

## Article

# Removal of Safranin O from Water by UV/TiO<sub>2</sub>/IO<sub>3</sub><sup>-</sup> Advanced Oxidation Process: Parametric Study and Impact of Inorganic Ions and Humic Acid

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**Abstract:** In the present paper, the influence of iodate (IO<sub>3</sub><sup>-</sup>) ions on the photocatalytic process using titanium dioxide (UV/TiO<sub>2</sub>) was systematically examined. The innovative studied system (UV/TiO<sub>2</sub>/IO<sub>3</sub><sup>-</sup>) demonstrated high performance in the elimination of safranin O (SO), a model dye, from water due to the implication of iodine radicals (IO<sub>3</sub><sup>•</sup>, IO<sub>2</sub><sup>•</sup>, IO<sup>•</sup>, etc.). The degradation was assessed by monitoring the change in initial substrate concentration (5–30 mg·L<sup>-1</sup>), TiO<sub>2</sub> loading (0.01–3 g·L<sup>-1</sup>), IO<sub>3</sub><sup>-</sup> concentration, liquid temperature, and initial pH. Further enhancement of oxyanion amount was beneficial for the initial rate of degradation (r<sub>0</sub>) over the range 0.1–50 mM, such that r<sub>0</sub> rose from 0.724 to 1.12 mg·L<sup>-1</sup>·min<sup>-1</sup>. However, a concentration of 100 mM IO<sub>3</sub><sup>-</sup> slowed the removal kinetics. Low pH values were found to be favorable for pollutant removal. Furthermore, a variety of inorganic and organic substances was employed to clarify the effect of the UV/TiO<sub>2</sub>/IO<sub>3</sub><sup>-</sup> process in natural waters. The findings revealed a negative impact of chloride excess in seawater and a decline in SO degradation in mineral water as a result of HCO<sub>3</sub><sup>-</sup> presence at more than 1 mM. At high concentrations of natural organic matter, the heterogeneity and the strong adsorption of humic acid on the TiO<sub>2</sub> surface were found to be harmful for SO decay.



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**Keywords:** degradation; safranin O; UV/TiO<sub>2</sub>/IO<sub>3</sub><sup>-</sup> process; parametric study; inorganic ions; humic acid; real water matrices

## 1. Introduction

The world is currently suffering from natural water contamination due to the detrimental effects of industrial activities. Wastewater from textile manufacture is highly contaminated with significant amounts of chemicals. The release of these compounds into water streams can cause complex ecological and environmental problems owing to their toxicity, non-biodegradability, and potential carcinogenicity [1]. Safranin O is regarded as a model compound representative of dyes that are released in the effluent of the textile and food industries [2]. It is extensively used for dyeing tannin, mordanted cotton, bast fibers, wool, silk, leather and paper, and for coloring candies and cookies [2–4]. This new paradigm of recalcitrant pollutants and their associated problems requires researchers to improve their in-depth understanding of the remediation technologies. Heterogeneous photocatalysis is one of the more promising advanced oxidation processes (AOP) developed in the past 20 years in alternative to conventional processes for water treatment [5]. Based on the in situ production and use of highly reactive species such as •OH and O<sub>2</sub><sup>•-</sup> with rate constants in the range of 118–1011 M<sup>-1</sup>·s<sup>-1</sup> [6], irradiated photocatalysts could efficiently degrade a wide range of hazardous contaminants. The high activity, non-toxicity, low cost, and excellent durability of titanium dioxide (TiO<sub>2</sub>) make it the most widely employed photocatalyst in environmental applications. The intensification of the photocatalytic effectiveness by

the involvement of inorganic oxidants such as  $\text{H}_2\text{O}_2$ ,  $\text{ClO}_3^-$ ,  $\text{BrO}_3^-$ ,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{IO}_4^-$ , and  $\text{IO}_3^-$ , has attracted increasing attention. These compounds could enhance the quantum efficiencies either by charge separation through scavenging conduction-band electrons at the surface of  $\text{TiO}_2$  or offering an additional oxygen atom as an electron acceptor to form the superoxide radical ion ( $\text{O}_2^{\bullet-}$ ) or reactive radical intermediates [7]. Chen et al. [1] investigated the system involving visible light  $\text{TiO}_2$  photocatalysis (Vis/ $\text{TiO}_2$ ) in the presence of peroxymonosulfate (PMS,  $\text{HSO}_5^-$ ). The proposed system (Vis/ $\text{TiO}_2$ /PMS) demonstrated high efficiency in the removal of Acid Orange 7 compared to the conventional process [1]. In their study, Wu et al. [8] evaluated the effects of different oxidants, including  $\text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{S}_2\text{O}_8$ ,  $\text{NaBrO}_3$  and  $\text{NaIO}_4$ , on the degradation ability of UV/ $\text{TiO}_2$  toward Reactive Red 198 and reported that the implication of periodate was more effective. Similar studies confirmed the beneficial effect of oxyanions on photocatalytic treatment in water [9–12]. However, limited research can be found about the use of iodate anion in  $\text{TiO}_2$ -mediated photocatalysis for eliminating emergent pollutants. To improve the decay rates of *o*-chloroaniline (*o*-CIA) by the illuminated Degussa P25, Choy et al. [13] used  $\text{ClO}_3^-$ ,  $\text{BrO}_3^-$ , and  $\text{IO}_3^-$ . Substantial enhancement was observed in the order  $\text{IO}_3^- > \text{BrO}_3^- > \text{ClO}_3^-$ . In complementary work, Choy et al. [7] discussed the effect of iodate in successive dosing, and the degradation pathway of *o*-CIA was proposed according to the detection of organic intermediates. In a recent work, Zhang et al. [14] investigated the degradation of carbamazepine (CBZ) using UV/ $\text{IO}_3^-$  and UV/ $\text{TiO}_2$ / $\text{IO}_3^-$  systems. They indicated that iodine radicals ( $\text{IO}^\bullet$ ,  $\text{IO}_2^\bullet$  and  $\text{IO}_3^\bullet$ ) were mainly involved in the degradation of CBZ in the UV/ $\text{TiO}_2$ / $\text{IO}_3^-$  process, which was found to be the most efficient process when compared to some other photocatalytic systems (UV/ $\text{ClO}_3^-$ / $\text{TiO}_2$ , UV/ $\text{BrO}_3^-$ / $\text{TiO}_2$ ).

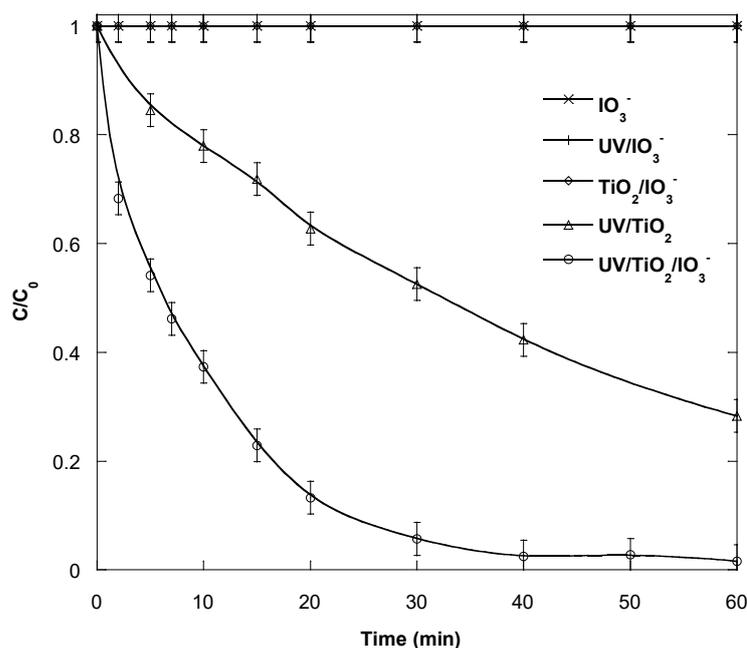
The UV/ $\text{TiO}_2$ / $\text{IO}_3^-$  process has received very limited attention. Moreover, while the improving impact of using a UV/ $\text{TiO}_2$ / $\text{IO}_3^-$  system has been shown to be significant, very little information is known about the influence of operating parameters on process effectiveness. Additionally, the viability of the process in the presence of inorganic and organic substances, as well as in real water matrices, such as mineral water and seawater, has not been examined earlier. All of these tasks have not been investigated previously, undoubtedly due to the novelty of the technique.

