

## Article

# Degradation Efficiency and Kinetics Analysis of an Advanced Oxidation Process Utilizing Ozone, Hydrogen Peroxide and Persulfate to Degrade the Dye Rhodamine B

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**Abstract:** In this study, the effectiveness of a rhodamine B (RhB) dye degradation process at a concentration of 20 mg/L in different advanced oxidation processes— $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{O}_3/\text{UV}$  and PDS/UV—has been studied. The use of UV in a photo-assisted ozonation process ( $\text{O}_3/\text{UV}$ ) proved to be the most effective method of RhB decolorization (90% after 30 min at dye concentration of 100 mg/L). The addition of sulfate radical precursors (sodium persulfate, PDS) to the reaction environment did not give satisfactory effects (17% after 30 min), compared to the PDS/UV system (70% after 30 min). No rhodamine B decolorization was observed using hydrogen peroxide as a sole reagent, whereas an effect on the degree of RhB degradation was observed when UV rays strike the sample with  $\text{H}_2\text{O}_2$  (33% after 30 min). The rhodamine B degradation process followed the pseudo-first-order kinetics model. The combined PDS/ $\text{O}_3/\text{UV}$  process has shown 60% color removal after 30 min of reaction time at an initial dye concentration of 100 mg/L. A similar effectiveness was obtained by only applying ozone or UV-activated persulfate, but at a concentration 2–5 times lower (20 mg/L). The results indicated that the combined PDS/ $\text{O}_3/\text{UV}$  process is a promising method for high RhB concentrations (50–100 mg/L) comparing to other alternative advanced oxidation processes.

**Keywords:** rhodamine B; dye; advanced oxidation process; radicals; kinetics



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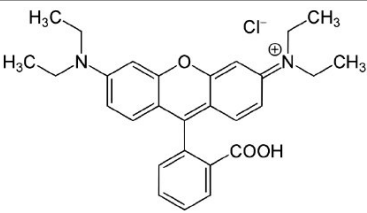
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## 1. Introduction

Synthetic dyes are used in different industrial sectors, in e.g., the textile, cosmetic, pharmaceutical, plastics, tanning, paper and food industries. Azo, anthraquinone, phthalocyanine and triphenylmethane dyes are some of the most commonly utilized dye groups in the textile industry [1], and the progression of the industrial revolution has led to an increase in their use. Moreover, as much as 50% of dyes are lost to the process wastewater as dyestuff residues during the dyeing and finishing process [2], causing a significant environmental pollution problem.

One of the dyes utilized in the chemical, textile, paper and paint industries is rhodamine B (RhB). The physicochemical properties of RhB are summarized in Table 1. Rhodamine B is part of the rhodamine dyes—organic chemical compounds of the triphenylmethane xanthene dye group—classified as micropollutants. These compounds exhibit toxicity after short-term exposure (acute toxicity), but the main research focus is concentrated on analyzing the long-term health effects resulting from their presence in the environment (chronic toxicity) [3]. RhB is irritating to the skin, eyes and upper respiratory tract. It also exhibits potential mutagenic and carcinogenic effects [4].

**Table 1.** Molecular structure and some physicochemical properties of RhB [5].

| Chemical Structure                                                                | Physicochemical Properties      |                                                                 |
|-----------------------------------------------------------------------------------|---------------------------------|-----------------------------------------------------------------|
|  | Chemical formula                | C <sub>28</sub> H <sub>31</sub> ClN <sub>2</sub> O <sub>3</sub> |
|                                                                                   | Molecular weight [g/mol]        | 479.00                                                          |
|                                                                                   | CAS number                      | 81-88-9                                                         |
|                                                                                   | Water solubility at 20 °C [g/L] | 15.0                                                            |
|                                                                                   | Dissociation constant (pKa) [-] | 3.7                                                             |
|                                                                                   | logK <sub>OW</sub> [-]          | 1.9–2.0                                                         |
|                                                                                   | λ <sub>max</sub> in water [nm]  | 554.0                                                           |

Due to high concentrations of dyes in process wastewater and their low biodegradability, it seems reasonable to develop new solutions of water and wastewater treatment, particularly from the perspective of removing colored pollutants that may pose significant environmental problems.

Advanced oxidation processes (AOPs) are proposed as an alternative solution to traditional water and wastewater treatment methods. AOPs utilizing physicochemical processes enable the total or partial elimination of hazardous substances through their mineralization into environmentally neutral carbon dioxide and water, as well as other simple chemical compounds [6]. AOPs generate highly reactive hydroxyl radicals •OH with a reduction potential of  $E_0 = 2.80$  V. Currently, there are a number of AOPs used for degradation of dyes such as rhodamine B, e.g., O<sub>3</sub>/UV, TiO<sub>2</sub>/UV (photocatalysis) or H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> (Fenton's reagent). In studies on the degradation of the rhodamine B dye from aqueous solutions using photo-Fenton and heterogeneous photocatalytic processes with an innovative Ni-Cu@MWCNT photocatalyst, Tariq et al. [7] achieved RhB dye degradation at levels of 86% and 98%, respectively. The high degradation percentage was achieved through the generation of large amounts of hydroxyl radicals under the influence of UV radiation. Similar results were also obtained by Dhahir et al. in their research [8].

