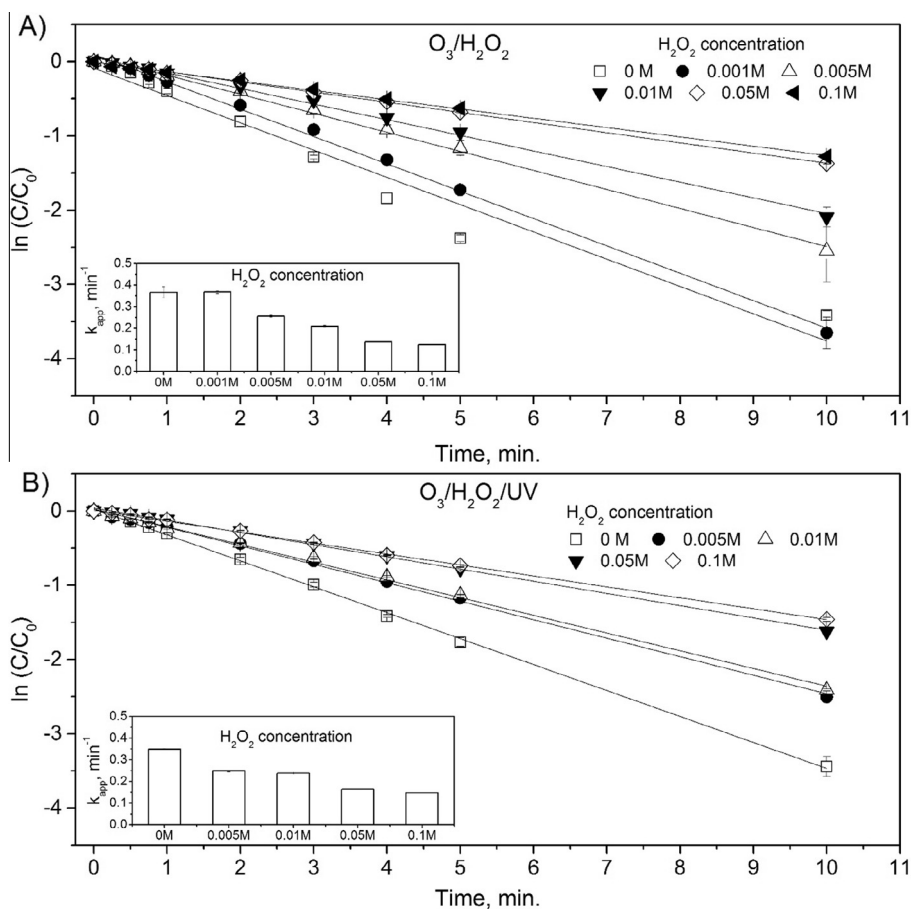
Fig. 2. H_2O_2 effect on RB5 decomposition pseudo-first order constant in the case of the O_3/H_2O_2 and $O_3/UV/H_2O_2$ processes; O_3 concentration in the inlet gas mixture C_{O3}^G = 42.3 g/Nm³; the gas flow Q_{in} = 40 L/h. C_0^{H2O2} = 0–0.01 M, pH 12, UVC lamp (15 W).

3.2. Comparison of the oxidation methods

The applied oxidation methods were compared for purified RB5 aqueous solutions (Fig. 3A) and both the diluted and undiluted industrial textile wastewater from the dyeing process that used Setazol Black DPT (Fig. 3B and C, respectively). The RB5 solutions were tested at a concentration of C_0^{RB5} = 125 mg/L and pH 12 (phosphate buffer) and pH 6.28 (MQ water) for ozone-based methods and H_2O_2/UV oxidation, respectively. This research conditions were selected based on the experiments, published in previous work [19]. The diluted industrial wastewater was characterized by the concentration of the dye at approximately 125 mg/L. This way results obtained for simulated and industrial wastewater could be compered more easily. The dye concentration of the industrial wastewater without dilution was 730 mg/L (the parameters of the wastewater are shown in Table 1). Diluted and undiluted wastewater at its natural pH were treated. In the case of the ozone-based oxidation processes, the O_3 concentration in inlet gas mixture was 42.3 g/Nm³, and the gas flow rate was Q_{in} = 40 L/h. An H_2O_2 concentration of 0.005 M (H_2O_2 concentration, which gave the highest reaction rate constant) and a 15W UVC lamp (used optionally) were applied. In the case of H_2O_2/UV oxidation, the hydrogen peroxide concentration was 0.2 M and 6 UVC lamps (7.2 W each) were used (reagent dosage explained in previous work [19]).

