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# Solar Chlorine Activation for Efficient Rhodamine B Removal in Strong Basic pH: Processing Conditions, Radicals Probing, and TiO<sub>2</sub> Nanocatalyst Effect

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Abstract: In recent years, there has been growing interest in the application of UV/chlorine advanced oxidation processes for wastewater treatment. However, few studies have investigated this process in a strongly basic medium (pH > 10), which is a common characteristic of many industrial effluents. In addition, the use of artificial UV lamps in these processes can be costly. To address these challenges, we investigated the use of solar light (referred to as Solar-L) in the Solar-L/chlorine process for the degradation of Rhodamine B (RhB) in a strongly basic medium (pH 11). We found that separate solar light or chlorination showed no degradation after half an hour, but the Solar-L/chlorine process effectively degraded RhB, with complete removal achieved in only 30 min, using 1000  $\mu$ M ClO<sup>-</sup>. The process also resulted in a significant reduction of TOC, i.e., 60% after 120 min and 80% after 240 min. Our results indicate that both •OH/O•- and reactive chlorine species (RCS) were involved in the degradation process, while O<sub>3</sub> played no role. The process performance improved with the decreasing initial contaminant concentration and increasing temperature (up to 55  $^{\circ}$ C). The addition of a TiO<sub>2</sub> nanocatalyst to the Solar-L/chlorine system significantly improved the RhB degradation efficiency by more than 30%. It was found that neither adsorption (on  $TiO_2$ ) nor Solar-L/TiO<sub>2</sub> photolysis contributed to the dye removal by the Solar-L/chlorine/TiO<sub>2</sub> system. Instead, the improvement associated with the Solar-L/chlorine/TiO<sub>2</sub> system was related to the involvement of hypochlorite in the photocatalytic reaction at the catalyst surface. A detailed discussion of the effect of  $TiO_2$ was carried out based on the physicochemical properties of RhB and TiO<sub>2</sub> catalyst with respect to the solution's pH. In conclusion, this study highlights the potential of solar light as a sustainable and efficient technology for the treatment of polluted water in strong basic media in the presence of chlorine and chlorine/TiO<sub>2</sub> as additives. These valuable findings provide a basis for the future research and development of this promising technology for water treatment applications.

**Keywords:** solar light; chlorine activation; strong basic pH; TiO<sub>2</sub>/chlorine photocatalysis; rhodamine B; degradation

## 1. Introduction

Water utilities face the challenge of treating drinking water sources contaminated with organic pollutants, such as pharmaceuticals, insecticides, and textile dyes, that are released into the environment from a variety of sources, including industrial manufacturing, agricultural runoff, and municipal wastewater [1–4]. Unfortunately, conventional water treatment methods are ineffective at removing these contaminants [5]. While UV irradiation alone may not completely remove these micropollutants, combining UV with oxidants such as  $H_2O_2$ ,  $S_2O_8^{2-}$ ,  $IO_4^{-}$ , and chlorine (HOC1/CIO<sup>-</sup>) can produce highly reactive radicals (e.g., •OH, SO4<sup>•-</sup>, iodine, and reactive chlorine species) that enhance the removal efficiency



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of these micropollutants [6–9]. For effective water treatment, UV-assisted processes such as  $UV/H_2O_2$ ,  $UV/S_2O_8^{2-}$ , and UV/chlorine are used. Although  $H_2O_2$  and persulfate-based AOPs can only utilize light in the UV-C interval due to their limited molar absorptivity, chlorine photolysis can be used for solar treatment because it absorbs light at longer wavelengths [10,11]. Additionally, chlorine photolysis uses a common disinfectant that is less expensive and easier to transport than hydrogen peroxide and persulfate [12]. In contrast to the UV/H<sub>2</sub>O<sub>2</sub> and UV/persulfate processes, the UV/chlorine system does not necessitate a residual chlorine quenching step to remove the rest of the chlorine [5]. The disinfection and oxidation mechanism of the UV/chlorine AOP treatment process is also enhanced in the presence of chloramines, which are formed from ammonia, a common contaminant in wastewater.

The chemistry of chlorine photolysis is complex due to the pH- and wavelengthdependent photolysis of chlorine and the subsequent pathways for oxidant production [13]. The pKa of HOCI/OCI<sup>-</sup> is 7.5, and HOCI dominates at pH 3–5, while OCI<sup>-</sup> dominates at pH > 9 [13]. HOCI absorbs maximally at 220 nm, while OCI<sup>-</sup> absorbs at about 290 nm [13]. The photolysis of chlorine can produce a group of highly reactive oxidants, including •OH and chlorine-reactive species (RCS: CIO•, CI•, and Cl<sub>2</sub>•<sup>-</sup>), which are capable of degrading organic water contaminants [11]. For example, the photolysis of HCIO can primarily produce •OH and Cl• radicals via HOCl + hv  $\rightarrow$  •OH + Cl• [14]. •OH and RCS are expected to be the main oxidants that play a significant role in the UV/chlorine system, especially at natural water pHs (pH 6–9) [11]. These radicals react with organic compounds at rates of about 10<sup>2</sup>–10<sup>6</sup> M<sup>-1</sup>s<sup>-1</sup> for Cl<sub>2</sub>•<sup>-</sup>, about 10<sup>7</sup>–10<sup>9</sup> M<sup>-1</sup>s<sup>-1</sup> for ClO•, and 10<sup>8</sup>–10<sup>11</sup> M<sup>-1</sup>s<sup>-1</sup> for •OH and Cl• [11,13]. The photolysis of chlorine is therefore a promising approach for the degradation of organic water contaminants, although its complex chemistry requires careful consideration to optimize its use in water treatment applications.