Recent literature data [9–13] indicates that current research is focused on a new class of oxidizers—peroxyacids, including inorganic peroxyacid salts (peroxymonosulfate, PMS; and persulfate, PS). The primary target of using peroxyacids is to generate sulfate radicals. The sulfate radical (SO<sub>4</sub>•<sup>−</sup>) is characterized by an oxidizing potential  $E_0 = 2.50$ – $3.10$  V and is produced as a result of the interaction of various energy sources (e.g., heat, UV radiation) with the SO<sub>4</sub>•<sup>−</sup> sulfate radical precursor (e.g., sodium persulfate Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) or as a result of the reactions of transition metal ions (e.g., Fe<sup>2+</sup>, Co<sup>2+</sup>) with the SO<sub>4</sub>•<sup>−</sup> radical precursor. In sulfate radicals-based processes, it is possible to achieve organic pollutant degradation under the influence of both sulfate and hydroxyl radicals. Activation of PS or PMS results in the generation of sulfate radicals, or both sulfate and hydroxyl radicals, for PS and PMS respectively [14–16].

Zawadzki [17] investigated the degradation of RhB in the presence of ultrasound (US) and sodium persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) activated by visible light (Vis). The performed study proved that a hybrid sono-visible light-sodium persulfate system is an interesting alternative for treatment of solutions containing rhodamine B at varying dye concentrations (up to 20 mg/L). Heidarpour et al. [18] improved the RhB decolorization process by increasing the oxidative capacity of the reaction system through simultaneous photocatalysis and heterogeneous persulfate activation, thereby confirming the significant role of sulfate radicals in the RhB degradation process.

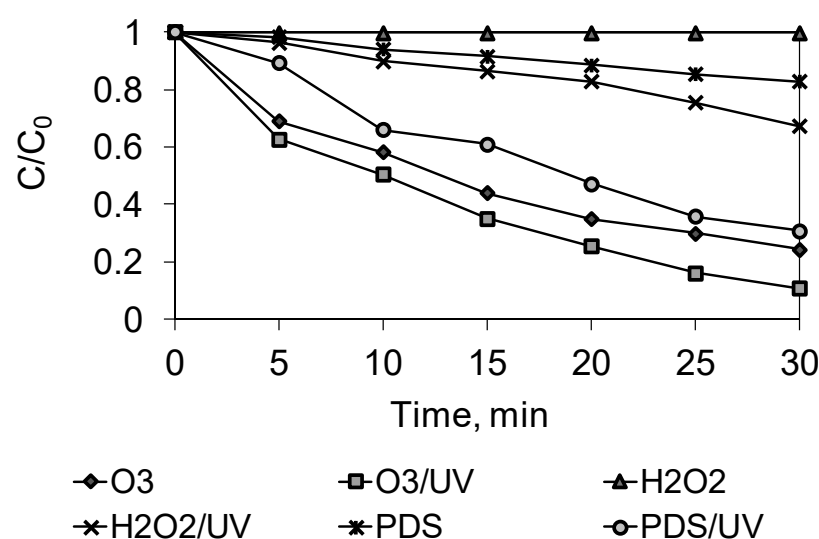
Considering the broad application of rhodamine B in various branches of industry, and therefore the presence of this substance in process wastewater and the problems related to its removal, the aim of this study was to assess the effectiveness of rhodamine B degradation in an advanced oxidation process: H<sub>2</sub>O<sub>2</sub>/UV, O<sub>3</sub>/UV, PDS/UV. The concentration of dyes in textile effluents depends on several parameters such as the type of dyeing process, dyes used, the nature of the effluent. Dye concentrations in industrial wastewater have been determined at varying levels, usually from about 10 to 200 mg/L, however concentrations between 600 and 7000 mg/L was also reported [19]. Therefore, the combined

PDS/O<sub>3</sub>/UV process was investigated to determine the ability to remove RhB over a wide concentration range (from 20 to 100 mg/L). The results of the combined PDS/O<sub>3</sub>/UV process were compared with other literature data in order to show the advantage of the proposed method.

## 2. Results and Discussion

### 2.1. Advanced Oxidation Study

The rhodamine B degradation using the following processes: H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>/UV, O<sub>3</sub>, O<sub>3</sub>/UV as well as PDS and PDS/UV was investigated. The results are presented in Figure 1. It was observed that the degree of rhodamine B degradation increased simultaneously over time, independently of the treatment system. For example, the H<sub>2</sub>O<sub>2</sub>/UV system degrades the RhB at a level of 14% and 33%, after 15 and 30 min respectively. On the other hand, the application of sodium persulfate (PDS) enabled to degrade the RhB at a level of 6% and 12% after 10 and 20 min.



**Figure 1.** Photodegradation of rhodamine B during different AOP. Conditions: C<sub>0</sub>[RhB] = 20.0 mg/L; V = 0.5 L; T = 298.0 K; p = 1013.0 hPa; pH = 6.0; t = 0–30 min.