As shown in Fig. 3A, for all of the tested methods, a high discoloration of the RB5 solutions, close to 100%, was achieved in a relatively short time (20 min). The best effect was obtained for ozonation. No synergy effect of various oxidizing together was noted. In the case of the simultaneous use of O_3 and H_2O_2, a decrease was observed in the degradation rate of RB5 aqueous solution, which could be explained by the scavenging effect of hydroxyl radicals caused by hydrogen peroxide.

For the diluted industrial textile wastewater containing RB5 (dyebath with Setazol Black DPT – Kyma Setas), the discoloration effect was very close to that achieved for RB5 aqueous solution (Fig. 3B). The exception was the UV/H_2O_2 process. Based on this observation, it can be concluded that the presence of textile auxiliary agents in wastewater – NaCl and SAA inhibited the decolorization with the UV/H_2O_2 cleaning method. The inhibition of decolorization (Fig. A3) and both TOC (Fig. A4) and COD decay (Fig. A5) is shown in the Supplementary Materials. The ozone-based AOPs were not influenced by these factors, as shown in the Supplementary Materials (Fig. A1). The influence of textile auxiliaries had been discussed wider in our previous work [19]. For the wastewater without dilution, complete discoloration was not achieved, even after 60 min, with any of the tested methods. Approximately 90% color reduction was obtained for ozonation and the O_3/H_2O_2, O_3/UV and $O_3/UV/H_2O_2$ processes after this time. Because of the fact that in the O_3/UV system a slightly greater amount of hydroxyl radicals could have been produced, in this case the efficiency of decolorization was a bit higher than in the processes without the light, but still the ozone concentration was too low relative to the amount of dye. The UV/H_2O_2 process was not effective. Slightly more than 30% color reduction was noted after 1 h. The influence of textile auxiliary agents was significant in this case. What is more the molecules of dyes have high UV absorption capacity. When the dye concentration is high, the
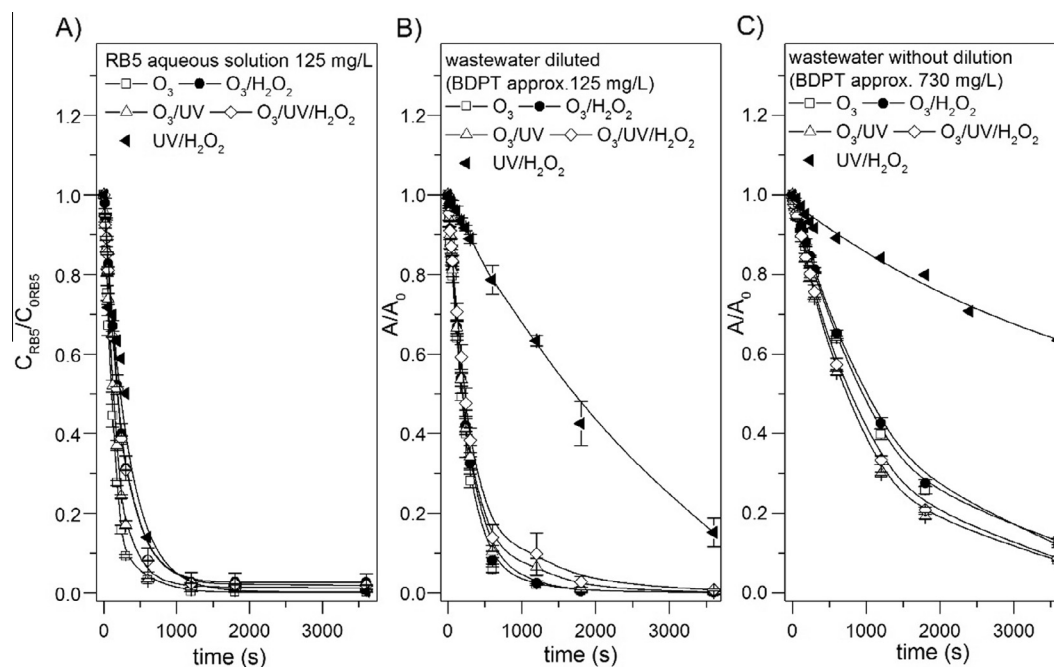
Fig. 3. O_3, O_3/H_2O_2, $O_3/UV/H_2O_2$ and UV/H_2O_2 processes for: A) RB5 solution 125 mg/L, B) diluted industrial wastewater (Setazol Black DPT approx. 125 mg/L), C) textile wastewater without dilution (Setazol Black DPT approx. 730 mg/L); ozone concentration $C_{O_3}^G$ =42,3 gO_3/Nm^3, gas flow Q_{in} = 40 L/h, C_0^{H2O2} = 0.005 M, pH = 12, UVC lamp (15 W).