Although the UV/chlorine process has demonstrated its efficiency for the degradation of refractory organic pollutants in acidic to slightly basic media ( $3 \le pH \le 10$ ), its efficiency in strongly basic media has rarely been addressed. The first flash photolysis experiments by Buxton and Subhani [14] showed that the hypochlorite ion (ClO<sup>-</sup>) produces chloride ion,  $^{\circ}OH/O^{\bullet-}$ , Cl<sup>-</sup>, and O( $^{3}P$ ) as its primary photoproducts at 253.7, 313, and 365 nm when the medium is basic. While O( $^{1}D$ ) was produced at 253.7 nm and 313 nm, it was not observed at 365 nm [14]. Once formed, primary photoproducts of ClO<sup>-</sup> begin to degrade into unstable, transient species such as ClO<sup>•</sup>, Cl<sub>2</sub><sup>•-</sup>, Cl<sub>2</sub>O, and Cl<sub>2</sub>O<sub>2</sub>, as well as stable by-products such as O<sub>2</sub>, Cl<sup>-</sup>, ClO<sub>2</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, and ClO<sub>4</sub><sup>-</sup>, with secondary oxidants such as O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and ClO<sub>2</sub> also being formed. Buxton and Subhani [14] proposed a series of reactions to explain how Cl<sup>-</sup>, O<sub>2</sub>, ClO<sub>2</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, and O<sub>3</sub> are produced by the photolysis of ClO<sup>-</sup> (Reactions 1–24). The reactive species generated as primary photoproducts of ClO<sup>-</sup> initiate the chain reaction. The hypochlorite ion is oxidized by  $^{\circ}OH/O^{\bullet-}$  and Cl<sup>•</sup> to form ClO<sup>•</sup> (Reactions 4–6), which rapidly dimerizes to form Cl<sub>2</sub>O<sub>2</sub> (Reaction 7).

Considering that the majority of AOPs are inefficient in strong basic media [15], we would like to investigate the viability of the UV/chlorine process under these conditions. In fact, several industrial processes generate strong alkaline effluents that require specific neutralization treatment prior to oxidation [16]. Furthermore, the use of solar light (Solar-L) as an energy source for the UV/chlorine process offers several advantages over traditional artificial light sources. Solar light is abundant and renewable, and its use can significantly reduce operating costs and environmental impact. Therefore, investigating the effectiveness of the UV/chlorine process under solar irradiation in strong alkaline media can have important implications for the development of sustainable and cost-effective wastewater treatment technologies.

$$ClO^{-} + hv \to O(^{3}P) + Cl^{-}$$
(1)

$$\mathrm{ClO}^- + hv \to \mathrm{O}^{\bullet-} + \mathrm{Cl}^{\bullet} \tag{2}$$

$$ClO^{-} + hv \rightarrow Cl^{-} + O(^{1}D)$$
(3)

$$OCl^{-} + {}^{\bullet}OH \to ClO^{\bullet} + OH^{-}$$
(4)

$$OCl^- + O^{\bullet-} \to ClO^{\bullet} + O^{2-}$$
(5)

$$+ \operatorname{OCl}^{-} \to \operatorname{Cl}^{-} + \operatorname{ClO}^{\bullet} \tag{6}$$

 $2 \operatorname{ClO}^{\bullet} \rightleftharpoons \operatorname{Cl}_2 \operatorname{O}_2 \tag{7}$ 

$$Cl_2O_2 + H_2O \to ClO_2^- + ClO^- + 2H^+$$
 (8)

Cl•

$$Cl_2O_2 + H_2O \rightarrow Cl^- + O_2 + ClO^- + 2H^+$$
 (9)

$$Cl_2O_2 + ClO_2^- \rightarrow ClO_3^- + Cl_2O \tag{10}$$

$$Cl_2O + H_2O \rightleftharpoons 2 HOCl$$
 (11)

$$^{\bullet}\text{OH} + \text{ClO}_2^{-} \rightarrow \text{ClO}_2 + \text{HO}^{-}$$
(12)

$$O^{\bullet-} + ClO_2^- \to ClO_2 + O_2^- \tag{13}$$

$$^{\bullet}\text{OH} + \text{ClO}_3^{-} \rightarrow \text{Products}$$
(14)

$$O^{\bullet-} + ClO_3^- \to Products$$
 (15)

$$O(1D) + H_2O \to H_2O_2 \tag{16}$$

$$ClO^{-} + H_2O_2 \rightarrow O_2 + Cl^{-} + H_2O$$
 (17)

$$O(^{3}P) + ClO^{-} \rightarrow ClO_{2}^{-}$$
(18)

$$O(^{3}P) + ClO^{-} \rightarrow Cl^{-} + O_{2}$$
<sup>(19)</sup>

$$O(^{3}P) + ClO_{2}^{-} \rightarrow ClO_{3}^{-}$$
<sup>(20)</sup>

$$O(^{3}P) + ClO_{2}^{-} \rightarrow Cl^{-} + O_{2} + O(^{3}P)$$
 (21)

$$O(^{3}P) + O_{2} \rightarrow O_{3} \tag{22}$$

$$O^{\bullet-} + O_2 \rightleftharpoons O_3^{\bullet-} \tag{23}$$

$$ClO^{\bullet} + O_3^{\bullet-} \to O_3 + ClO^-$$
(24)

Rhodamine B (RhB), a basic dye, is a fluorescent organic compound that is used for many applications, including biological stains, pH indicators, and tracers [17]. It has also been used as a colorant in the textile and food industries. However, RhB poses a significant environmental threat due to its toxicity and persistence in water [18,19], as well as causing phototoxic and photoallergic reactions. It has been experimentally shown to be carcinogenic, a reproductive and developmental toxicant, a neurotoxicant, and a chronic toxicant to both humans and animals [1]. Consequently, several studies have focused on the removal of RhB from wastewater and environmental matrices [20–24]. However, there was no previous study on applying UV/chlorine to degrade this effective water pollutant, especially with using solar light.