The objective of this study was to evaluate the aqueous degradation of safranin O (SO) dye using the UV/ $\text{TiO}_2$ / $\text{IO}_3^-$  process. For the first time, the process performance was examined under diverse experimental parameters, namely, substrate charge, photocatalyst mass,  $\text{NaIO}_3$  loading, liquid temperature, and initial pH. The degradation efficiency was also tested in the presence of some inorganic anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{NO}_2^-$ ) and humic acid as natural organic matter. In the last part, the removal of SO from seawater and mineral water was discussed, utilizing our findings on the effect of additives.

## 2. Results

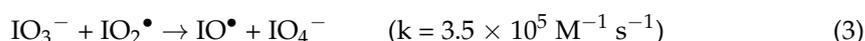
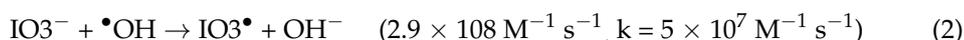
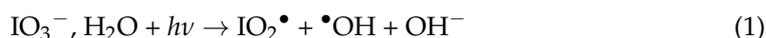
### 2.1. Photocatalytic Degradation of Safranin O through Iodate Process

In order to improve the performance of the  $\text{TiO}_2$ -mediated photocatalytic process to treat an aqueous solution of  $10 \text{ mg}\cdot\text{L}^{-1}$  of safranin O dye, the iodate anions ( $\text{IO}_3^-$ ) were added. First, the effect of iodate was tested in the presence of the oxyhalogen ( $\text{IO}_3^-$ ) alone, under UV irradiation, and with the  $\text{TiO}_2$  suspension. Figure 1 exhibits the obtained results. According to these results, no change in initial concentration of dye was noticed over time under  $\text{IO}_3^-$  alone, under illuminated iodate, or with the  $\text{TiO}_2$ / $\text{IO}_3^-$  system. These findings can be attributed to the fact that the photon energy provided at 365 nm was not sufficient to photo-activate the oxyanion for producing efficient free radicals for dye destruction. Choy et al. [13] found a negligible effect of illuminated iodate (300 nm) in the degradation of *o*-chloroaniline.



**Figure 1.** Effect of iodate on SO degradation in different systems ( $[\text{IO}_3^-] = 0.15 \text{ mM}$ ,  $[\text{TiO}_2] = 0.4 \text{ g}\cdot\text{L}^{-1}$ ,  $[\text{SO}] = 10 \text{ mg}\cdot\text{L}^{-1}$ ,  $T = 25 \pm 2 \text{ }^\circ\text{C}$  and  $\text{pH}\sim 6$ ).

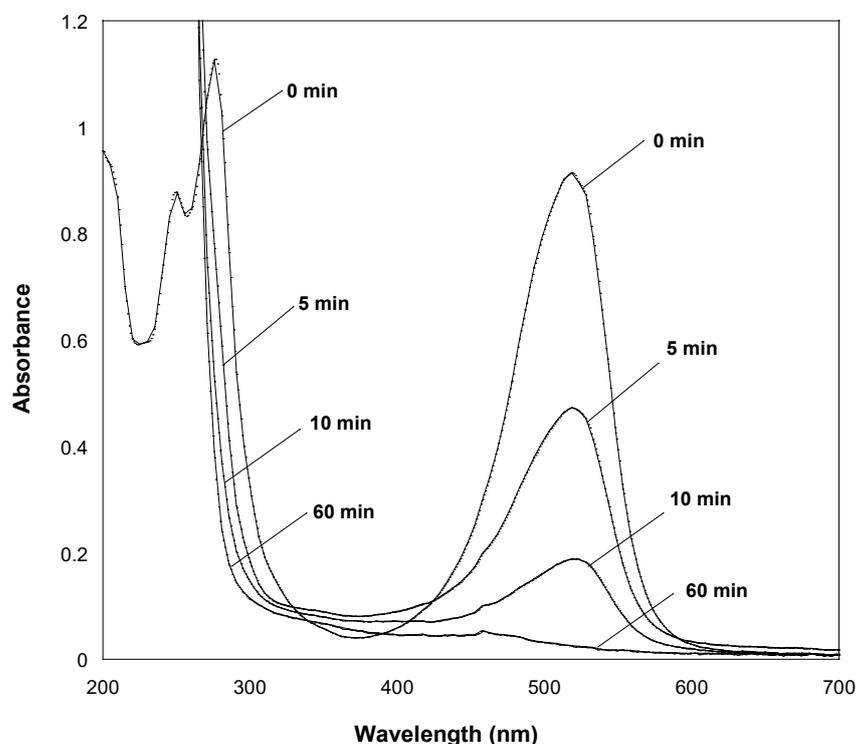
The introduction of 0.15 mM of iodate into the UV/TiO<sub>2</sub> system substantially accelerated the SO degradation. After one hour of reaction, almost the entirety of the organic compound disappeared through the UV/TiO<sub>2</sub>/IO<sub>3</sub><sup>−</sup> process, versus 72% in the absence of iodate. Kinetically, the initial rate of SO degradation was substantially improved in the presence of 0.15 mM of the oxyanion, which is probably due to the involvement of new free radicals in the degradation process. Amichai and Treinin [15] detected the formation of IO<sub>3</sub><sup>•</sup>, IO<sub>2</sub><sup>•</sup>, and IO<sup>•</sup> in an iodate-containing solution that undergoes a flash photolysis at neutral pH. These radicals can be yielded by the photodecomposition of iodate, as well as by secondary reactions involving the parent ions [15]. In the second way, IO<sub>3</sub><sup>−</sup> reacts with <sup>•</sup>OH and IO<sub>2</sub><sup>•</sup> to produce IO<sub>3</sub><sup>•</sup> and IO<sup>•</sup>, respectively (Equations (1)–(3) [15,16]), and other reactive species.



In support of these findings, Haddad et al. [17] reported that the photodegradation of light green SF yellowish (LGSFY) dye was significantly improved in the presence of iodate, attributing these results to the efficient contribution of IO<sub>2</sub><sup>•</sup> and IO<sup>•</sup>. Choy et al. [7] investigated the removal of o-chloroaniline by iodate, chlorate, and borate-assisted photocatalysis. They found a considerable enhancement in degradation rate in the order of UV/TiO<sub>2</sub>/IO<sub>3</sub><sup>−</sup> > UV/TiO<sub>2</sub>/BrO<sub>3</sub><sup>−</sup> > UV/TiO<sub>2</sub>/ClO<sub>3</sub><sup>−</sup>. This observation was justified by the ability of iodate to trap more conduction band electrons compared to the other oxyhalogens. In another study, Choy et al. [7] deduced that the target molecule was mainly degraded by the attack of <sup>•</sup>OH radicals. Recently, Zhang et al. [14] indicated that IO<sub>3</sub><sup>−</sup> can delay the recombination of electrons and holes through trapping e<sup>−</sup> ejected from the surface of TiO<sub>2</sub>. Furthermore, the longer half-life of h<sub>νB+</sub> and the additional reactive radical can create additional pathways to boost the degradation of substrate.