extent of UV absorbed by it can be high and affected the process, as it could be observed in our experiment. At the same time the direct photolysis was not observed (Fig. A2).

3.3. Mineralization and biodegradability

For the tested wastewater samples and RB5 solutions with prior O_3, O_3/H_2O_2, O_3/UV, $O_3/UV/H_2O_2$, or UV/H_2O_2 treatment, the degree of mineralization was assessed (Fig. 4). The reduction of organic compounds, as expressed by COD and the mineralization extent, was satisfactory for RB5 aqueous solutions. Between 80% and 90% COD reduction and 50% TOC reduction was observed after 60 min of treatment. For the UV/H_2O_2 treatment, the COD reduction was 25% (Fig. 4A). In the cases of diluted and undiluted industrial wastewater, the reduction of organic compounds obtained after treatment was much lower than those obtained for the oxidation of RB5 aqueous solutions (in the case of all tested methods). Approximately 50% COD and 30% TOC reduction were achieved for diluted industrial wastewater (Fig. 4B). In spite of the fact that RB5 concentration in simulated and diluted industrial wastewater was approximately the same, COD and TOD reductions were not comparable for these two samples. Therefore, in case of research focused on industrial application real research conditions, should be taken under consideration. For undiluted industrial wastewater, there was only a 10% COD and 20% TOC reduction (Fig. 4C) due to the greater initial load of the industrial wastewater (compared to the dye aqueous solution). In some cases, the COD reduction was smaller than the TOC reduction due to the occurrence of compounds, which are not oxidized by the dichromate method (as used in the LCK 514 COD test).

The biodegradability study was performed for the simulated mixtures containing 125 mg/L of RB5 and for the diluted industrial wastewater corresponding to the concentration of the industrial dye (approximately 125 mg/L). Although the transformation products were not identified, the degradation of RB5 into other by-products was monitored by the change in the degree of oxidation,

which is an indicator of the oxidation degree of complex solutions and provides indirect information on their probability of biodegradation. Therefore, based on the COD/TOC, BOD$_5$/COD values and average oxidation state (AOS), biodegradability was evaluated. The AOS value was calculated following Reyes et al. [33] by using Eq. (7), where TOC and COD are expressed in mM of C and O_2, respectively.