The main objective of this work was to investigate the effectiveness of the Solar-L/chlorine process for the degradation and mineralization of Rhodamine B (RhB) under strong alkaline conditions. The experimental conditions and radical scavenger assays were investigated to determine the primary reactive species involved in the degradation process (Solar-L/chlorine at strong basic pH). In addition, the performance of the process was evaluated by introducing a TiO<sub>2</sub> photocatalyst to determine the potential enhancement of pollutant degradation by combining Solar-L/chlorine photolysis and TiO<sub>2</sub> photocatalysis under strong basic conditions.

#### 2. Results and Discussion

#### 2.1. Solar-Light/Chlorine Process Efficiency in Basic Medium

The degradation of RhB at pH 11 was studied using solar irradiation alone, chlorine alone (as hypochlorite ions), and a combination of solar irradiation and chlorine. The

degradation kinetics were followed as a function of time for 30 min. The results are shown in Figure 1a-c. No degradation occurred with solar light and chlorine (different doses) separately, but complete removal was achieved by combining the two systems (with 1000 µM chlorine) in 30 min, with an exponential decay of the dye concentration over time, reflecting a pseudo-first-order kinetic law (C/C<sub>0</sub> =  $e^{-kt}$ ). The  $t_{1/2}$  for the combined system was 4 min and 13 min for 500 and 1000 µM chlorine, respectively, with pseudo-first-order rate constants of k = 0.077 and 0.174 min<sup>-1</sup>, respectively. However, the combined system was insignificant at low doses of chlorine (below 300 µM), where maximum RhB removal of less than 20% was achieved. This suggests that the system depends on a threshold concentration of chlorine to achieve the efficient degradation of RhB. The beneficial effect of the combined solar light/chlorine system was certainly attributed to the formation of reactive species (hydroxyl and RCS) upon chlorine photolysis by the UV portion of the solar spectrum. The Suntest modulator used in this study generates UV radiation with wavelengths between 290 and 400 nm (UVB and UVA part of the solar spectrum), which represents about 7% of the global solar spectrum. Overall, these results demonstrate the potential of the solar UV/chlorine process for the degradation of RhB (and similar



persistent textile dyes) in a strong alkaline medium.

**Figure 1.** RhB degradation upon (a) solar light irradiation (Solar-L), (b) chlorine, and (c) Solar-L/chlorine systems ( $C_0 = 10 \mu$ M, pH 11, and temp.  $25 \pm 2 \degree$ C).

The degradation of RhB was confirmed by analyzing the UV-Vis spectra and TOC reduction during the treatment of RhB (5 mg/L) at pH 11. The changes in UV-Vis spectra and TOC removal results are shown in Figure 2a (60 min treatment) and Figure 2b (250 min treatment), respectively. The initial RhB spectrum (t = 0) showed two bands with maxima at 550 and 290 nm. During treatment, the 550 nm band disappeared after 30 min, while the absorbance at 290 nm decreased from 0.6 to 0.164 (72% decrease) and continued to decrease to 0.084 for more than 45 min. From Figure 2b, the TOC decreased by 6% at 15 min, 16% at 30 min, 43% at 60 min, 60% at 120 min, 73% at 180 min, and 80% at

240 min. The disappearance of the 550 nm band is attributed to the degradation of the chromophoric group. The 290 nm band is associated with the aromatic or naphthenic group, and its disappearance is explained by the formation of intermediates that can absorb at this wavelength or by the formation of smaller molecules that do not have this chromophore. The decay of the 290 nm band was slower than that of the 550 nm band due to the preference of  $^{\circ}OH/O^{\circ-}$  and RCS to react primarily with the chromophoric group rather than with the aromatic rings of the dye. However, the decay of the 290 nm band strongly indicates RhB degradation (destruction), not just decolorization, and provides evidence of mineralization, which is confirmed by the TOC results in Figure 2b. However, the removal of TOC took a longer time because it is related not only to the degradation of the dye molecules but also to the degradation by-products existing along with the dye present in the solution (degradation by-products).



**Figure 2.** Change in (**a**) RhB's UV-Vis spectra and (**b**) TOC abatement during the treatment with the Solar-L/chlorine process ( $C_0 = 10 \mu$ M, pH 11, and temp. 25 ± 2 °C).

