

Detoxification of diluted azo-dyes at biocompatible pH with the oxone/ Co^{2+} reagent in dark and light processes

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Abstract

Accelerated bleaching and photobleaching of diluted solutions of Methyl Orange and other dyes occur only when Co^{2+} -ions are present in solution mediating oxone ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) decomposition. The bleaching of Methyl Orange, Orange II and Methylene Blue dyes in dilute solutions (0.01 mM) proceeds within a few minutes and occurs at biocompatible pH leading to a decrease in the toxicity of the initial solution under simulated daylight radiation. A reduction in the toxicity of 35% was observed at biocompatible pH-values when a solution Orange II (0.01 mM) was irradiated in the presence of oxone (0.06 mM)/ Co^{2+} (0.004 mM). Only traces of Co^{2+} were necessary to accelerate the decomposition of the dyes in the presence of oxone in the dark and even more under daylight irradiation. The photobleaching proceeds with a photonic efficiency of ~ 0.24 . The solution parameters were optimized for the photobleaching of azo-dyes by the oxone/ Co^{2+} reagent. H_2O_2 generation was observed to be possible only as long as Orange II was present in the solution. The decomposition kinetics of H_2O_2 was followed under solar radiation. The dye decomposition was also investigated as a function of the applied light intensity. No saturation effects were observed when simulated solar light with 90% AM1 was applied. The photobleaching reaction proceeded with acceptable kinetics with light intensities 5–10 times lower than AM1. This makes the photocatalytic treatment suitable under diffuse daylight.

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1. Introduction

Dyes and organic compounds decomposition in waste water effluents by Advanced Oxidation Technologies has become an important subject of research during the last decade [1]. This subject has actively been the focus of research out of many laboratories and practical solutions for industrial processes able to sustain long-term efficient operation have to be found [2].

The objective of this study is to explore, optimize, and test the experimental parameters for the oxone/ Co^{2+} reagent that allows the degradation of commercial textile dyes at a low concentration. By this approach, no costly pH adjustment is needed before or after the photocatalytic pre-treatment. The detoxification introduced by the dyes and the catalytic reagent will be assessed by a routine method used in toxicological studies. Recently, light enhanced homogeneous Fenton systems have

been widely reported. But either initial acidification of polluted wastewaters and post-neutralization of the iron species precipitation was necessary in Fenton systems. This is costly in terms of time, chemical reagents and labor.

The catalytic decomposition of oxone by Mn^{2+} and Cu^{2+} -ions [3] and also in the presence of Co^{2+} -ions have been known for some time [4–6]. The present investigation addresses the kinetics of the photobleaching of azo dyes diluted solution. The observed kinetics was drastically accelerated when Co^{2+} -ions mediate the photocatalysis under daylight irradiation. In the presence of Co^{2+} -ions, oxone has been reported [5–7,9] to generate a variety of highly oxidative sulphate radicals in aqueous solution.

Oxone is an oxidant used in organic synthesis, analytical chemistry, catalysis and degradation of organic pollutants [3–9]. The redox potential of the radical generated by oxone [5,10,11], $\text{HSO}_5^- \rightarrow \text{HO}^\bullet + \text{SO}_4^{\bullet-}$, $E^0 = 1.82 \text{ eV}$ is higher than the potential of the radicals generated by H_2O_2 ($\text{H}_2\text{O}_2 \rightarrow 2\text{HO}^\bullet$, $E^0 = 1.76 \text{ eV}$ when used as the oxidant in dark or in the light activated decomposition of dyes and organic compounds.

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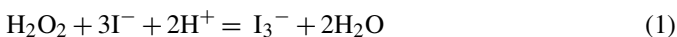
2. Experimental

2.1. Materials

Methyl Orange, Orange II, Methylene Blue, oxone ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, NaOH and KI were Fluka products and used as received. Solutions were prepared by dissolving in Milli-Q water.

2.2. Bleaching reactions and analytical methods

Solutions were prepared by mixing appropriate concentration of the appropriate dye, Co^{2+} , and oxone in this sequential order. The dye bleaching reactions were followed by measuring the optical density at the peak of Methyl Orange, Orange II and Methylene Blue absorption bands at $\lambda = 465$, 486 and 665 nm, respectively in a Hewlett-Packard 38620N diode array spectrophotometer. The pH-values were measured by pH meter Copenhagen 701. H_2O_2 concentration was measured using the colorimetric method developed by Hochanadel [13,14]. The iodide-ion was oxidized in neutral or slightly acidic solution and the absorption of I_3^- was measured at $\lambda = 354$ nm. The iodide reagent was prepared immediately before using by mixing equal volumes of two solutions containing: (a) 66 g KI, 2 g NaOH and 0.4 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ /l with (b) 20 g $\text{KHC}_8\text{H}_4\text{O}_4$ /l. A measured volume of the sample was diluted to a specified volume with distilled water and the reagent used. The optical densities for sample and blank were measured following the I_3^- absorption peak with $\epsilon = 26,000 \text{ M}^{-1} \text{ cm}^{-1}$ (354 nm). The iodide reacts in a 3:1 ratio with H_2O_2 according to the relation



The Merckoquant (Merck AG) test for quantitative determination of peroxides was used as a second method to confirm the results obtained by the iodometric test.