$$AOS = \frac{4(TOC - COD)}{TOC} \tag{7}$$

The results are shown in Fig. 5(A, B, C: RB5 aqueous solution, D, E, F: diluted industrial wastewater). The COD/TOC reduction results obtained for the dye solution were satisfying and confirmed that fewer complexed by-products were present after AOP treatment, which resulted in the mineralization of RB5 (Fig. 5A). The COD/TOC reduction for wastewater was not as high but was still significant (Fig. 5. D). For the BOD$_5$/COD values of RB5 solutions after AOP treatments, a visible increase was observed from the value close to zero (0 min) up to 0.8 (60 min). The best results were obtained for the O_3/0.005 M H_2O_2 process and O_3 at 0.8 and 0.75, respectively. For the diluted wastewater, BOD$_5$/COD increased after using AOPs. However, the increase of these values was not significantly high. The largest enhancement in biodegradability was found for the ozonation of the wastewater (Fig. 5F). Moreover, when using a higher concentration of H_2O_2, a positive effect on biodegradability was achieved. The AOS values are presented in Fig. 5B and E (for the dye solution and the wastewater, respectively). The AOS is a valuable parameter that can be used as a general oxidation measure of complex mixtures (where various oxidation products are present). Therefore, AOS was considered. AOS can take values between +4 CO_2 (the most oxidized state of C) and −4 for CH_4 (the most reduced state of C). All of the tested AOPs resulted in significant increases in the AOS values for the dye solution and lower increases for wastewater. A higher general oxidation degree (covering the main compound and its oxidation products) was achieved in the case of AOPs when H_2O_2 was used in addition to ozone. With respect to COD/TOC, BOD$_5$/COD and
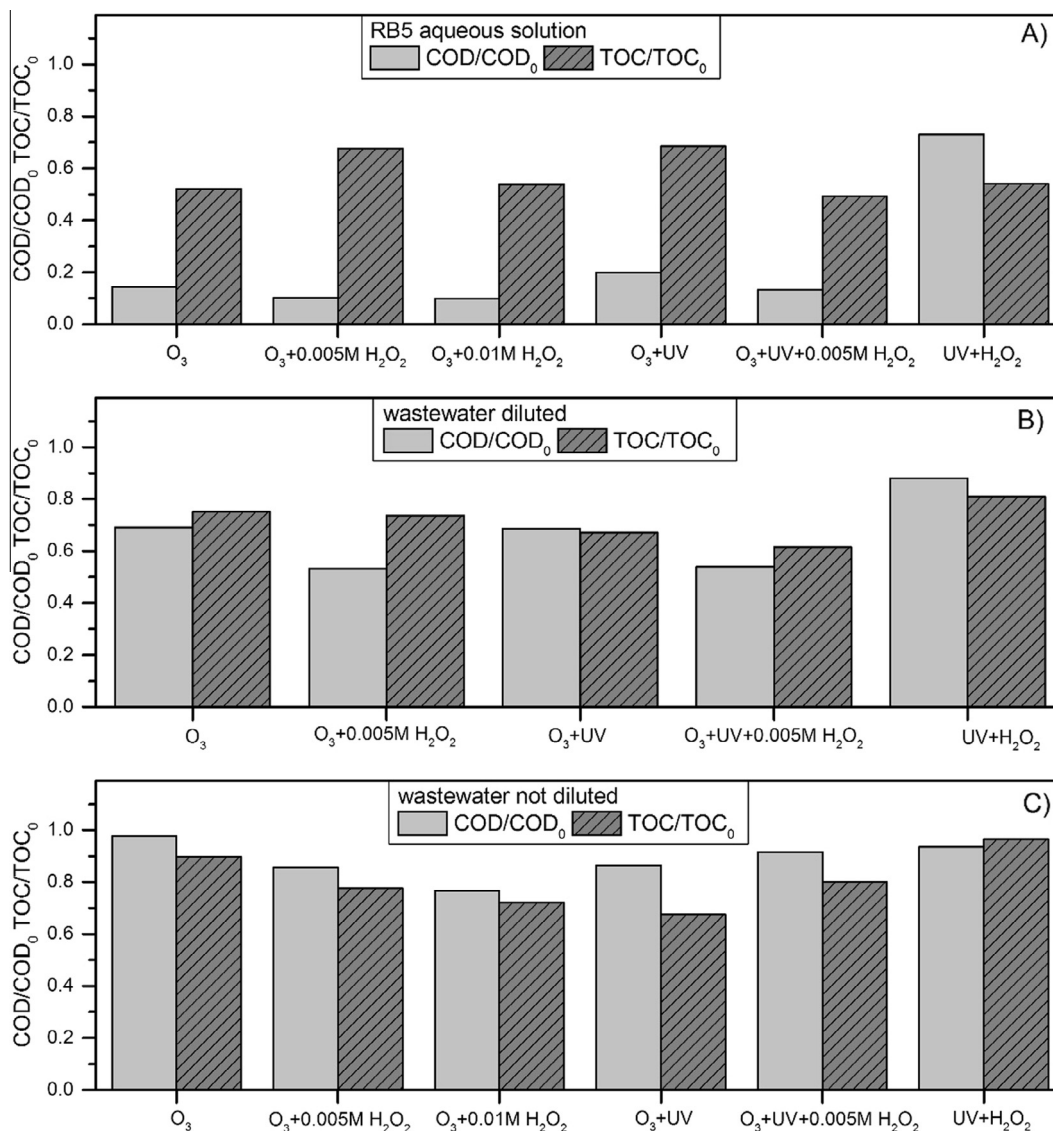
Fig. 4. TOC and COD removal for the decolorization of RB5 aqueous solutions A) and textile wastewater containing Setazol Black DPT: diluted one B) and not diluted one C) by ozonation, UV/H$_2$O$_2$, O$_3$/H2O2, UV/O$_3$/H$_2$O$_2$ (C$_0^{RB5}$ = 125 mg/L, C_{in}^{O3} = 42.3 g/Nm^3, Q$_{in}$ = 40 L/h, pH = 12, UVC lamp 15 W, C$_0^{H2O2}$ = 0.005 and 0.01 M) and H$_2$O$_2$/UV process (for dye aqueous solution: C$_0^{RB5}$ = 125 mg/L, C$_0^{H2O2}$ = 0.2 M, pH = 6.28; for wastewater C$_0^{H2O2}$ = 0.2 M, pH = 11.23).