## 2.2. Probing the Reactive Species Involved in RhB Degradation by Solar-L/Chlorine Process

As described in Section 2, when aqueous hypochlorite is exposed to irradiation with wavelengths between 300 and 400 nm at a basic pH, this leads to the formation of reactive species such as  ${}^{\bullet}OH/O{}^{\bullet-}$ , RCS (Cl ${}^{\bullet}$ , Cl $O{}^{\bullet}$ , Cl $2{}^{\bullet-}$ ), and O<sub>3</sub> by photolysis. These species play a critical role in the degradation of water contaminants by the UV/chlorine process [11,13]. To determine the specific roles of these radicals, radical scavengers such as ascorbic acid, benzoic acid (BA), tert-butanol (TBA), and  $N_2$  saturation were used.  $N_2$  saturation was used to remove dissolved O<sub>2</sub>, which is responsible for O<sub>3</sub> production via Reactions 22–24. Thus, N<sub>2</sub> saturation provides information on the role of ozone in the overall degradation rate of the dye. Ascorbic acid is well-known as a common reductant (scavenger) of all oxidants [25,26]. It was used to confirm the free radical pathway in the degradation of RhB. TBA, on the other hand, can scavenge  ${}^{\bullet}OH/O^{\bullet-}$  (k = 6.0 × 10<sup>8</sup>/5.0 × 10<sup>8</sup> M<sup>-1</sup>s<sup>-1</sup>), Cl<sup>•</sup>  $(k = 3.0 \times 10^8 \text{ M}^{-1} \text{s}^{-1})$ , and ClO<sup>•</sup>  $(k = 1.3 \times 10^7 \text{ M}^{-1} \text{s}^{-1})$ , with a negligible effect on Cl<sub>2</sub><sup>•-</sup>  $(k = 7 \times 10^2 \text{ M}^{-1} \text{s}^{-1})$  and  $O_3$  (k  $\leq 3 \times 10^{-3} \text{ M}^{-1} \text{s}^{-1}$ ), providing insight into the plausible role of  $\text{Cl}_2^{\bullet-}$  [27]. BA is capable of scavenging  $^{\bullet}\text{OH/O}^{\bullet-}$  (k~1.8 × 10<sup>9</sup> M<sup>-1</sup>s<sup>-1</sup>) and Cl<sup>•</sup> (k =  $3.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ ), but it has a negligible effect on ClO<sup>•</sup> [k = (0.2–1.8) × 10<sup>8</sup>  $M^{-1}s^{-1}$ ] and  $Cl_2^{\bullet-}$  (k < 3.0 × 10<sup>6</sup>  $M^{-1}s^{-1}$ ), allowing determination of the contribution of  ${ClO}^{+} + {Cl}_{2}^{-}$  [27]. Finally, the contributions were calculated by comparing the pseudofirst-order degradation constants  $(min^{-1})$  in the absence and presence of scavengers. These constants are calculated as follows:

$$k_{\rm Cl2}^{\bullet-} = k_{\rm TBA} \tag{25}$$

$$k_{\rm O3} = k_{\rm contol} - k_{\rm N2} \tag{26}$$

$$k_{(\text{ClO}\bullet+\text{Cl2}\bullet-)} = k_{\text{BA}} \tag{27}$$

$$k_{(\bullet OH/O}^{\bullet -} + Cl_{\bullet}) = k_{contol} - k_{BA} - k_{O3}$$
<sup>(28)</sup>

where  $k_{\text{Cl2}}^{\bullet-}$ ,  $k_{O3}$ ,  $k_{(\text{ClO}+\text{Cl2}\bullet-)}$ , and  $k_{(\bullet\text{OH}/O}^{\bullet-} + \text{Cl}\bullet)$  are the specific degradation rate constants (min<sup>-1</sup>) of RhB with Cl<sub>2</sub><sup>\bullet-</sup>, O<sub>3</sub>, {ClO<sup>\bullet</sup> + Cl<sub>2</sub><sup>\bullet-</sup>}, and { $^{\bullet}\text{OH}/O^{\bullet-} + \text{Cl}^{\bullet}$ }, respectively;  $k_{\text{BA}}$ ,  $k_{\text{TBA}}$ , and  $k_{\text{N2}}$  are the degradation rate constants calculated in the presence of BA, TBA, and N<sub>2</sub> purging. The radicals' contributions are calculated as follows:

$$Cl_2^{\bullet-}$$
 contribution (%) =  $100 \times k_{Cl2}^{\bullet}/k_{contol}$  (29)

$$O_3 \text{ contribution } (\%) = 100 \times k_{O3}/k_{\text{contol}}$$
 (30)

$$ClO^{\bullet} \text{ contribution } (\%) = 100 \times [k_{(ClO_{\bullet+} Cl2_{\bullet-})} - k_{Cl2}^{\bullet-}]/k_{contol}$$
(31)

$$\{{}^{\bullet}\text{OH/O}{}^{\bullet-} + \text{Cl}{}^{\bullet}\} \text{ contribution } (\%) = 100 \times k_{(\bullet\text{OH/O}}{}^{\bullet-} + \text{Cl}{}^{\bullet})/k_{\text{contol}}$$
(32)

The photodegradation of RhB using the Solar-L/chlorine process was studied in the presence and absence of ascorbic acid, BA, and TBA, with 1000  $\mu$ M chlorine and fixed concentrations of 1 mM for ascorbic acid and BA and 100 mM for TBA. These scavenger concentrations were in high excess compared to the 10  $\mu$ M RhB used. The results, which are shown in Figure 3, indicate that the scavengers significantly reduced the rate of dye removal, with complete quenching observed with ascorbic acid, confirming the radical pathway for RhB. The quenching rate increased from BA to TBA, but degradation was not affected by N<sub>2</sub> saturation. BA reduced RhB degradation to a lesser extent than TBA. The calculated pseudo-first-order rate constants were  $k_{contol} = 0.0174 \text{ min}^{-1}$ ,  $k_{N2} = 0.173 \text{ min}^{-1}$ ,  $k_{BA} = 0.045 \text{ min}^{-1}$ , and  $k_{TBA} = 0.009 \text{ min}^{-1}$ . These values suggest an insignificant role for O<sub>3</sub>, a 5% contribution for Cl<sub>2</sub><sup>•-</sup>, 20.7% for ClO<sup>•</sup>, and a 74.3% contribution for  $^{\bullet}\text{OH}/\text{O}^{\bullet-}$  and Cl<sup>•</sup> together. Therefore, both hydroxyl and reactive chlorine radicals are involved in the efficient degradation process of RhB using Solar-L photoactivated hypochlorite.



**Figure 3.** Scavenger tests using BA, TBA, ascorbic acid, and N<sub>2</sub>-saturation during the degradation of RhB by the system Solar-L/chlorine at pH 11 (conditions:  $C_0 = 10 \ \mu\text{M}$ , [TBA]<sub>0</sub> = 100  $\mu\text{M}$ , [Asc.A]<sub>0</sub> = [BA] = 1 mM, N<sub>2</sub> saturation 10 min before the run up to run completion (30 min), temp. 25 °C).