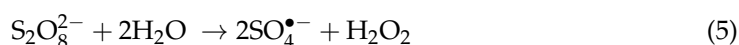
Addition of oxidizers (O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, PDS) into the reaction environment results in the initiation of reactions generating oxidative radicals (hydroxyl •OH or sulfate SO<sub>4</sub><sup>•−</sup>). There are two methods of pollutant elimination in the case of the sole ozonation process [20]. The first, the direct oxidation route, consists in a reaction of the ozone with the pollutant. Direct oxidation is more selective and the most appropriate for acidic conditions. In neutral reaction environment (pH = 6.0–7.0), the available methods include both direct as well as indirect oxidation, which consists in oxidation by means of hydroxyl radicals. For this reason, the reaction environment pH after the addition of the rhodamine B standard was maintained at a level of about 6.0. Due to the certain limitations characteristic of ozonation in water and wastewater technologies (e.g., low ozone transfer rate, ozone production costs) [21], one of the methods used to assist the ozonation reaction is the application of UV radiation. Ozone has a molar absorptivity (ε) of 2952 cm<sup>2</sup>/M at λ = 254 nm [22]. For this reason, UV radiation is used in order to accelerate the decomposition of ozone and hydroxyl radical generation, as shown in Equations (1) and (2). This effect was documented by authors [23,24]. In this study, the use of UV irradiation-assisted ozonation made it possible to increase the degree of rhodamine B decolorization from 75% to 90% after 30 min of reaction time:



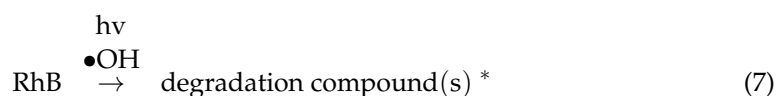
The next studied processes were PDS and PDS/UV systems involving sulfate radical generation. Literature data indicates that sulfate radicals find application not only in dye decolorization [25], but also in the removal of a number of other organic substances, e.g., pharmaceutical substances [26] and pesticides [27] as well as liquid media, such as landfill leachate [28].

The effects of sole sulfate radical precursors (sodium persulfate, PDS) did not bring about satisfactory results of rhodamine B decolorization effects, as can be observed in Figure 1. Only 17% of dye degradation was achieved after 30 min of reaction time. Nevertheless, it should be noted that the effectiveness of sole PDS was only 5% lower compared to the H<sub>2</sub>O<sub>2</sub> process catalyzed by UV radiation (H<sub>2</sub>O<sub>2</sub>/UV). As indicated in the literature [29,30], persulfates are capable of reacting via direct reactions with organic compounds without the presence of catalysts, but the degree of pollutants elimination is lower compared to the one obtained through the use of activated persulfate [31]. The reason for this is that the reaction in the presence of radicals generated as a result of persulfate activation is faster by a factor of 103–105 compared to the sole presence of the persulfate without activation [32].

The energy transferred to the persulfate anion results in the breaking of the peroxide bond and the generation of two sulfate radicals (Equation (3)). Sodium persulfate activation by UV irradiation results in reactions according to Equations (4) and (5) [2]. The application of UV radiation for PDS activation made it possible to shorten the time necessary to achieve rhodamine B degradation compared e.g., to the H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>/UV and PDS processes. For example, after 10 min of the PDS/UV process, the obtained effectiveness was similar to the PDS system after 30 min of reaction time. A reaction time of 30 min in the PDS/UV system made it possible to achieve twice the effectiveness of the H<sub>2</sub>O<sub>2</sub>/UV process:



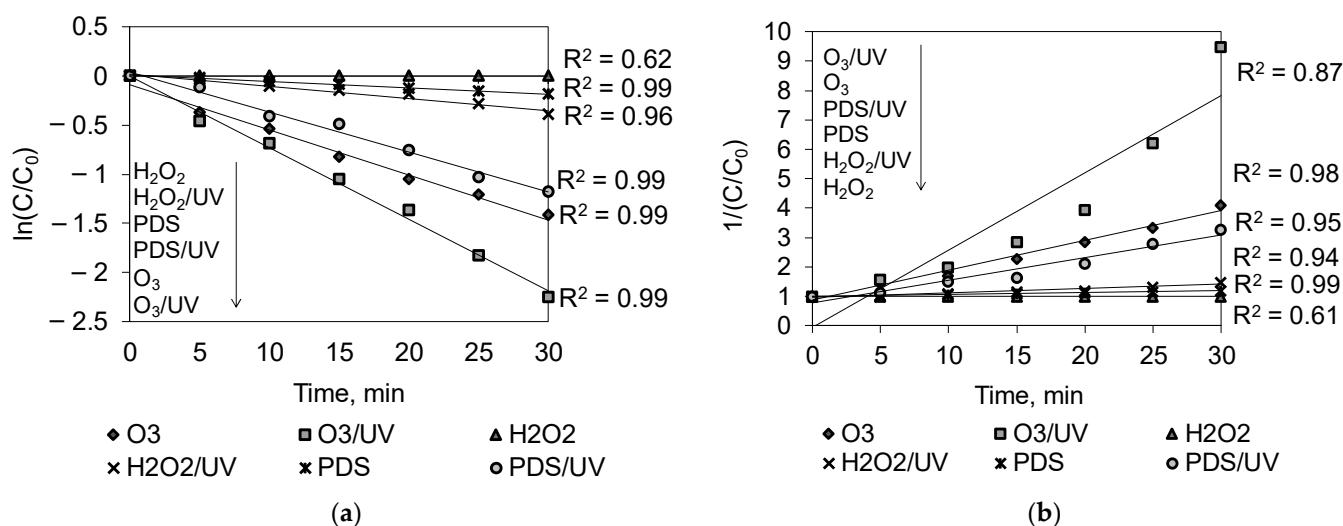
No rhodamine B decolorization was observed during the process of hydrogen peroxide as the sole source of radicals, as can be seen in Figure 1. Although hydrogen peroxide finds wide application as a low cost and commercially available oxidant, it shows certain practical limitations, e.g., it does not oxidize some types of organic pollutants. For example, the effectiveness of anthraquinone dye decolorization in literature [33] did not depend on the initial dose of H<sub>2</sub>O<sub>2</sub>. A double increase in the dose of hydrogen peroxide resulted in an increase of the decolorization effectiveness from 5.8% to 7.8% after 45 min of reaction time. However, the obtained results indicate that UV irradiation increases the RhB degradation effectiveness from <1% to 33% after 30 min of reaction time. The RhB degradation in the H<sub>2</sub>O<sub>2</sub>/UV process is achieved through the reactions of hydroxyl radicals formed through irradiation of H<sub>2</sub>O<sub>2</sub> (Equation (6)). Literature data [34,35] indicates that the RhB degradation in the H<sub>2</sub>O<sub>2</sub>/UV system takes places primarily through radical mechanisms, however conversion via UV radiation absorption cannot be excluded as well (Equation (7)):