AOS, the O$_3$ and O$_3$/0.005 M H$_2$O$_2$ treatments resulted in more oxidized by-products that could be assimilated by microorganisms in both cases: RB5 aqueous solution and wastewater containing RB5.

3.4. Toxicity

Although high AOS values are frequently associated with biocompatibility of the solutions, it does not necessarily must be related to the formation of by-products characterized by low toxicity. The toxicity assessment was conducted by a screening test and an EC$_{50}$ test for the decomposition of RB5 aqueous solutions and diluted wastewater containing industrial dye. The results of the screening test for ozonation, O$_3$/H$_2$O$_2$ and UV/O$_3$/H$_2$O$_2$ of RB5 aqueous solutions are shown in Fig. 6. Using oxidation methods with higher concentrations of H$_2$O$_2$ (0.01 M) and coupling O$_3$, H$_2$O$_2$ and UV resulted in nontoxic mixtures. However, the use of O$_3$ and O$_3$/0.005 M H$_2$O$_2$ resulted in a less significant decrease in toxicity (Table 2 shows the EC$_{50}$ values). Moreover, the tested dyestuff was characterized by very high toxicity. The EC$_{50}$ value was

3.86 ± 0.32 mg/L, which is in in agreement with the values obtained by other authors for the sodium dithionite form of RB5 [34]. This form of the dye has also been identified by us using mass spectroscopy.

The toxicity of the RB5 aqueous solution during ozonation was also investigated. A short ozonation time increased the toxicity only slightly, i.e., from EC$_{50}$ = 2.81% at the beginning to 2.55% after 5 min (very low EC$_{50}$ value), which suggests the appearance of some toxic by-products during the initial ozonation phase. Then, after 60 min of treatment and the application of 1.68 g/L ozone, the toxicity decreased more than five times, and the EC$_{50}$ was 19.62%.