#### 2.3. Process Efficiency with Variation of Initial Dye Concentration

The effect of the initial RhB concentration on the efficiency of the combined Solar-L/chlorine process at pH 11 was investigated. The initial RhB concentration ranged from 2 to 25  $\mu$ M, while the chlorine concentration was kept constant at 1000  $\mu$ M. The

degradation kinetics and the initial degradation rate vs. initial RhB concentration were plotted in Figure 4a,b, respectively. The results showed that the degradation kinetics of RhB decreased with the increasing initial RhB concentration (Figure 4a). The degradation rate constant (*k*) decreased from 0.309 min<sup>-1</sup> at 5  $\mu$ M to 0.174 min<sup>-1</sup> at 10  $\mu$ M, 0.072 min<sup>-1</sup> at 15  $\mu$ M, 0.043 min<sup>-1</sup> at 20  $\mu$ M, and 0.033 min<sup>-1</sup> at 25  $\mu$ M. The t<sub>1/2</sub> also decreased from 21 min at 25  $\mu$ M to 16, 8, 5, and 2 min at 20, 15, 10, and 5  $\mu$ M, respectively. However, the initial RhB degradation rate versus initial RhB concentration (Figure 4b) increased from 0.4  $\mu$ M/min at 2  $\mu$ M to 0.79  $\mu$ M/min at 5  $\mu$ M and reached a plateau of 1  $\mu$ M/min at 10, 15, 20, and 25  $\mu$ M RhB. These observations indicate that the combined Solar-L/chlorine process is more effective at lower initial concentrations of RhB and can efficiently degrade RhB at concentrations as low as 2  $\mu$ M.



**Figure 4.** Initial RhB concentration effect on its degradation: (**a**) removal kinetics and (**b**) initial rate of degradation,  $r_0$  ( $C_0 = 5-25 \mu$ M, pH 11, and temp.  $25 \pm 2 \degree$ C).

The decrease in the degradation rate constant with the increasing initial RhB concentration (Figure 4a) indicates that the system follows pseudo-first-order kinetics. According to this kinetic model, the reaction rate is proportional to the concentration of the dye. Therefore, as the initial concentration of dye increases, the number of active sites available for the reaction becomes limited, resulting in a decrease in the reaction rate. In addition, as the initial concentration of RhB increases, the dye molecules become more concentrated in the reaction mixture, resulting in a filter effect. This effect occurs when the dye molecules block incident solar radiation from reaching the hypochlorite ions, thereby reducing the rate of hypochlorite ion photolysis and consequently the production of reactive species. Furthermore, competition between dye molecules and their degradation intermediates for available radicals may also contribute to the observed effect. At higher concentrations of RhB, a greater number of intermediates are formed, increasing the competition for reaction with radicals.

The increase in the initial RhB degradation rate with the increasing initial RhB concentration is the second effect of the initial RhB concentration (Figure 4b). This effect is due to the higher concentration of RhB molecules available for a reaction with the generated radicals in the combined system. At low RhB concentrations, there are fewer RhB molecules available for a reaction, resulting in a slower degradation rate. However, as the RhB concentration increases, more RhB molecules are available for a reaction, resulting in a faster degradation rate. The plateau observed in Figure 4b suggests that the reaction has reached its maximum rate, and further increases in RhB concentration do not result in a further increase in degradation rate. Similar trends have been reported for several contaminants degraded by different AOPs, such as sonolysis, UV/persulfate, UV/periodate, UV/chlorine, and others [8,18,28–32].

It is important to note that the first effect (decrease in rate constant with increasing initial RhB concentration) and the second effect (increase in initial RhB degradation rate with increasing initial RhB concentration) are not contradictory. The first effect is a result of

limited active sites for the reaction and a filter effect due to the higher concentration of dye molecules, whereas the second effect is due to the higher concentration of RhB molecules available for reaction with generated radicals. Together, these effects contribute to the overall degradation kinetics observed in the system. Both scenarios, with respect to the initial contaminant concentration, have been reported for several AOPs [8,18,25,28–34].

## 2.4. Process Efficiency Dependence of Liquid Temperature

The effect of liquid temperature on the Solar-L/chlorine degradation of RhB (10  $\mu$ M) was investigated at temperatures of 25, 35, 45, and 55 °C, using chlorine at 1000  $\mu$ M. The degradation results are shown in Figure 5a, while the effect of the same temperature values on dye chlorination (without light) is shown in Figure 5b. The results of Figure 5a showed that the degradation rate increased with increasing temperature. Comparing the degradation rate constants at different temperatures with that at 25 °C, we find that the increase in the degradation rate constant is quite significant, especially between 45 and 55 °C. The degradation rate constant increased from 0.174 min<sup>-1</sup> at 25 °C to 0.184 min<sup>-1</sup> at 35 °C (5.7% increase), 0.218 min<sup>-1</sup> at 45 °C (25.3% increase), and 0.33 min<sup>-1</sup> at 55 °C (89.6% increase). The effect of the beneficial temperature was more pronounced at the beginning of the treatment. In addition,  $t_{1/2}$  decreased significantly with the increasing temperature. Moreover, the  $t_{1/2}$  value decreased from 5 min at 25 °C to 3, 1.8, and 1.2 min at 35, 45, and 55 °C, respectively. These results highlight the significant effect of solution heating on the Solar-L/chlorine treatment of RhB. It should be noted that the contribution of direct chlorination to the high temperature effect is marginal up to 45 °C, as no effect of chlorine alone on RhB removal was observed (Figure 5b). However, at 55 °C, direct chlorination may help to accelerate RhB removal in the combined system, as the chlorination process of micropollutants can be enhanced at higher temperatures. In our case, approximately 35% of the Rhodamine B was removed after the chlorination treatment (Figure 5b).