where \* indicates that identification of degradation products was beyond the scope of this study

## 2.2. Kinetics Studies

The linear relationships  $[\ln(C/C_0)]$  and  $[1/(C/C_0)]$  as functions of reaction time (min) are presented in Figure 2. As shown in the studies [36,37], the pseudo-first-order model is not always the best model to describe the reaction kinetics. For example, Haddad et al. [36] showed that the pseudo-second-order model showed a better fit in the Fenton process compared to the pseudo-first-order model. The above observations were also confirmed by Aljuboury and Palaniandy [37]. It is therefore justified to study both pseudo-first and pseudo-second order kinetics.



**Figure 2.** Kinetics of rhodamine B degradation (a—pseudo-first-order; b—pseudo-second-order). Conditions:  $C_{0[RhB]} = 20.0$  mg/L;  $V = 0.5$  L;  $T = 298.0$  K;  $p = 1013.0$  hPa;  $pH = 6.0$ ;  $t = 0$ –30 min.

For each treatment systems, kinetic reaction parameters were determined based on the analyzed kinetic models (Table 2). As can be observed in Figure 2 and Table 2, the  $R^2$  values obtained for the pseudo-first-order model exhibit better fitting compared to the pseudo-second-order model. There is a very good relationship between  $\ln(C/C_0)$  and  $t$  (except for the  $H_2O_2$  process), therefore the rhodamine B degradation followed a pseudo-first-order model. Satisfactory fitting (60–80%) was obtained only for the  $H_2O_2$  process, as a result of the very low RhB degradation effectiveness (under 1%).

**Table 2.** Kinetic parameters of the advanced oxidation process.

| Model               | Parameter | Process  |             |        |        |        |          |
|---------------------|-----------|----------|-------------|--------|--------|--------|----------|
|                     |           | $H_2O_2$ | $H_2O_2/UV$ | PDS    | PDS/UV | $O_3$  | $O_3/UV$ |
| pseudo-first-order  | k, 1/min  | 0.00     | 0.0065      | 0.0126 | 0.0408 | 0.0459 | 0.0726   |
|                     | $R^2$     | 0.62     | 0.99        | 0.96   | 0.99   | 0.99   | 0.99     |
| pseudo-second-order | k, 1/min  | 0.00     | 0.0070      | 0.0150 | 0.0768 | 0.1022 | 0.2625   |
|                     | $R^2$     | 0.61     | 0.99        | 0.94   | 0.95   | 0.98   | 0.87     |