The toxicity assessment was also conducted for the diluted industrial wastewater. The results of the screening test and the EC$_{50}$ test are shown in Table 3. Each AOP treatment resulted in decreased toxicity. However, the wastewater was not as toxic as it was before the treatment as for the RB5 aqueous solution. According to Gottlieb et al [34], the parent RB5 (EC$_{50}$ = 27.5 mg/L) and its hydrolyzed form (EC$_{50}$ = 11.4 mg/L) are characterized by a
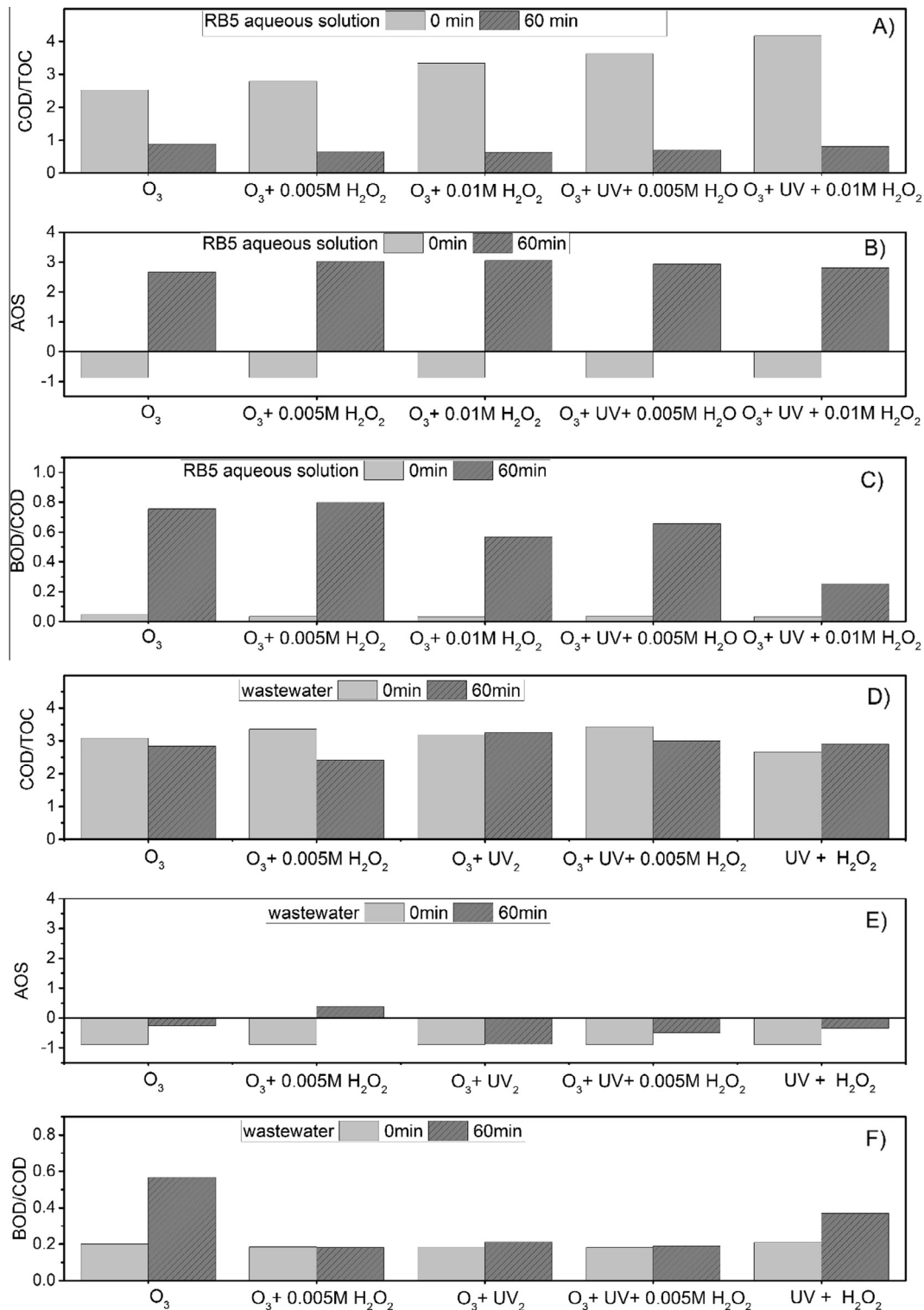
Fig. 5. COD/TOC A), AOS B), BOD₅/COD values obtained for the decomposition of RB5 aqueous solutions and COD/TOC D) AOS E), BOD₅/COD F) values obtained for the decomposition of diluted wastewater by ozonation, O_3/H_2O_2, $UV/O_3/H_2O_2$ (C_0^{RB5} = 125 mg/L, C_{O3}^G = 42.3 g/Nm³, Q_{in} = 40 L/h, pH = 12, UVC lamp 15 W, C_0^{H2O2} = 0.005 and 0.01 M).

lower toxicity than the sodium dithionite form of RB5. During the industrial dyeing process, the sodium salt of the dye is used (technical product with four Na atoms), and hydrolyzation of the dye occurs due to the high temperature dyeing conditions and alkaline pH, which explains the differences between the toxicity of RB5 in aqueous solution and the toxicity of the wastewater.

3.5. Costs evaluation

The efficiency factor of several ozone-based AOP methods has been discussed from a practical point of view; the cost factor is also important. In industrial practice, efficiency related to costs is an indicator for choosing the best treatment method. In previous
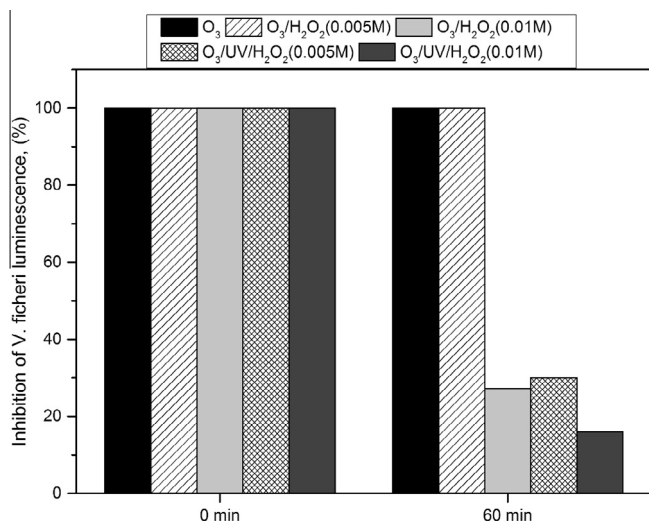
Fig. 6. Toxicity assessment for the oxidation of RB5 aqueous solutions by ozonation, O_3/H_2O_2, $UV/O_3/H_2O_2$ (C_0^{RB5} = 125 mg/L, C_{O3}^G = 42.3 g/Nm^3, Q_{in} = 40 L/h, pH = 12, UVC lamp 15 W, C_0^{H2O2} = 0.005 and 0.01 M).