**Figure 5.** Temperature effect on RhB degradation by (**a**) Solar-L/chlorine and (**b**) chlorine processes ( $C_0 = 10 \mu$ M, pH 11, and temp. 25–55 °C).

The effect of liquid temperature is relatively complex. On the one hand, the quantum yield of chlorine photolysis can be affected by temperature changes, although it is primarily pH rather than temperature dependent. At a basic pH, chlorine photolysis occurs primarily by direct photolysis, which involves the dissociation of hypochlorous acid into hypochlorite and hydroxyl and chlorine radicals. The quantum yield of this process is known to be high, typically in the range of 0.3–0.7 at pH values above 8 [11]. However, Bendjama et al. [35] reported that the intensity of the absorbed UV254 nm light in aqueous solution increased with the increasing liquid temperature, providing evidence that chlorine photolysis (even

using Suntest UV-A and B) in basic media can be increased with liquid temperature. Overall, our results show that liquid temperature plays a significant role in accelerating the degradation of RhB by combining Solar-L photolysis and chlorine in a strong basic medium.

## 2.5. Effect of TiO<sub>2</sub> Nanocatalyst

The effect of adding  $TiO_2$  nanocatalyst (average particle size: 30 nm) to the reacting system (Solar-L/chlorine/RhB) was evaluated at pH 11 and ambient temperature (25 °C). The resulting Solar-L/TiO<sub>2</sub>/chlorine system is a combination of several single and binary systems, including Solar-L/TiO<sub>2</sub>, Solar-L/chlorine, TiO<sub>2</sub>/chlorine, and TiO<sub>2</sub> alone. Therefore, in order to demonstrate the net effect of chlorine on the photolytic process  $(Solar-L/TiO_2)$ , a comparison of the different systems in terms of RhB removal is necessary, as shown in Figure 6. Based on the results presented in Figure 6, it can be concluded that neither TiO<sub>2</sub> alone nor TiO<sub>2</sub>/chlorine can effectively degrade RhB, indicating that RhB adsorption on  $TiO_2$  is insignificant. This can be attributed to the repulsive electrostatic forces between RhB molecules and the  $TiO_2$  surface at a basic pH of 11. The point of zero charge (pzc) of the TiO<sub>2</sub> used in this study (Degussa P25) is at pH 6.8 [36], which means that the TiO<sub>2</sub> surface is positively charged in acidic media (pH < pzc) and negatively charged in alkaline conditions (pH > pzc). RhB exists in two forms, cationic (RhB+) and zwitterionic  $(RhB\pm)$ , as shown in Figure 7. At pH values higher than the pKa of RhB, i.e., 3.70 [18], the zwitterionic form dominates, especially at a strongly basic pH (pH 11). Therefore, both TiO<sub>2</sub> and RhB were predominantly negatively charged, which can explain the repulsive force between them.



**Figure 6.** Comparison of different photolytic and photocatalytic processes on the degradation of RhB ( $C_0 = 10 \mu$ M, pH 11, and temp. 25–55 °C).

On the other hand, similar to the first results, photolysis with  $100 \text{ mg/L TiO}_2$  has no significant effect on the degradation of RhB. This is probably due to the fact that the dye molecules are far away from the catalyst surface (repulsive forces), where oxidizing radicals are generated from the excitation of the catalyst surface. It was confirmed in [34] that solar light can effectively generate photocatalytic activity on the TiO<sub>2</sub> surface. However, the effectiveness of this activity depends on various parameters, such as the pH of the solution (a major influencing factor), the initial dye concentration, the amount of catalyst used, etc.

In the case of 100 mg/L TiO<sub>2</sub>, the absence of RhB degradation in the solar photocatalytic process can be attributed to the fact that RhB molecules are positioned at a certain distance from the catalyst surface (due to repulsive forces), where radicals are formed following the formation of electrons ( $e^-_{CB}$ ) and holes ( $h^+$ ) during the photo-excitation ( $\lambda < 400$  nm) of the TiO<sub>2</sub> semiconductor (Reactions 33–42).



Figure 7. Rhodamine B forms in water [18].

$$\mathrm{TiO}_{2} + hv \to h^{+}_{\mathrm{VB}} + e^{-}_{\mathrm{CB}}$$
(33)

$$OH^-_{ads} + h^+_{VB} \rightarrow {}^{\bullet}OH_{ads}$$
 (34)

$$H_2O_{ads} + h^+_{VB} \to {}^{\bullet}OH_{ads} + H^+$$
(35)

$$O_2 + e^-{}_{CB} \to O_2^{\bullet^-} \tag{36}$$

$$O_2^{\bullet-} + H^+ \to HO_2^{\bullet} \tag{37}$$

$$\mathrm{HO_2}^{\bullet} + \mathrm{HO_2}^{\bullet} \to \mathrm{H_2O_2} \tag{38}$$

$$O_2^{\bullet-} + HO_2^{\bullet} \to HO_2^- + O_2 \tag{39}$$

$$\mathrm{HO}_2^- + \mathrm{H}^+ \to \mathrm{H}_2\mathrm{O}_2 \tag{40}$$

$$H_2O_2 + e^-_{CB} \to {}^{\bullet}OH + OH^-$$
(41)

$$H_2O_2 + O_2^{\bullet-} \rightarrow {}^{\bullet}OH + OH^- + O_2$$

$$\tag{42}$$

Note that, in the above reaction scheme, Equations (34) and (35) were proposed as the main pathway for photogeneration of  $^{\bullet}$ OH radicals on the TiO<sub>2</sub> surface [37].