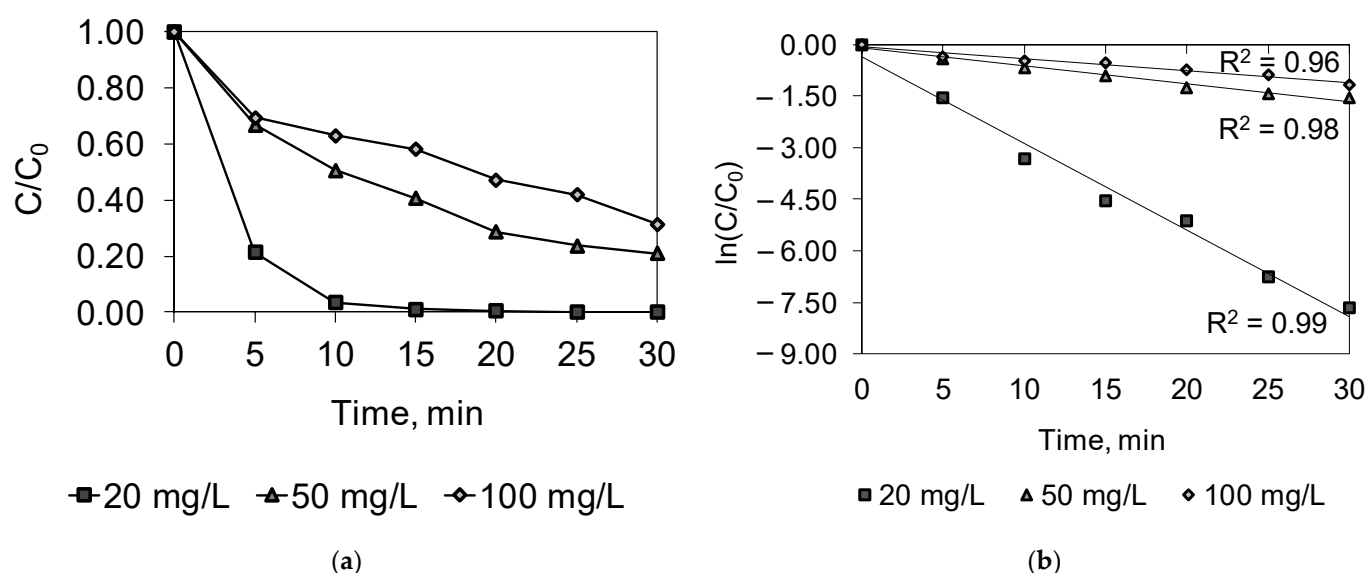
A phenomenon characteristic of advanced oxidation processes is the occurrence of (typically) two time intervals for the conducted oxidation reactions [38]. Other authors [39,40] observed a similar phenomenon as well, resulting most likely from the indirect reactions of oxidizing components with the pollutant degradation products. Based on the linear relationship analysis, it was found that this phenomenon does not occur in the studied AOP methods, as it is primarily characteristic of heterogeneous oxidation processes (e.g.,  $TiO_2$  photocatalysis) or other processes conducted in the presence of solid catalysts (e.g., the  $Cu(II)$ -polyampholyte heterogeneous catalyst) [41]. In these types of processes, the first, “rapid” stage occurs due to the high availability of active centers in the catalyst and the simultaneous availability of a high number of oxidative radicals. As the reaction

proceeds, the number of active centers becomes less available due to blockage of catalyst pores and lower radicals generation, which results in a transition to the second, “slow” stage of the reaction.

The obtained results demonstrate that each of the applied treatment methods is characterized by different kinetic parameter values. The  $O_3/UV$  system exhibited the greatest steady reaction rate, which was a result of the ozone oxidation path, involving direct oxidation with ozone and radical oxidation with the  $\bullet OH$  radical.

### 2.3. Combined PDS/ $O_3/UV$

In the final stage of the studies, the model solution containing the rhodamine B dye standard at an initial concentration of 20, 50 and 100 mg/L was subjected to treatment in a combined PDS/ $O_3/UV$  process. The process was carried out for 30 min. The results are presented in Figure 3a. The use of hydrogen peroxide was omitted in order to minimize the risk of oxidation process inhibition by an excessive quantity of  $H_2O_2$ , which may result in  $\bullet OH$  radical recombination and the auto-decomposition of  $H_2O_2$  into  $H_2O$  and  $O_2$ , as evidenced [42–44].



**Figure 3.** Photodegradation of rhodamine B during different AOP (a) and reaction kinetics (b). Conditions:  $C_{0[RhB]} = 20\text{--}100$  mg/L;  $V = 0.5$  L;  $T = 298.0$  K;  $p = 1013.0$  hPa;  $pH = 6.0$ ;  $t = 0\text{--}30$  min.

Based on the obtained results, it was concluded that the decolorization degree depends on the initial dye concentration. For example, after 15 min, at concentrations of 20, 50 and 100 mg/L, the degree of RhB degradation was 42%, 59% and 99% respectively. The experimental conditions were the same for each of the analyzed systems (temperature, reaction, atmospheric pressure, reaction vessel volume, reaction vessel shape), so, presumably the quantity of the generated oxidative radicals was stable and decreased simultaneously with the increase in RhB concentration. This phenomenon was also confirmed in other publications [45,46], and it is influenced by e.g., dye particle density, which blocks UV penetration into the treated solution. Another reason for the decreased decolorization effect is the reduced likelihood of oxidative radical and dye particle collisions, or the fact that the radicals are first used for oxidizing the by-products of the oxidation process [47]. Also high concentration of dye molecules causes greater consumption of radicals resulting in an insufficient amount of radicals to decompose the excess of RhB. Moreover, intermediates may consume active species, which results in a poor dye decolorization (competitiveness effect). However, a detailed study of the possible formation of oxidation by-products should be carried out. Despite the high efficiency of AOPs for degradation of many pollutants, particular attention should be paid to the by-products of the oxidation process, which are often more toxic and dangerous than the original compounds [48].

The effectiveness of RhB degradation may also be influenced by the composition of wastewater, e.g., solid particles suspended in the treated wastewater, or the inorganic ions, such as  $\text{Cl}^-$  ions;  $\text{CO}_3^{2-}$ ;  $\text{HCO}_3^-$  or  $\text{NO}_3^-$  and  $\text{NO}_2^-$ . Solid particles can increase the consumption of reagents needed for the oxidation of pollutants and absorb UV radiation. In turn, the ions can inhibit RhB degradation as a result of scavenging  $\text{SO}_4^{\bullet-}$  and/or  $\bullet\text{OH}$  radicals [49].

Although the advanced oxidation process was conducted at high dye concentrations (50–100 mg/L), the combined PDS/ $\text{O}_3$ /UV process, RhB removal of 69–79% after 30 min of reaction time was achieved. A similar effectiveness was obtained by only applying ozone or UV-activated persulfate, but at a concentration 2–5 times lower (20 mg/L).