Figure 2 shows the evolution of the UV-vis. spectra of SO solution (10 mg L<sup>−1</sup>) prior to and during the oxidative treatment with UV/TiO<sub>2</sub>/IO<sub>3</sub><sup>−</sup> using 0.15 mM of IO<sub>3</sub><sup>−</sup> and 0.4 g·L<sup>−1</sup> of TiO<sub>2</sub> at 25 °C and pH~6. As can be observed from this figure, the initial SO solution has two distinct bands: the first is that of the chromophoric group and is located

in the visible region, with  $\lambda_{\max} = 519$  nm, and the second is that of the aromatic rings and is located in the UV region, with  $\lambda_{\max} = 275$  nm. The characteristic band in the visible region declined with increasing reaction time until no peak was further observed. This implies the degradation of the dye upon attack by oxidative moieties. The increase in absorption in the UV region 228–238 nm is explained by the formation of by-products absorbing in this UV region.

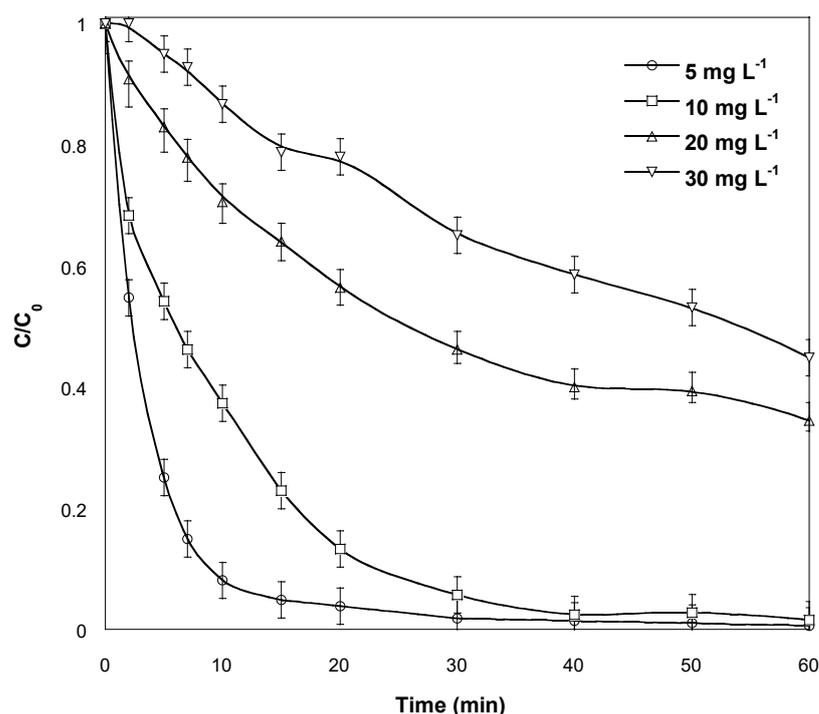


**Figure 2.** Temporal variation of the UV–Vis. spectra of SO solution upon treatment with UV/TiO<sub>2</sub>/IO<sub>3</sub><sup>−</sup> process ([IO<sub>3</sub><sup>−</sup>] = 0.15 mM, [TiO<sub>2</sub>] = 0.4 g·L<sup>−1</sup>, [SO] = 10 mg·L<sup>−1</sup>, T = 25 ± 2 °C and pH~6).

## 2.2. Effect of Operational Conditions

### 2.2.1. Effect of Initial Concentration of SO

This section elucidates the effect of initial concentration of dye on the performance of the UV/TiO<sub>2</sub>/IO<sub>3</sub><sup>−</sup> process to remove SO from water. For that, batch experiments were carried out at four initial substrate concentrations: 5, 10, 20, and 30 mg·L<sup>−1</sup>. The other operational parameters were fixed at 0.4 g·L<sup>−1</sup> of TiO<sub>2</sub>, 0.15 mM of iodate, 25 °C, and natural liquid pH. The experimental findings are presented in Figure 3. This figure shows that the degradation efficiency was reduced in high dye concentration. For example, for an initial concentration of 5 mg·L<sup>−1</sup>, the abatement rate after 10 min of irradiation was almost total (92%), while it was only 13% for C<sub>0</sub> = 30 mg·L<sup>−1</sup>. The same behavior was reported in the presence of periodate instead of iodate and under classical photocatalysis [12]. Table 1 presents the variation of initial degradation rate (r<sub>0</sub>) as a function of initial concentration of SO. The initial degradation rate values decreased gradually from 1.131 to 0.308 mg·L<sup>−1</sup>·min<sup>−1</sup> with the increase in dye quantity in water from 5 to 30 mg·L<sup>−1</sup>. These results can be explained by the strong competition of the substrate molecules with the reactive species, whose number remained unchangeable as long as the same operational conditions were kept in all trials.



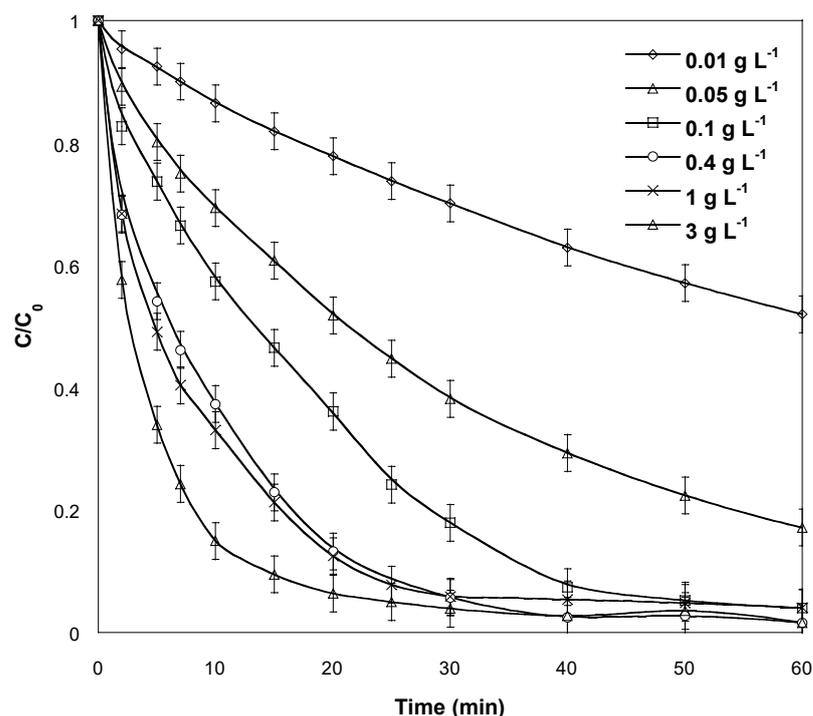
**Figure 3.** Effect of initial substrate concentration on SO degradation by UV/TiO<sub>2</sub>/IO<sub>3</sub><sup>−</sup> process ([IO<sub>3</sub><sup>−</sup>] = 0.15 mM, [TiO<sub>2</sub>] = 0.4 g·L<sup>−1</sup>, [SO] = 10–30 mg·L<sup>−1</sup>, T = 25 ± 2 °C and pH~6).