Alternatively, as previously demonstrated (Figure 1a), solar light irradiation alone is insignificant for the removal of RhB. However, when coupled with hypochlorite, it becomes effective (Figure 1c); the dye was removed in 30 min with a pseudo-first-order reaction rate of 0.174 min<sup>-1</sup>. The reason for this trend is well explained in Sections 2.1 and 2.2. The addition of TiO<sub>2</sub> to the solar L/C system increased the RhB degradation rate, with the ratio of the initial degradation rate ( $r_0$ , in  $\mu$ M/min) with and without TiO<sub>2</sub> being 2.0/1.35  $\approx$  1.48. The degradation rate constant (k) in the presence of TiO<sub>2</sub> is 0.23 min<sup>-1</sup> compared to 0.174 min<sup>-1</sup> without TiO<sub>2</sub>. The ratio of k is 0.23/0.174  $\approx$  1.321. This means that the addition of TiO<sub>2</sub> improved the initial dye removal rate ( $r_0$ ) by 48% and the degradation rate constant (k) by 32%.

The beneficial effect of the solar-L/ClO<sup>-</sup>/TiO<sub>2</sub> ternary system could be attributed to the involvement of hypochlorite in the photochemical reactions taking place at the catalyst surface (Reactions 33–42). In fact, ClO<sup>•</sup> can reach the catalyst surface even in the presence of repulsive forces between the catalyst surface (negative at pH 11) and hypochlorite anions due to the too-high dosage of aqueous ClO<sup>•</sup> (1000  $\mu$ M). At the catalyst surface, ClO<sup>•</sup> can react with e<sup>-</sup> and •OH according to Reactions 43–44. A number of other subsequent reactions may result, leading to the formation of other reactive species such as Cl<sup>•</sup>, Cl<sub>2</sub> and Cl<sub>2</sub><sup>•-</sup>, as well as chlorinated products such as Cl<sub>2</sub>O<sub>2</sub> (Reactions 43–53). It should be noted that these chlorine species, especially Cl<sup>•</sup>, ClO<sup>•</sup>, Cl<sub>2</sub>, and Cl<sub>2</sub><sup>•-</sup>, can generate many secondary reactions at the TiO<sub>2</sub> surface, but what we are interested in is the reactivity of

these reactive species with our substrate (RhB) under the operating conditions of a strongly basic medium (pH 11).

C1-

C1 .

$$\mathrm{ClO}^{-} + e^{-}(\mathrm{TiO}_{2}) \to \mathrm{O}^{\bullet-} + \mathrm{Cl}^{-}$$

$$\tag{43}$$

$$^{\bullet}OH_{ad} + ClO^{-} \rightarrow ClO^{\bullet} + OH^{-}$$
(44)

$$\mathrm{Cl}^- + h^+(\mathrm{TiO}_2) \to \mathrm{Cl}^{\bullet}$$
 (45)

$$Cl^{\bullet} + H_2O \rightarrow HClO^{\bullet-} + H^+$$
 (46)

$$\mathrm{Cl}^{\bullet} + \mathrm{OH}^{-} \to \mathrm{ClO}^{\bullet} + \mathrm{O}^{\bullet^{-}}$$

$$\tag{47}$$

$$HClO^{\bullet-} \rightleftharpoons {}^{\bullet}OH + Cl^{-}$$
(48)

$$CI + CIO \rightarrow CIO + CI \tag{49}$$

$$\operatorname{Cl}^{\bullet} + \operatorname{Cl}^{-} \rightleftharpoons \operatorname{Cl}_{2}^{\bullet^{-}}$$
 (50)

$$\operatorname{Cl}^{\bullet} + \operatorname{Cl}^{\bullet} \rightleftharpoons \operatorname{Cl}_{2}$$
 (51)

$$2\operatorname{Cl}_2^{\bullet-} \to \operatorname{Cl}_2 + 2\operatorname{Cl}^- \tag{52}$$

$$ClO^{\bullet} + ClO^{\bullet} \to Cl_2O_2 \tag{53}$$

The ultrafast recombination of electron/hole pairs ( $h^+_{VB} + e^-_{CB} \rightarrow hv$ , 1 ps [38]) is a major drawback in the application of TiO<sub>2</sub>-based photocatalysis in water treatment. This is because the recombination process limits the availability of radicals that can react with RhB molecules. However, hypochlorite (ClO<sup>-</sup>) can be used as an efficient electron acceptor to prevent the  $e^{-}/h^{+}$  recombination, as shown in Equation (43), and increase the concentration of radicals in the bulk solution. Similar effects have been observed with other oxidants, such as H<sub>2</sub>O<sub>2</sub> and persulfate [39-44]. In addition, Reaction 44 can replace inactive •OH<sub>ad</sub> with ClO<sup>•</sup>, which is likely to diffuse widely in the bulk solution to react with RhB molecules and enhance their degradation. In fact, reactive chlorine species have longer lifetimes than •OH (i.e., 5  $\mu$ s for Cl<sup>•</sup> [45] and fractions of milliseconds for Cl<sub>2</sub><sup>•-</sup> [45] versus ~1 ns for •OH), making them more efficient at degrading contaminants [46]. In addition, chloride ions, the main product of hypochlorite photolysis in bulk solution [14], can act as  $h^+$  scavengers (reaction 45), preventing  $e^{-}/h^{+}$  recombination and generating an excess of chlorine radicals in the reaction medium. Overall, hypochlorite can greatly enhance the reactivity of the photocatalyst even in the presence of repulsive forces caused by the high basification of the medium.