2.3. Irradiation procedures

The photochemical reactor consisted of 80 ml cylindrical Pyrex flask each containing 60 ml of solution. Irradiation of the cylindrical reactor were carried out in the cavity of a Suntest solar simulator (Hanau, Germany) air cooled at 45°C . The Suntest lamp emitted 5–6% of the photons between 290 and 400 nm. The profile of the photons emitted between 400 and 800 nm followed the solar spectrum with a light intensity at 70 mW/cm^2 corresponding to 70% of AM1 full solar light intensity. The radiant flux was monitored by an ISI Corporation power meter of Yellow Springs, Co., USA.

2.4. Toxicity determination via the *Vibrio fischeri* bio-assay

The effect of Orange II and the intermediates produced in the solution during the photocatalytic pre-treatment on the luminescence of the bacterium *Vibrio fischeri* (Microtox test) was carried according to AFNOR NFT 90-320 (Fluorescence Test in Bacteria, German Din-Norms 38412 (L 34) 1991). Essentially, this test measures the luminescence inhibition of *Vibrio fischeri*.

The concentration that inhibits 50% of the bacterial luminescence is expressed as CE_{50} and this value is converted in (units of toxicity) by the expression $\text{UT}_{50} = 100/\text{CE}_{50}$. These toxicity units are dimensionless and always take into consideration the value of the control sample. The control sample was the growth medium of *Vibrio fischeri*. During the pre-treatment of the dye Orange II, the residual H_2O_2 produced in solution was eliminated by the addition of peroxidase. The initial pH for the five samples pre-treated at different times for the toxicology determination was adjusted to 6.5 by a solution of NaOH (0.1 M) before the carrying out the Microtox test. The measurements were carried out in a salt solution (2% NaCl) since the bacteria used is of marine origin.

3. Results and discussion

3.1. Effect of Co^{2+} and oxone concentration on the bleaching and photobleaching of Methyl Orange

Fig. 1A shows the bleaching (dark process) of diluted Methyl Orange (0.01 mM) in the presence of oxone (0.06 mM) as a function of the increasing concentration of Co^{2+} -ion. The bleaching increases with the concentration of Co^{2+} -ion added up to trace (f) for the highest Co^{2+} concentration added in solution. The control experiment in Fig. 1A (trace a) indicates that no Methyl Orange bleaching takes place in the absence of oxone. Fig. 1A also shows that the bleaching of Methyl Orange dye in the presence of Co^{2+} was accelerated in relation to the bleaching observed when oxone was added in the absence of the Co^{2+} (Fig. 1A, trace b), the oxone decomposition becomes faster due to the added Co^{2+} -ions as recently reported [7–9]. In the case of relatively concentrated solutions of dyes and oxone [9], the solutions contained about 20 times higher concentrations of azo dye and about 100 times higher concentration of oxone in relation to Co^{2+} -ion concentration. The initial pH dropped from pH 5.9 to about 2 upon oxone addition. In the present study by using much lower concentrations of Methyl Orange and oxone (Fig. 1A), the pH of the solution did not change with respect to the initial pH of 4.3 after the bleaching process (Fig. 1A, traces b–f). This makes possible to carry out the azo dye bleaching using the oxone/ Co^{2+} reagent at biocompatible pH values as it will be shown in later sections of this study. Doubling the concentration of oxone (0.06 mM) did not accelerate of the photobleaching kinetics of Methyl Orange.

Fig. 1B shows the bleaching of Methyl Orange under the same experimental conditions as used in Fig. 1A, but at an initial pH of 10.5. This pH was observed to remain constant during the bleaching process. The bleaching kinetics and efficiency was observed to be lower than the one observed in Fig. 1A, but Methyl Orange bleaching increased as a higher concentration of Co^{2+} -ions were added to the solution.

Fig. 1C shows the photobleaching (Suntest light, 70 mW/cm^2) of diluted of Methyl Orange (0.01 mM) in the presence of oxone (0.06 mM) as a function of increasing concentration of Co^{2+} -ion. The results show that the photobleaching kinetics is considerably enhanced with respect to the bleaching kinetics reported in Fig. 1a. Nevertheless the TOC