**Table 1.** Dependence of initial degradation rate on SO initial concentration in the range (5–30 mg·L<sup>−1</sup>) through UV/TiO<sub>2</sub>/IO<sub>3</sub><sup>−</sup> process.

| Initial SO Concentration (mg·L <sup>−1</sup> )          | 5   | 10    | 20    | 30  |
|---|-----|-------|-------|-----|
| r <sub>0</sub> (mg·L <sup>−1</sup> ·min <sup>−1</sup> ) | 1.5 | 0.765 | 0.342 | 0.1 |

### 2.2.2. Effect of Photocatalyst Concentration

Optimizing the mass of the catalyst is an essential step in the study of photocatalytic processes. Therefore, it is necessary to determine the value for which the quantity of the photocatalyst is minimal and the reaction rate is the highest. The efficiency of the UV/TiO<sub>2</sub>/IO<sub>3</sub><sup>−</sup> (0.15 mM) system to eliminate 10 mg·L<sup>−1</sup> of SO was examined at different concentrations of TiO<sub>2</sub>, namely, 0.01, 0.05, 0.1, 0.4, 1, and 3 g·L<sup>−1</sup>. The mixture temperature was kept constant at 25 °C with a pH of approximately 6. The abatement of SO concentration over the reaction time in every suspension of TiO<sub>2</sub> is displayed in Figure 4. Contrary to our previous study related to periodate-assisted photocatalysis [12], the greater the amount of the photocatalyst, the higher the degradation yield in the adopted range (0.01–3 g·L<sup>−1</sup>). After 15 min of irradiation, approximately 78% of the initial concentration was removed from the solutions containing 0.4 and 1 g·L<sup>−1</sup> of titanium dioxide, versus 90.5% when [TiO<sub>2</sub>]<sub>0</sub> = 3 g·L<sup>−1</sup>. The dependence of initial degradation rate on TiO<sub>2</sub> loading was also noticed (Table 2). The increase in photocatalyst mass led to the acceleration of the destruction reaction, so that r<sub>0</sub> increased from 0.15 to 1.32 mg·L<sup>−1</sup>·min<sup>−1</sup> when TiO<sub>2</sub> concentration increased from 0.01 to 3 g·L<sup>−1</sup>. These findings are the consequence of an increase in the active surface of TiO<sub>2</sub> by increasing the number of illuminated particles, thus producing a greater number of “electron-hole” pairs and, therefore, a greater quantity of oxidizing entities effective in the destruction of the pollutant. Additionally, the increase in photocatalytic activity with catalyst loading is indicative of a heterogeneous catalytic regime since the fraction of incident light absorbed by the catalyst increases as the amount of TiO<sub>2</sub> increases in a suspension [14,18].



**Figure 4.** Effect of  $\text{TiO}_2$  loading ( $0.01\text{--}3\text{ g}\cdot\text{L}^{-1}$ ) on SO degradation by UV/ $\text{TiO}_2$ / $\text{IO}_3^-$  process ( $[\text{IO}_3^-] = 0.15\text{ mM}$ ,  $[\text{SO}] = 10\text{ mg}\cdot\text{L}^{-1}$ ,  $T = 25 \pm 2\text{ }^\circ\text{C}$  and  $\text{pH}\sim 6$ ).

**Table 2.** Dependence of initial degradation rate on  $\text{TiO}_2$  loading in the range  $0.01\text{--}3\text{ g}\cdot\text{L}^{-1}$  through UV/ $\text{TiO}_2$ / $\text{IO}_3^-$  process.

| $[\text{TiO}_2]_0\text{ (g}\cdot\text{L}^{-1})$         | 0.01 | 0.05  | 0.1   | 0.4   | 1     | 3    |
|---|------|-------|-------|-------|-------|------|
| $r_0\text{ (mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1})$ | 0.15 | 0.397 | 0.526 | 0.765 | 1.017 | 1.32 |

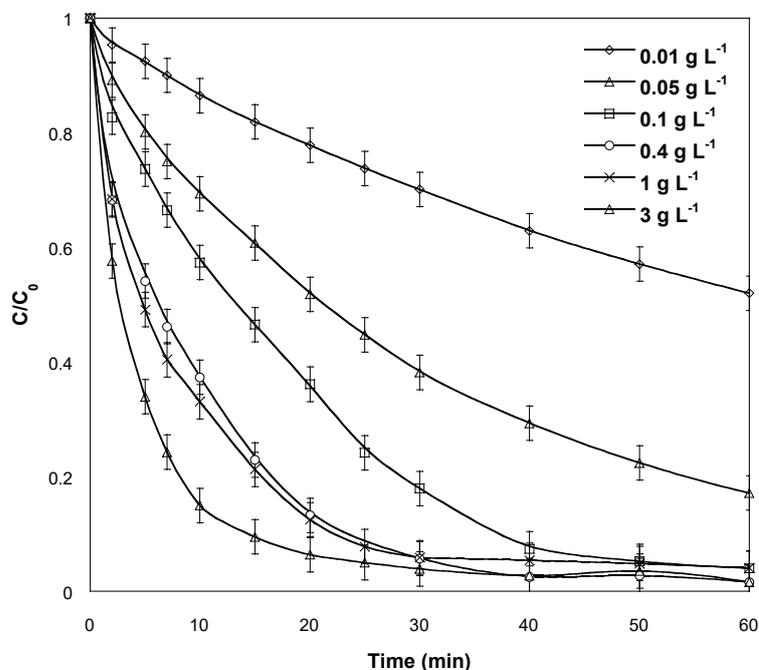
In the present work, because only a slight increase in the degradation rate of SO occurred when the  $\text{TiO}_2$  concentration was increased from  $0.4\text{ g/L}$ , Degussa P25 concentration was set to  $0.4\text{ g}\cdot\text{L}^{-1}$  for the next experiments.

### 2.2.3. Effect of Iodate Loading

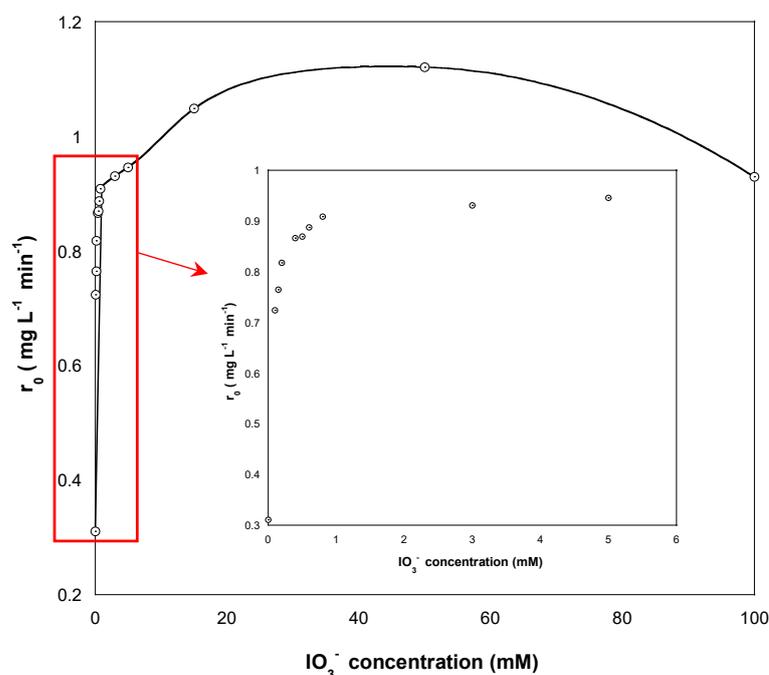
The investigation of  $\text{IO}_3^-$  loading effect on the efficiency of photocatalytic treatment has not yet been reported. In order to examine the photocatalytic response as a function of oxyhalogen dose for SO degradation, experiments were conducted in an aerated aqueous solution of dye ( $10\text{ mg}\cdot\text{L}^{-1}$ ) containing  $0.4\text{ g}\cdot\text{L}^{-1}$  of  $\text{TiO}_2$  at a controlled temperature ( $25\text{ }^\circ\text{C}$ ) and near-neutral pH. The concentration of  $\text{IO}_3^-$  was varied over the range  $0.1\text{--}100\text{ mM}$ . Results were reported in Figure 5.