A kinetic study was also performed in order to investigate the PDS/ $\text{O}_3$ /UV process dynamics. Since it was demonstrated that the rhodamine B degradation followed a pseudo-first-order model, the analysis of RhB decolorization dynamics was performed based on this model. The relationship between  $[\ln(C/C_0)]$  and the process time  $t$  is presented in Figure 3b. As expected, the process performed at the lowest dye concentration showed the highest value of reaction rate constant  $k$  (Table 3). The high RhB concentrations resulted in an increase of the half-life ( $t/2$ ) from 2.8 min ( $C_{0[\text{RhB}]} = 20$  mg/L) to 13.3 min and 20.3 min at concentrations of 50 and 100 mg/L respectively.

**Table 3.** Kinetic parameters of the combined advanced oxidation process (PDS/ $\text{O}_3$ /UV) in a different dye concentrations.

| Parameter   | Dye Concentration, mg/L |        |        |
|-------------|-------------------------|--------|--------|
|             | 20                      | 50     | 100    |
| $k$ , 1/min | 0.2513                  | 0.0523 | 0.0341 |
| $R^2$       | 0.99                    | 0.98   | 0.96   |
| $t/2$       | 2.8                     | 13.3   | 20.3   |

Table 4 presents the chemical reaction rate classification based on the mathematically calculated half-life  $t/2$ . Reactions of RhB decolorization in the concentration range of 20–50 mg/L were classified as moderate ( $1\text{--}10^3$  s), whereas at a concentration of 100 mg/L were classified as slow ( $10^6\text{--}10^3$  s), whereas the mathematically calculated half-life, expressed in seconds, was 1218 s.

**Table 4.** Classification of reaction rates based on half-lives [50].

| Half-Life, s                | Time Span for Near-Completion | Rate Classification |
|-----------------------------|-------------------------------|---------------------|
| $10^{-15}\text{--}10^{-12}$ | ps or less                    | ultra fast rate     |
| $10^{-12}\text{--}10^{-6}$  | $\mu\text{s}$ or less         | very fast rate      |
| $10^{-6}\text{--}1$         | seconds                       | fast rate           |
| $1\text{--}10^3$            | minutes or hours              | moderate rate       |
| $10^6\text{--}10^3$         | weeks                         | slow rate           |
| $>10^6$                     | weeks or years                | very slow rate      |

### 3. Comparison with Other AOPs

This study showed that the combined PDS/ $\text{O}_3$ /UV is a promising method for high rhodamine B concentrations (50–100 mg/L). The high concentration of the dye did not make it difficult to obtain over 50% RhB decomposition within 30 min. In this study, also ozone or UV-activated persulfate were also examined but at a concentration of 20 mg/L and similar efficiencies were obtained. As presented in Table 5, combined PDS/ $\text{O}_3$ /UV is an interesting alternative to eliminate RhB in comparison with other studies. As is shown, the PDS/ $\text{O}_3$ /UV process has great potential for the degradation of rhodamine B, particularly where the dye concentrations are high (up to 100 mg/L). Relatively short reaction time (30 min) is benefit of using this method. The reaction time needed to achieve 60% decolorization is two times shorter compared with the research performed by Rakesh et al. [51]. In

turn, in a study by Jinisha et al. [52], it took 180 min to decompose approximately 98% of the RhB. The result obtained was found even better than those reported by Natarajan et al. [53], although the authors investigated the degradation of RhB at a lower concentration (about 50 mg/L).

**Table 5.** The summary of different AOPs applied for RhB degradation.

| AOP                                                                 | Conditions                                                                                                                                                                                                | Removal Efficiency, % | References |
|---------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|------------|
| PDS/O <sub>3</sub> /UV                                              | C <sub>0</sub> [RhB] = 100 mg/L<br>pH = 6.0<br>time = 30 min<br>O <sub>3</sub> flow = 10 mL/min<br>T = 295.0 K<br>Lamp = 10 W<br>H <sub>2</sub> O <sub>2</sub> dose = 40 mg/L<br>PDS dose = 20 mM         | 60.0                  | This study |
| PDS/Vis/US                                                          | C <sub>0</sub> [RhB] = 10 mg/L<br>pH = 6.0<br>time = 60 min<br>T = 295.0 K<br>US = 40 kHz, 60 W<br>PDS dose = 20 mM<br>Lamp = 10 W                                                                        | 85.0                  | [17]       |
| Peroxide assisted photocatalytic degradation in the presence of ZnO | C <sub>0</sub> [RhB] = 5 mg/L<br>time = 90 min<br>Catalyst dose = 500 mg/L<br>lamp (300 W)                                                                                                                | 60.0                  | [51]       |
| Electro-Fenton                                                      | C <sub>0</sub> [RhB] = 10 mg/L<br>pH = 2.0<br>time = 180 min<br>Electrode dose = 15 mg/L<br>Voltage = 8 V                                                                                                 | 97.7                  | [52]       |
| Carbon aerogel/persulfate                                           | C <sub>0</sub> [RhB] = 10 mg/L<br>pH = 7.0<br>time = 60 min<br>Persulfate dose = 1.0 mM<br>Carbon aerogel dose = 100 mg/L                                                                                 | 80.0                  | [53]       |
| UV-LED/TiO <sub>2</sub>                                             | C <sub>0</sub> [RhB] = 49 mg/L<br>time = 180 min<br>pH = 3.05<br>TiO <sub>2</sub> = 1.6 g/L<br>Lamp = LED (5)<br>luminous intensity = 350 mcd<br>radiant flux = 10–12 mW at 20 mA                         | 51.0                  | [54]       |
| O <sub>3</sub> /UV                                                  | C <sub>0</sub> [RhB] = 100 mg/L<br>pH = 3.0<br>time = 15 min<br>ozone flow = 30 mL/min<br>Lamp = 16 W                                                                                                     | 99.8                  | [55]       |
| Ti/SnO <sub>2</sub> -Sb electrode                                   | C <sub>0</sub> [RhB] = 50 mg/L<br>pH = 3.0<br>time = 20 min<br>at a constant current density of 20 mA/cm <sup>2</sup><br>with a 10 mmol/L Na <sub>2</sub> SO <sub>4</sub> supporting electrolyte solution | 97.8                  | [56]       |
| Fe(0)-based Fenton process with H <sub>2</sub> O <sub>2</sub>       | C <sub>0</sub> [RhB] = 49 mg/L<br>Time = 30 min<br>pH = 4.0<br>Fe(0) = 1.0 g/L<br>H <sub>2</sub> O <sub>2</sub> = 2.0 mM                                                                                  | 100.0                 | [57]       |