Table 2
RB5 aqueous solution toxicity assessment, EC$_{50}$ test.

Method	Time (min)	EC$_{50}$ (% v/v)
O_3	0	3.31
	60	19.72
O_3/H_2O_2 (0.005 M)	0	3.15
	60	21.61

Table 3
Diluted wastewater toxicity assessment, screening test and EC$_{50}$ test.

Method	Time (min)	Luminescence inhibition after exposure to effluent for 15 min (%)	EC$_{50}$ (95% CI in brackets) (% v/v)
O_3	0	67.51	46.63 (40.77–53.33)
	60	1.59	Not calc.
O_3/H_2O_2 (0.005 M)	0	90.77	40.13 (32.19–66.38)
	60	Not calc.	Not calc.
O_3/UV	0	70.16	46.30 (34.57–62.02)
	60	2.70	Not calc.
$O_3/UV/H_2O_2$ (0.005 M)	0	53.70	76.05 (52.21–84.71)
	60	Not calc.	Not calc.
UV/H_2O_2 (0.2 M)	0	58.02	59.77 (48.59–79.01)
	60	12.87	Not calc.

studies the electrical energy per order (EE/O) indicator has been used for this purpose. In most cases, this evaluation is related to laboratory-scale experiments [22,29,35]. A cost evaluation performed in this way can be far different from the industrial-scale process. In this study, the costs of the tested treatment methods were estimated on the basis of real industrial conditions. The industrial-scale AOP plant implemented in one of the Polish dye houses (Bilinski Co.) that used an APP Thies ozone apparatus was the model for the cost evaluation. The operating and investment costs were calculated for all of the tested ozone-based AOPs. The input data are shown in Table 4. The operating costs were related to the ozone dose used in the experiment (1.69 g/L). The industrial

Table 4
Cost evaluation input data.

Parameter	Value
Ozone dose in gas phase	250 g/Nm^3
Gas flow-rate	10 Nm^3/h
Reaction time	0.67 h
Reactor volume	1 m^3
UV lamp energy	16 kW
H_2O_2 0.005 M	0.51 L(H_2O_2 30% a.s.)/m^3
H_2O_2 0.01 M	1.02 L(H_2O_2 30% a.s.)/m^3

process time was calculated following Chung & Kim [28] using Eq. (8).

$$Total\ Ozone\ Dose = \frac{O_3\ dose \cdot Gas\ flow - rate \cdot Reaction\ time}{Reactor\ volume}\ (g/L) \qquad (8)$$

In Fig. 7, the investment and operating costs of the several tested ozone-based AOPs are shown. The investment costs (Fig. 7A) of the ozonation plant are high. In the case of O_3/H_2O_2, the cost of the H_2O_2 dose is negligible compared to that of ozonation. In contrast, the UV lamp equipment significantly increases the investment costs. The operating costs (Fig. 7B) of the ozonation and O_3/H_2O_2 processes are comparable and are approximately 50% the cost of fresh water and discharge industrial wastewater to the city's sewage. Therefore, using the O_3 and O_3/H_2O_2 process can be economically reasonable, especially when the possibility of environmental penalty is considered (in textile wastewater, the main problem is an excessive chloride concentration). The cost of using O_3/UV and $O_3/UV/H_2O_2$ is 80% that of fresh water and discharge industrial wastewater to the city's sewage, industrial implementation is not recommended. These differences are due to the UV lamp application. The investment costs and the efficiency of these methods do not provide incentives.

The total ozone dose (TOD = 1.69 g/L) can be far too high when an industrial ozone treatment plant is considered. Due to mass transfer, the limitation ozone was overdosed during the laboratory-scale experiment. The industrial ozone reactor (APP by Thies) is equipped with an ozone injecting system, and mass transfer between the gas (O_3 and O_2 mixture) and liquid phases (wastewater) is enhanced. Therefore, industrial research should be conducted, the exact industrial TOD should be estimated and the reaction time could be much shorter.