As shown in Figure 5, the removal efficiency increased proportionally with the amount of iodate involved over  $0.1\text{--}50\text{ mM}$ . After 15 min of illumination, the system revealed its highest performance in the presence of iodate at 15 and 50 mM with a degradation rate of 92%. However, a slight drop in degradation extent was seen using 100 mM of oxyanion, estimated at 2.5% after a half hour of treatment. Kinetically, the initial degradation rates were also calculated a few minutes after starting the reaction. The dependence of the initial degradation rate on  $\text{IO}_3^-$  concentration was depicted in Figure 6. It was observed that the dye destruction kinetics were significantly improved by increasing the amount of iodate added. For  $\text{IO}_3^-$  contents of 0.1, 0.15, 0.5, and 3 mM, the  $r_0$  were, respectively, equal to 0.724, 0.764, 0.87, and 0.93  $\text{mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$ . The initial rate of degradation continued to evolve very rapidly up to a value of  $1.12\text{ mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$  which corresponds to  $[\text{IO}_3^-]_0 = 50\text{ mM}$ . This trend is the result of the increasing production of active oxygen species ( $\bullet\text{OH}$ ,  $\text{O}_2^{\bullet-}$ ,

$\text{IO}_3^\bullet$ ,  $\text{IO}_2^\bullet$ ,  $\text{IO}^\bullet \dots$ ) in the presence of more oxyhalogen in the solution. Otherwise, a detrimental effect of iodate concentration up to 10 mM was observed by Haddad et al. [17] on the photo-decomposition of LGSFY dye. In excess of  $\text{IO}_3^-$ , the iodate radicals could react with each other to produce low efficient species in SO destruction, which explains the decline of  $r_0$  at 100 mM of  $\text{KIO}_3$ . For the rest of the manipulations, a concentration of 0.15 mM iodate was adequate.



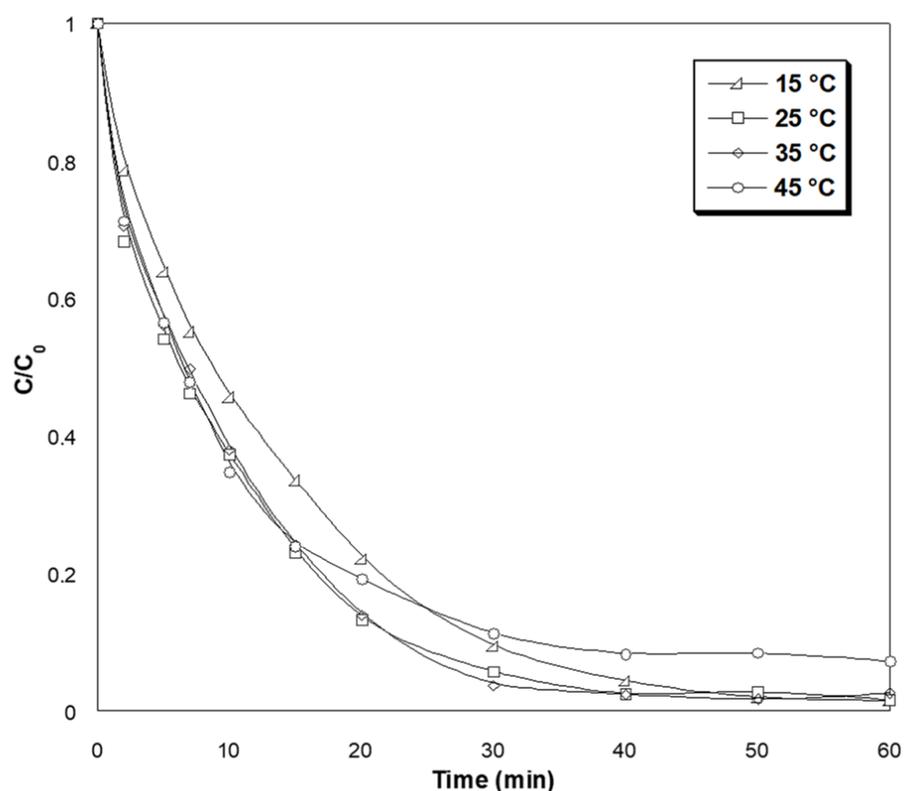
**Figure 5.** Influence of iodate concentration in the range of 0.1–100 mM on the degradation of SO ( $10 \text{ mg}\cdot\text{L}^{-1}$ ) by UV/ $\text{TiO}_2/\text{IO}_3^-$  process ( $[\text{TiO}_2] = 0.4 \text{ g}\cdot\text{L}^{-1}$ ,  $T = 25 \pm 2^\circ\text{C}$  and  $\text{pH}=6$ ).



**Figure 6.** Dependence of initial rate of SO degradation on  $\text{IO}_3^-$  concentration in the range 0.1–100 mM by UV/ $\text{TiO}_2/\text{IO}_3^-$  process ( $[\text{TiO}_2] = 0.4 \text{ g}\cdot\text{L}^{-1}$ ,  $[\text{SO}] = 10 \text{ mg}\cdot\text{L}^{-1}$ ,  $T = 25 \pm 2^\circ\text{C}$  and  $\text{pH}=6$ ).

#### 2.2.4. Effect of Liquid Temperature

For the first time, the impact of medium temperature on the iodate-assisted photocatalysis potential to eliminate organic pollutants is discussed. To examine the influence of this parameter on the removal of SO, five aqueous solutions of dye ( $10 \text{ mg}\cdot\text{L}^{-1}$ ) were set at different temperatures: 15, 25, 35, and 45 °C. The photocatalytic treatment was performed in the presence of 0.15 mM of  $\text{IO}_3^-$ ,  $0.4 \text{ g}\cdot\text{L}^{-1}$  of photocatalyst, and at the natural pH of the solutions. Figure 7 depicts the change in SO concentration during illumination time.

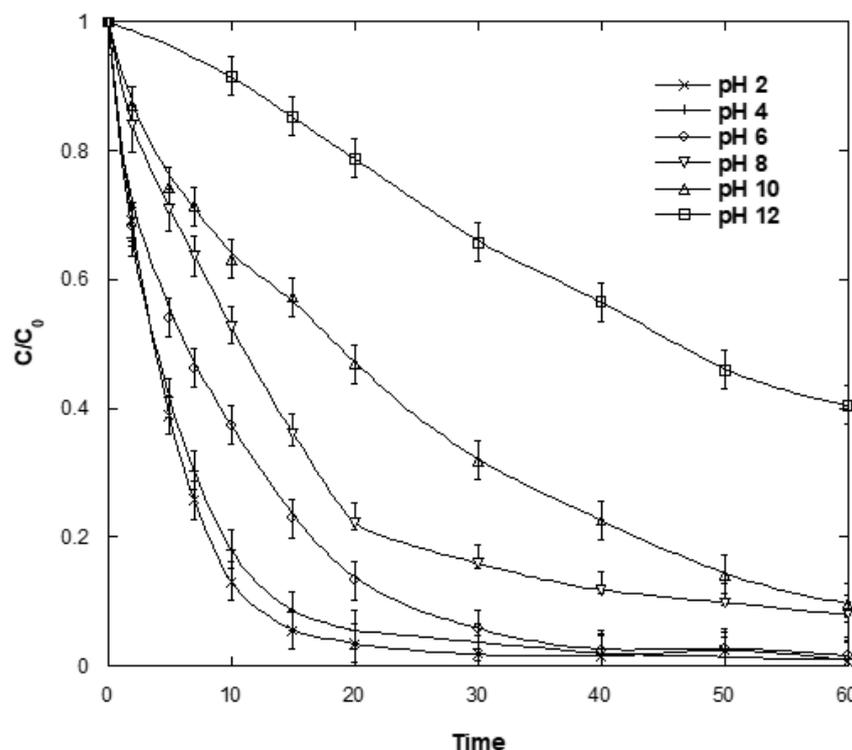


**Figure 7.** Effect of liquid temperature in the range of 15–45 °C on the degradation of SO by UV/TiO<sub>2</sub>/IO<sub>3</sub><sup>−</sup> process ([IO<sub>3</sub><sup>−</sup>] = 0.15 mM, [TiO<sub>2</sub>] = 0.4 g·L<sup>−1</sup>, [SO] = 10 mg·L<sup>−1</sup> and pH~6).