This proposed process is characterized also by simplicity and low consumption of chemical reagents (excluding  $O_3$  and UV, only PDS is needed). Although not all of the dye was removed, this study was designed to use lower ozone flow (10 mL/min) comparing to 30 mL/min in the study by Cuiping et al. [55]. It can be assumed that the use of higher ozone flow would increase the efficiency of the process. Similar conclusions can be considered when analyzing higher lamp power. Another essential advantage of the combined PDS/ $O_3$ /UV (under the experimental conditions) is the energy-saving power lamp. Although a lower energy lamp (10 W) was used in this study, satisfactory decolorization effects were obtained without the need for a higher wattage lamp (e.g., 16 W in the study by Cuiping et al. [55] or 300 W in the study by Rakesh et al. [51]). Hence, RhB need less energy consumption for degradation.

What distinguishes the use of PDS/ $O_3$ /UV from other solutions presented in the table is the neutral reaction environment (pH = 6.0). It can be seen that most of the experiments shown in the table were performed in the very low pH range (2 to 4). The technology proposed in this article is based on carrying out the reaction at a pH close to neutral (pH = 6.0). Therefore, the costs of a potential pH correction are negligible.

It is worth noting that the PDS/ $O_3$ /UV combination did not use solid catalysts (e.g.,  $TiO_2$ ). Recent literature reports [58–60] identify titanium (Ti) as a contaminant due to the drastic increase in the use of Ti in personal care products (cosmetics, sunscreens), environmental applications (photocatalysts), and drug delivery systems. Sodium persulfate (PDS) is not expected to bioaccumulate (it decomposes into ions ubiquitous in the environment) and will not be absorbed into soil or sediments due to its dissociation and high water solubility [61], whereas ozone and UV radiation are commonly used in water disinfection. In addition, despite the possibility of regeneration of catalysts, such as titanium dioxide (washing with solvents, hydrogen peroxide and thermal treatment), their lifetime is limited, and the problem of their disposal after the process still remains. PDS readily dissolves in water, as mentioned above.

In conclusion, the use of various sources of free radicals (ozone, PDS, UV) can be useful to reduce the costs necessary to remove rhodamine B (60% at the initial concentration of 100 mg/L). As can be deduced from the above discussion, proposed technology is compatible with the principles of green chemistry, including: use of catalysts (PDS), design for degradation (degradation of RhB), waste prevention and less hazardous chemical (no chemical residues, lack of nanomaterials), energy efficiency (e.g., low energy-consumption lamp).

## 4. Materials and Methods

### 4.1. Materials

Aqueous solutions were prepared by dissolving the dye standard at a concentration of 20 mg/L (purity of >97%) in distilled water. This dye concentration (20 mg/L) can be identified in the raw wastewater from the textile industry as reported in Section 1. The dye was obtained from Chempur (Tarnowskie Góry, Poland). The pH of the model solution before and after the addition of the dye solution was pH = 6.0. Any deviations from this value, before and after the addition of any reagents, were corrected with 0.1 mol/L HCl or 0.1 mol/L NaOH from Sigma-Aldrich (Poznań, Poland). The aim of the study was to analyze the oxidation at initial pH = 6.0. The change in pH during the oxidation process was not controlled. The RhB degradation was carried out using persulfate and hydroxyl radicals generated from sodium persulfate ( $Na_2S_2O_8$ ), ozone and hydrogen peroxide. The chemical reagents used during the experiment were obtained from Sigma-Aldrich.