At the end of this section, it is important to emphasize that the effect of  $TiO_2$  was evaluated for varying initial RhB concentrations (5–25  $\mu$ M with 100 mg/L TiO<sub>2</sub>) and TiO<sub>2</sub> loadings (up to 500 mg/L with 10  $\mu$ M RhB). In all cases, the trends reported and discussed earlier (and in Figure 6) were observed. The TiO2-induced enhancement of RhB degradation in Solar-L/chlorine at pH 11 was consistently between 30 and 35%, with no significant effect of Solar-L/TiO<sub>2</sub> on the degradation process. This suggests that the effect of electrostatic repulsive forces between the catalyst surface (negative) and the zwitterionic form of RhB was maintained even with varying TiO<sub>2</sub> loading or initial RhB concentration. Therefore, the only enhancement mechanism is the involvement of hypochlorite in the photocatalytic reactivity at the photocatalyst surface, as discussed above.

#### 3. Experimental

#### 3.1. Reagent

Rhodamine B (abbreviation, RhB; C.I. number, 45170; and molecular formula, C<sub>28</sub>H<sub>31</sub>N<sub>2</sub>O<sub>3</sub>Cl, MW: 479.01 gmol-1) was procured from Sigma-Aldrich (St. Louis, MO, USA) Sodium hypochlorite (NaOCl) solution (available chlorine ~16%) was supplied by Henkel (Dély Ibrahim, Algeria). P-25 TiO<sub>2</sub> nonporous powder (80% anatase and 20% rutile, average particle size of 30 nm, and specific surface area of 50 m<sup>2</sup> g<sup>-1</sup>) was supplied by Degussa Corporation (Düsseldorf, Germany) and used as received. All other reagents (tert-butanol, Benzoic acid, ascorbic acid, NaOH, and H<sub>2</sub>SO<sub>4</sub>) were commercial products of the purest grade available (Sigma-Aldrich).

## 3.2. Setup

The experimental setup, as shown in Figure 8, consisted of a water-jacketed Pyrex glass reactor (250 mL) located in a chamber of a commercial Suntest simulator (Suntest CPS+, Atlas, Mount Prospect, IL, USA). This simulator was equipped with an Xe arc lamp with an emission range limited to wavelengths between 280 and 800 nm, and an irradiance of 500 W was maintained. The lamp had a spectral distribution of approximately 0.5% of the emitted photons at wavelengths shorter than 300 nm and about 7% between 300 and 400 nm. The emission spectrum between 400 and 800 nm followed the solar spectrum. The distance between the solution surface and the light source was fixed. The experiments were carried out in the temperature range of 25–55 °C, with the temperature monitored by a thermocouple immersed in the reaction medium and maintained at the desired value by circulating water from a thermostatic bath (RC6 Lauda, Abcoude, The Netherlands) through a jacket surrounding the cell. The pH of the solution was monitored during the reaction, using a pH meter (Jenway 3505- Keison Products, Chelmsford, UK).



**Figure 8.** Experimental setup scheme. (1) Solar simulator 'Suntest CPS+', (2) irradiation lamp, (3) command panel, (4) water-jacketed glass reactor, (5) magnetic stirring plate, (6) pH-meter, (7) thermostatic bath (8) heat/flow rate controller, and (9) connection piping.

#### 3.3. Procedures

Deionized water was used to prepare all solutions. Batch degradation experiments were performed under different conditions, using a constant solution volume of 200 mL. Stock solutions of RhB (10 mM) and chlorine (10 mM) were prepared and stored in the dark at 4 °C. The desired operating concentrations were obtained by making appropriate dilutions from these stocks. In all photocatalytic runs, TiO<sub>2</sub> was added to the RhB solution, and the suspension was allowed to stand in the dark with stirring for 15 min to ensure the adsorption/desorption equilibrium of the pollutant. After this period, known amounts of chlorine were added to the reactor, and the Suntest lamp (Suntest CPS+, Atlas, Mount Prospect, IL, USA) was turned on to mark the start time of the reaction. The suspension was continuously stirred at moderate speed (~300 rpm), using a magnetic stirrer. Aliquots (3 mL) were removed from the photoreactor at different time intervals, filtered through 0.45  $\mu$ m Millipore filters (non-adsorber of RhB), and analyzed using a UV-Vis spectrophotometer (Jasco V-730, Tokyo, Japan) equipped with 1 cm light-path quartz cuvettes. The concentration of RhB was measured at 550 nm, which is its maximum absorption wavelength in the visible band. The pH of the solution was adjusted to pH 11, using sodium hydroxide. All experiments were repeated three times to ensure the reproducibility of the experimental results, and the data were averaged (error bars represent the 95% confidence interval).

#### 4. Conclusions

The obtained results highlight the effectiveness of the Solar-L/chlorine process in degrading Rhodamine B, emphasizing the cost-saving advantages of utilizing solar light instead of artificial UV lamps. While solar light or chlorination alone did not exhibit a noticeable impact on RHB removal, the combined Solar-L/chlorine process demonstrated remarkable efficiency, achieving complete degradation within just 30 min of using 1000  $\mu$ M ClO<sup>-</sup>. The process also demonstrated an effective reduction of the total organic carbon (TOC), with a 60% reduction observed after 120 min and 80% reduction after 240 min. Notably, higher temperatures (55 °C) resulted in an enhanced degradation performance. Furthermore, the inclusion of a TiO<sub>2</sub> nanocatalyst in the Solar-L/chlorine system significantly improved the efficiency of RhB degradation, showcasing an enhancement of over 30%.

To enhance the practical implementation of the Solar-L/chlorine process, it is crucial for future research to identify the by-products generated during degradation and assess their potential environmental impact. Furthermore, conducting a toxicity analysis of the final effluent is essential to ensure the safety of the treated water for discharge. Additionally, an economic cost evaluation of the process is necessary to evaluate its feasibility for large-scale industrial applications. These important findings serve as a foundation for further advancements and optimization of this promising technology in the field of water treatment, offering valuable insights for its future development and application.

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