The process seemed to be less sensitive to the temperature variation in the studied interval, according to Figure 7. However, the degradation was slightly inhibited at 15 °C, such that 66.5% was eliminated after 15 min, compared to 76% when the solution was heated to 25, 35, and 45 °C. Like periodate, iodate is thermally stable and does not decompose under the conditions adopted in this study. In heterogeneous photocatalysis, low temperatures affect the adsorption of molecules on the surface of the photocatalyst [19,20], which may justify the small reduction in degradation efficiency at 15 °C.

#### 2.2.5. Effect of Initial Solution pH

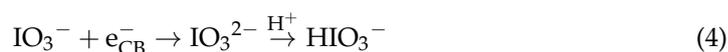
Since initial solution pH is a controlling factor in photocatalytic reactions for dye removal, the effect of media acidity on safranin O ( $10 \text{ mg}\cdot\text{L}^{-1}$ ) decay in the presence of iodate (0.15 mM) was examined. The change in media protonation can modify the surface charge of both the pollutant and the photocatalyst, as well as the speciation of an aqueous inorganic oxidant. Figure 8 shows the plot of degradation efficiency during the experiment at every pH value, ranging in the interval of 2–12.



**Figure 8.** Effect of initial solution pH (2–12) on the removal efficiency of SO through UV/TiO<sub>2</sub>/IO<sub>3</sub><sup>−</sup> process ([IO<sub>3</sub><sup>−</sup>] = 0.15 mM, [TiO<sub>2</sub>] = 0.4 g·L<sup>−1</sup>, [SO] = 10 mg·L<sup>−1</sup>, and pH~6).

The results revealed that the process was more efficient in acidic medium. The dye was completely degraded after only 30 min at pH 2, 40 min at pH 4, and 50 min at pH 6, while 92%, 90%, and 59.5% of the initial concentration of pollutant were destroyed, respectively, at pH 8, 10, and 12 after one hour of illumination. These findings are opposed to what has been reported in conventional and periodate-assisted photocatalysis, where the alkaline pH was the most favorable [9,21,22].

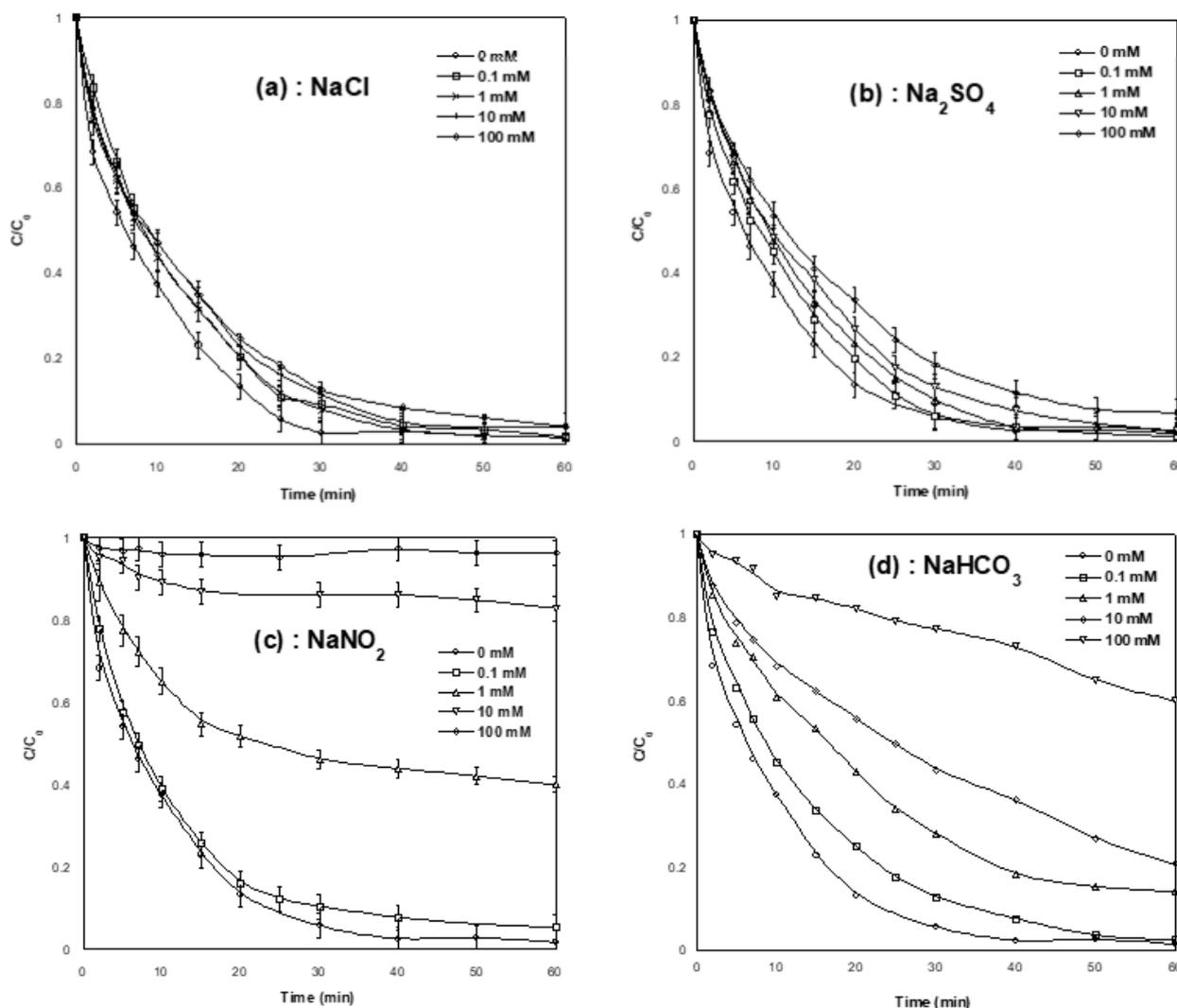
Buxton et al. [23] reported that the iodic acid anion (HIO<sub>3</sub><sup>−</sup>) could be indirectly formed when IO<sub>3</sub><sup>−</sup> captured an electron in a protonated medium, following Equation (4). At lower pH, the presence of HIO<sub>3</sub><sup>−</sup> was probably effective in the degradation of the SO dye. The amount of iodic acid produced decreases in alkaline media, which may justify the decline in treatment efficiency at pH 8, 10, and 12. Additionally, according to reactions 1–3, the increase in OH<sup>−</sup> concentration resulted into a low yield of IO<sub>2</sub><sup>•</sup>, or IO<sub>3</sub><sup>•</sup> and IO<sup>•</sup>. In a recent study, synthesized defective TiO<sub>2</sub>-HIO<sub>3</sub><sup>−</sup> revealed a higher reactivity towards organic pollutants compared to the nicked titania [24]. Furthermore, Fkhmi et al. [25] observed that the reaction of IO<sub>3</sub><sup>−</sup> with iodide was pH-dependent and only took place in acidic medium. The accumulation of iodide ions (I<sup>−</sup>) with a pH higher than 5.5 could probably trap a large number of reactive radicals, resulting in low system efficiency. At pH 12, the possibility of agglomeration of the TiO<sub>2</sub> particles was one more reason to have a low conversion percent of the pollutant.