4. Conclusions

In this study, the wastewater stream after the industrial reactive dyeing process was taken into consideration. Due to high salinity, high pH and intense color, it is the most problematic textile wastewater type from an environmental perspective. It was indicated that, using O_3 or O_3 combined with a moderate concentration of H_2O_2 (below 0.005 M) results in good color reduction and an increase in mineralization, biodegradability and a reduction in the toxicity of hazard compound RB5. In turn, for the AOPs in which higher concentrations of H_2O_2 and/or UV irradiation were used, lower values of BOD$_5$/COD ratio were found. Treating after-dyeing discharge by ozone-based AOPs can be a first stage in the textile wastewater purification process, e.g., prior to biological treatment, or it can be the only operation when the purified after-dyeing discharge is used as a source of concentrated brine (ready to use). Moreover, treating the selected textile wastewater stream, in this case, after-dyeing discharge, by using a customized method can be economically reasonable for industry. It should be noticed that conducting the research focused only on the oxidation
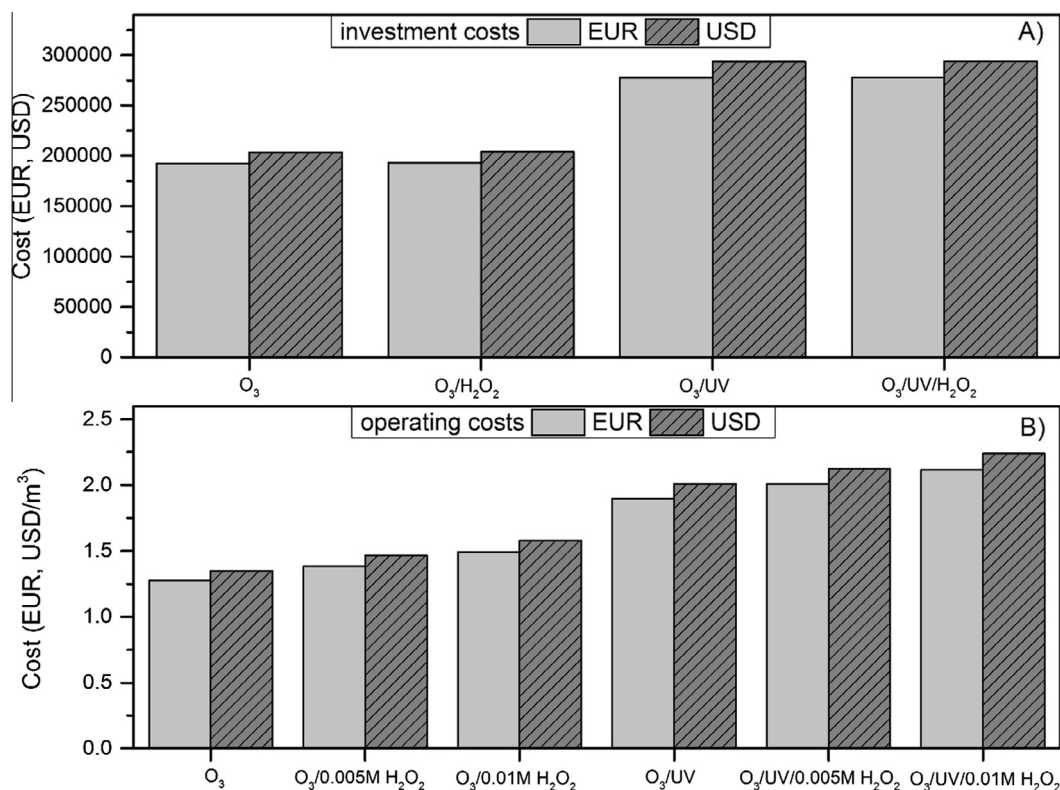
Fig. 7. The investment A) and operating B) costs of ozone-based AOPs.

of aqueous dye solutions without considering the conditions in industrial textile wastewater can give distorted results; reliance on these results can be confusing when designing an industrial process.

Based on experimental results and costs evaluation, the use of ozone or ozone with very low concentration of H_2O_2 (0.005 M) can be recommended to textile industry. In contrast to the O_3/UV process, the investment and operating costs of the O_3/H_2O_2 process are not much higher than ozonation itself. When greater mineralization is considered, O_3/H_2O_2 is a good option, but ozonation is the best one.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2016.07.100.

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