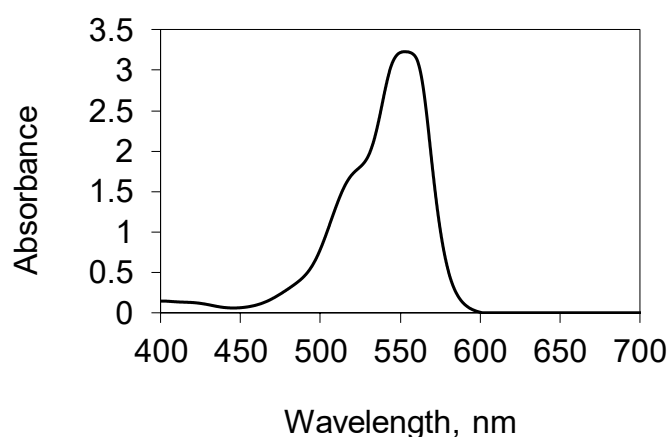
### 4.2. Advanced Oxidation Experiments

The advanced oxidation processes were conducted in glass vessels. The sodium persulfate oxidation (PDS) was assisted by a CUV-510 ultraviolet lamp (Grech, Maao, China) with a power of 10 W (PDS/UV). The dose of sodium persulfate ( $Na_2S_2O_8$ ) was set to 20 mM. Higher doses of sodium persulfate did not cause a significant increase in RhB degradation. The use of lower doses (2–10 mg/L) resulted in the removal efficiency of RhB

ranging from 2–47 times less. A ZY-H103 ozone generator (Eltom, Warsaw, Poland) with a power of 20 W (ozone flow 10 mL/min) was used in the  $O_3$ ,  $O_3$ /UV experiments. The dose of ozone was set to 100 mg/L. The  $O_3$  dose was similar to [62], but it should be noted, that ozone dose may vary depending on the specific application. Ozone was continuously fed to the reactor. In each experiment, the decolorization studies were conducted in glass vessels containing the RhB dye at a concentration of 20 mg/L (model solution). The dose of hydrogen peroxide was set to 40 mg/L ( $H_2O_2$ ,  $H_2O_2$ /UV). The  $H_2O_2$  dosage was similar to a dose range (30–2250 mg/L) tested by [63]. The hydrogen peroxide and PDS were added each time before the start of the experiment. A magnetic stirrer was used to ensure the optimal mixing of the model solutions. Reagents—radical precursors (sodium persulfate, ozone, hydrogen peroxide), were added into the model solutions. The PDS,  $O_3$  and  $H_2O_2$  doses were determined by preliminary studies, in which various AOPs at different catalysts dose, pH, reaction vessel volume, temperature, and different dye concentrations were tested. The decolorization process was conducted continuously for 30 min. Samples for analysis were collected at 5, 10, 15, 20, 25 and 30 min intervals. Experimental conditions, i.e., the temperature ( $T = 298.0$  K), reaction ( $pH = 6.0$ ), atmospheric pressure ( $p = 1013.0$  hPa), reaction vessel volume ( $V = 0.5$  L) and reaction vessel shape (borosilicate glass cylinder beakers), remained unchanged throughout each experiment.

#### 4.3. Instruments and Analytical Methods

At specific time intervals, the analytes were collected and analyzed with V-730 spectrophotometer (Jasco, Kraków, Poland). Figure 4 presents the obtained RhB absorption spectrum. The UV-Vis absorption spectrum was covered a range from approximately 400 to 700 nm. The compound absorption spectrum exhibits a peak at a wavelength  $\lambda_{max} = 554.0$  nm. The solutions were tested at the same wavelength ( $\lambda_{max} = 554.0$  nm). In solutions, in which the absorbance was more than 1, the suitable dilution was made to increase the sensitivity of quantitative analysis.



**Figure 4.** Absorption spectrum of rhodamine B standard (20 mg/L).

#### 4.4. Kinetics Studies

Although studies indicate the use of pseudo-first-order kinetic model (Equation (8)) [64] in order to assess the fit of rhodamine B degradation rate to the appropriate model, in this study the pseudo-second-order model (Equation (9)) was also studied. The integrated dye mass balance in batch reactor are presented in Table 6.

**Table 6.** The equation of kinetics.

| Model               | Plot                                                 | References |
|---------------------|------------------------------------------------------|------------|
| Pseudo-first-order  | $-\ln\left(\frac{C_t}{C_0}\right) \text{ VS } t$ (8) | [65]       |
| Pseudo-second-order | $\frac{1}{C_t/C_0} \text{ VS } t$ (9)                | [66]       |

where:  $C_t$ —concentration at time  $t$  (mg/L);  $C_0$ —initial concentration (mg/L);  $k_1$ —pseudo-first-order rate constant;  $k_2$ —pseudo-second-order rate constant.

## 5. Conclusions

The complexity and relevance of the problem of the presence of colored compounds in wastewater creates the urgent necessity to develop new and effective technologies for their elimination. Therefore, in this study the possibility of utilizing advanced oxidation processes (AOPs) for the degradation of the rhodamine B (RhB) dye was carried out. The advantage of AOPs for wastewater decolorization is the possibility of radical generation in various ways, which allow to select a more suitable method meeting the requirements for the treatment of colored solutions. The use of UV-assisted ozonation proved to be the most effective for RhB decolorization, i.e., at a concentration of 20 mg/L 90% of the dye was removed after 30 min of reaction time. Satisfactory results were also obtained in a combined PDS/O<sub>3</sub>/UV system (nearly 60% RhB removal at a concentration of 100 mg/L after 30 min). The results indicated that combined PDS/O<sub>3</sub>/UV method is promising for dyeing of rhodamine B aqueous solutions at a concentration up to 100 mg/L compared to other advanced oxidation processes.

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