### 2.3. Mineral and Organic Additives Impact on Degradation Efficiency

This part of the study examined the influence of some inorganic ions (Cl<sup>−</sup>, SO<sub>4</sub><sup>2−</sup>, HCO<sub>3</sub><sup>−</sup> and NO<sub>2</sub><sup>−</sup>) and natural organic matter (humic acid HA) on the degradation of SO by the UV/TiO<sub>2</sub>/IO<sub>3</sub><sup>−</sup> process. An appropriate amount of salt was added to 10 mg·L<sup>−1</sup> of aqueous dye in the range of 0.1–100 mM. The organic substance was used in three concentrations: 5, 10, and 20 mg·L<sup>−1</sup>. Corresponding experiments were run in a suspension

of  $0.4 \text{ g}\cdot\text{L}^{-1}$  of photocatalyst,  $0.15 \text{ mM}$  of iodate at  $25 \text{ }^\circ\text{C}$ , and natural pH. Experimental results are shown in Figure 9.



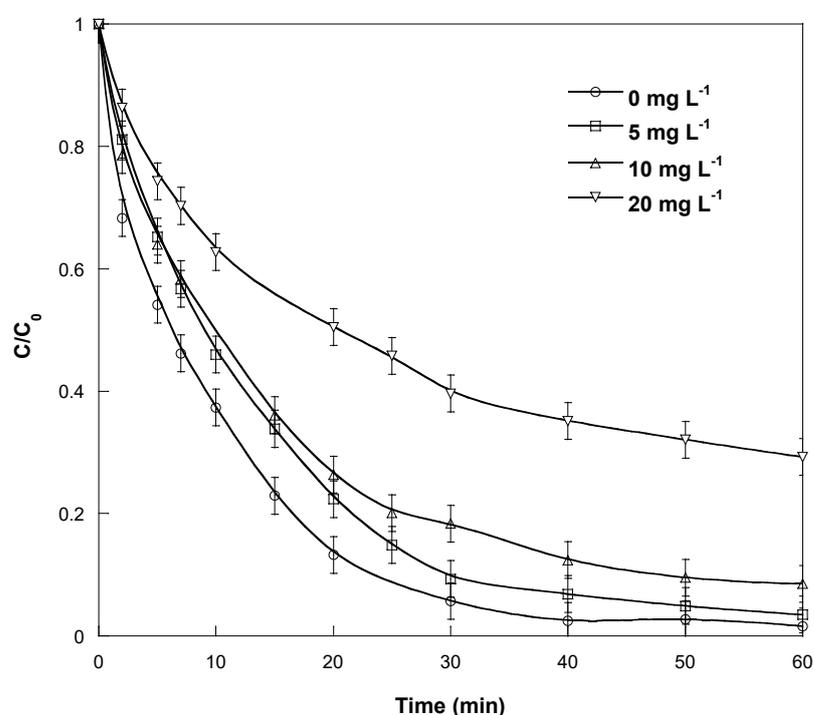
**Figure 9.** Effect of different additives on SO degradation by UV/TiO<sub>2</sub>/IO<sub>3</sub><sup>−</sup> process: (a) chloride, (b) sulfate, (c) nitrite, and (d) bicarbonate ([IO<sub>3</sub><sup>−</sup>] =  $0.15 \text{ mM}$ , [TiO<sub>2</sub>] =  $0.4 \text{ g}\cdot\text{L}^{-1}$ , [SO] =  $10 \text{ mg}\cdot\text{L}^{-1}$  and pH~6 (pH~8.3 for [HCO<sub>3</sub><sup>−</sup>] = 1, 10 and 100 mM)).

According to Figure 9, the presence of salts negatively affected the degradation efficiency in the order  $\text{Cl}^- < \text{SO}_4^{2-} \ll \text{HCO}_3^- < \text{NO}_2^-$ . The effect of both  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  was not very significant, even at 100 mM, i.e., a reduction of only 2% and 5% of degradation was observed for the ions, in order, after 60 min of treatment. These results suggest that chloride and sulfate ions are not reactive with effective iodine radicals. The weak effect of their addition can be attributed to the trapping of  $\bullet\text{OH}$ , whose contribution to SO degradation is relatively weak according to our previous studies (not yet published). In their study, Haddad et al. [17] reported that the degradation of light green SF yellowish (LGSFY) by the UV/IO<sub>3</sub><sup>−</sup> process was retarded by about half in the presence of  $\text{SO}_4^{2-}$  at more than 0.1 mM.

However, the implication of nitrite and bicarbonate ions drastically inhibited the SO destruction. As shown in Figure 9c,d, the negative impact increased with the increase of salt concentration while the entire inhibition was achieved at 100 mM of  $\text{NO}_2^-$  against 58.6% in the presence of the same dose of  $\text{HCO}_3^-$ . In classical photocatalysis (not documented), the negative effect of nitrite was also found to be important, which was probably due to

the strong adsorption of these ions on the surface of the catalyst, thus, less oxidant species could be formed. As for bicarbonate (Figure 9d), the change of solution alkalinity ( $\text{pH} > 8$ ) was probably responsible for the degradation rate reduction, since the addition of this ion at different a concentration had a negligible effect on the ability of the  $\text{UV}/\text{TiO}_2/\text{IO}_4^-$  system to eliminate the SO dye. It should be noted that no available data related to the effect of  $\text{NO}_2^-$  ions on photocatalysis effectiveness.

The presence of HA also altered the pollutant removal, as shown Figure 10. At  $20 \text{ mg}\cdot\text{L}^{-1}$ , half of the initial mass of the SO was degraded after 20 min; however, the degradation of the same quantity took 10 min at  $5 \text{ mg}\cdot\text{L}^{-1}$  and 12 min at  $10 \text{ mg}\cdot\text{L}^{-1}$  of natural organic matter, compared to 7 min in the HA-free solution. Humic substances are a mixture of compounds that absorb light more intensely in the UV field. At high concentrations, the presence of organic matter hampered the photocatalytic degradation as the number of photoactivated  $\text{TiO}_2$  particles decreased. Palmer et al. [26] attributed the dramatic effect of these compounds to their strong adsorption on the  $\text{TiO}_2$  surface.



**Figure 10.** Effect of humic acid on SO removal by  $\text{UV}/\text{TiO}_2/\text{IO}_3^-$  process ( $[\text{IO}_3^-] = 0.15 \text{ mM}$ ,  $[\text{TiO}_2] = 0.4 \text{ g}\cdot\text{L}^{-1}$ ,  $[\text{SO}] = 10 \text{ mg}\cdot\text{L}^{-1}$  and  $\text{pH} \sim 6$ ).

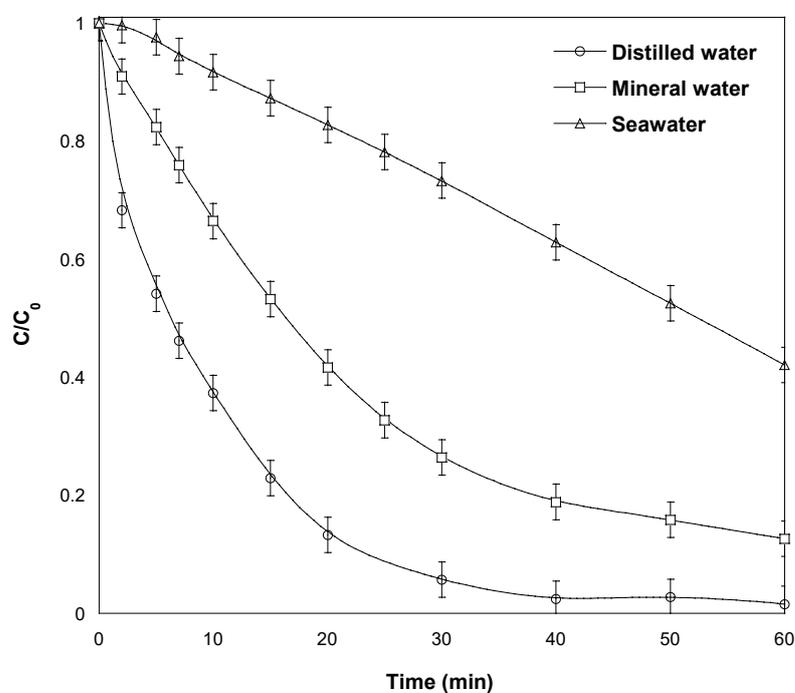
#### 2.4. Degradation in Real Water Matrices

Natural waters can also be contaminated by colored effluents. Thus, the efficiency of the studied process ( $\text{UV}/\text{TiO}_2/\text{IO}_3^-$ ) to remove SO from different water matrices, including mineral water and seawater, was tested. The seawater was collected in the region of Annaba, Algeria. Chemical composition and acidity of each matrix are given in Table 3. The experiments were carried out at natural pH under the same operational conditions adopted in distilled water. The corresponding results are compared and illustrated in Figure 11. As observed, the process performance diminished in natural waters where the negative effect was more pronounced in seawater. After one hour of reaction, the degradation percentage was reduced by 11% in mineral water and by about 40.5% in seawater. The influence of the different inorganic ions revealed that the bicarbonate and sulfate anions at more than 1 mM retarded the kinetics of the pollutant removal. Consequently, the presence of  $\text{HCO}_3^-$  at 4 mM and  $\text{SO}_4^{2-}$  at 0.7 mM (Table 3) are probably responsible for the reduction in degradation rate of SO in mineral water. In seawater, the excess of chloride ( $>500 \text{ mM}$ ) hampered the penetration of light, thus reducing the efficiency of the photon. Additionally,

the strong adsorption of organic matter on the  $\text{TiO}_2$  surface may be another reason for the diminution of SO degradation in seawater.

**Table 3.** Principal characteristics of water matrices used in this study.

|                    | Mineral Water                        | Seawater                           |
|--------------------|--------------------------------------|------------------------------------|
| pH                 | 7.2                                  | 7.5                                |
| $\text{Ca}^{2+}$   | $99 \text{ mg}\cdot\text{L}^{-1}$    | $0.4 \text{ g}\cdot\text{L}^{-1}$  |
| $\text{Mg}^{2+}$   | $24 \text{ mg}\cdot\text{L}^{-1}$    | $1.3 \text{ g}\cdot\text{L}^{-1}$  |
| $\text{K}^+$       | $2.1 \text{ mg}\cdot\text{L}^{-1}$   | -                                  |
| $\text{Na}^+$      | $15.8 \text{ mg}\cdot\text{L}^{-1}$  | $11.0 \text{ g}\cdot\text{L}^{-1}$ |
| $\text{HCO}_3^-$   | $265 \text{ mg}\cdot\text{L}^{-1}$   | -                                  |
| $\text{SO}_4^{2-}$ | $68 \text{ mg}\cdot\text{L}^{-1}$    | $3.0 \text{ g}\cdot\text{L}^{-1}$  |
| $\text{Cl}^-$      | $72 \text{ mg}\cdot\text{L}^{-1}$    | $20.0 \text{ g}\cdot\text{L}^{-1}$ |
| $\text{NO}_3^-$    | $15 \text{ mg}\cdot\text{L}^{-1}$    | -                                  |
| $\text{NO}_2^-$    | $<0.02 \text{ mg}\cdot\text{L}^{-1}$ | -                                  |



**Figure 11.** Removal of SO from real water matrices by UV/ $\text{TiO}_2/\text{IO}_3^-$  process ( $[\text{IO}_3^-] = 0.15 \text{ mM}$ ,  $[\text{TiO}_2] = 0.4 \text{ g}\cdot\text{L}^{-1}$  and  $[\text{SO}] = 10 \text{ mg}\cdot\text{L}^{-1}$ ).

### 3. Materials and Methods

#### 3.1. Reagents

All chemicals used in these experiments were of analytical reagent grade. The stock solutions of safranin O were prepared using distilled water. Safranin O (SO) was provided by Fluka (CAS 477-73-6, CI 50240, India).  $\text{TiO}_2$  Degussa P-25 (80% anatase and 20% rutile, average particle size: 30 nm, specific surface area:  $50 \text{ m}^2\cdot\text{g}^{-1}$ ) was employed as a photocatalyst and purchased from Evonik.  $\text{KIO}_3$  (Sigma-Aldrich, USA, CAS 7758-05-6), potassium nitrite (Sigma-Aldrich), sodium chloride (Prolabo), sodium sulfate (Sigma-Aldrich), and humic acids (Sigma-Aldrich) were used as received. For pH adjustment, NaOH (Sigma-Aldrich) and  $\text{H}_2\text{SO}_4$  (Sigma-Aldrich) were used.

#### 3.2. Photocatalytic Experiments and Apparatus

The photocatalytic trials were performed using the experimental setup described by Bendjama et al. [12]. The reactor consisted of a 500 mL Pyrex-jacketed cylinder. The irradiation

tion was performed using a low-pressure mercury lamp ( $15 \text{ mW cm}^{-2}$ , Oriel 6035) emitting mainly at 365 nm, placed in the middle of the reactor. The liquid temperature was controlled using a thermostatic immersion heater at  $25 \pm 2 \text{ }^\circ\text{C}$  in almost all experiments. Prior to irradiation, 200 mL of a solution/suspension of  $10 \text{ mg}\cdot\text{L}^{-1}$  safranin O (SO) and  $0.4 \text{ g}\cdot\text{L}^{-1}$   $\text{TiO}_2$  were magnetically stirred for 30 min in the dark to ensure adsorption–desorption equilibrium on the semiconductor surface. The concentration after the adsorption process is denoted as initial concentration ( $C_0$ ). Determined quantities of iodate and other additives were added to the reactor and the UV lamp was turned on for initiating the oxidation. During irradiation, samples were withdrawn and  $\text{TiO}_2$  particles were separated by centrifugation (10,000 rpm, 30 min), then analyzed using a UV-Vis spectrophotometer (Biochrom Lightwave II) at 519 nm. Moderate stirring was maintained throughout all experiments. The pH of the solution was adjusted using 0.1 N HCl and 0.1 N NaOH. In blank experiments, the influence of iodate was examined in the presence of  $\text{IO}_3^-$  alone, under UV irradiation, and with the  $\text{TiO}_2$  suspension.

#### 4. Conclusions

The primary aim of this study was to evaluate the performance of iodate-assisted photocatalysis to purify an aqueous solution of safranin O (SO). Based on what was presented in the experimental results, the studied system demonstrated a high efficiency of SO degradation compared to the other systems, namely  $\text{IO}_3^-$  sole, UV/ $\text{IO}_3^-$ , and UV/ $\text{TiO}_2$ . The degradation rates significantly accelerated with increasing  $\text{IO}_3^-$  and photocatalyst concentrations in the studied range. However, beyond 50 mM of  $\text{IO}_3^-$ , the degradation slowed. Though not expected, the acidic media was more favorable for SO destruction, whereas the temperature variation had a negligible influence. The investigation of the impact of inorganic anions on the process efficiency showed an adverse effect, which was less important in the presence of chloride ( $\text{Cl}^-$ )- and sulfate ( $\text{SO}_4^{2-}$ )-, and more pronounced in bicarbonate ( $\text{HCO}_3^-$ )- and nitrite ( $\text{NO}_2^-$ )-containing solutions. The addition of humic substances negatively affected the dye decay, especially at  $20 \text{ mg}\cdot\text{L}^{-1}$ , as a result of their strong adsorption on the  $\text{TiO}_2$  surface. These findings allowed us to clearly demonstrate the behavior of the UV/ $\text{TiO}_2$ / $\text{IO}_3^-$  system toward SO decay in various water matrices. The degradation inhibition in mineral water could be due to the presence of  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  at more than 1 mM. In seawater, the excess of chloride anions hampered the UV light penetration, thus limited oxidation occurred.

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