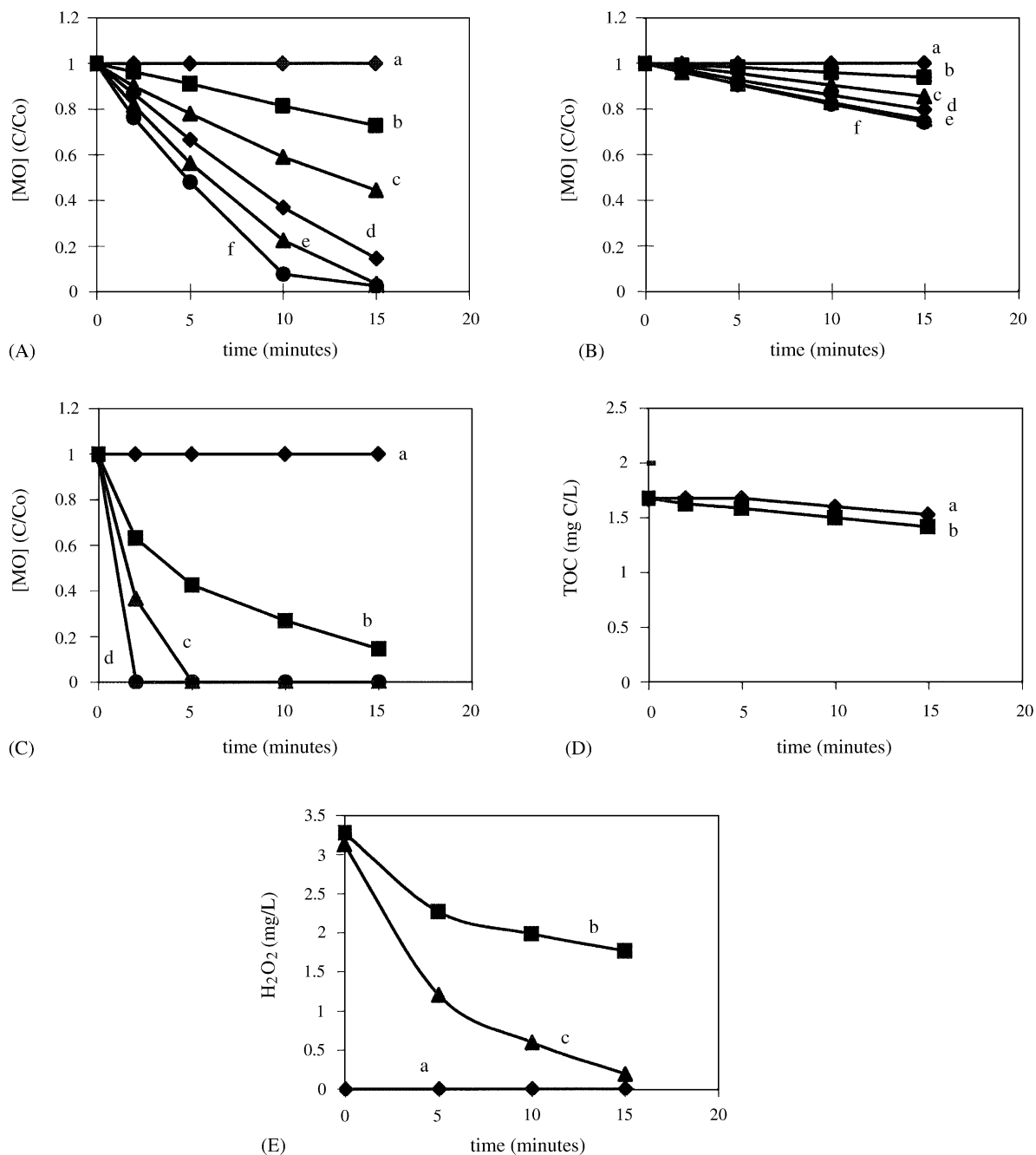


Fig. 1. (A) Bleaching of Methyl Orange (0.01 mM) at pH 4.3 in the dark: (a) Methyl Orange alone at pH 5.9, (b) Methyl Orange + oxone (0.06 mM), (c) (b) + Co²⁺ (0.001 mM), (d) (b) + Co²⁺ (0.002 mM), (e) (b) + Co²⁺ (0.003 mM) and (f) (b) + Co²⁺ (0.004 mM). (B) Bleaching of Methyl Orange (0.01 mM) at pH 10.5: (a) Methyl Orange at pH 10.7, (b) Methyl Orange + oxone (0.06 mM), (c) (b) + Co²⁺ (0.001 mM), (d) (b) + Co²⁺ (0.002 mM), (e) (b) + Co²⁺ (0.003 mM) and (f) (b) + Co²⁺ (0.004 mM). (C) Photobleaching (Suntest light, 70 mW/cm²) of Methyl Orange (0.01 mM) at pH 4.3: (a) Methyl Orange alone at pH 5.9, (b) Methyl Orange + oxone (0.06 mM), (c) Methyl Orange + oxone (0.06 mM) + Co²⁺ (0.001 mM) and (d) Methyl Orange + oxone (0.06 mM) + Co²⁺ (0.004 mM). (D) TOC decrease as a function of time: (a) Methyl Orange (0.01 mM) + oxone (0.06 mM) + Co²⁺ (0.004 mM) in the dark (pH 4.3) and (b) Methyl Orange (0.01 mM) + oxone (0.06 mM) + Co²⁺ (0.004 mM) under Suntest light (70 mW/cm²) (pH 4.3). (E) Decrease of H₂O₂ produced in solution containing Methyl Orange (0.01 mM) at pH 4.3 (Suntest light, 70 mW/cm²): (a) Methyl Orange alone at pH 5.9, (b) Methyl Orange + oxone (0.06 mM) + Co²⁺ (0.001 mM) and (c) Methyl Orange + oxone (0.06 mM) + Co²⁺ (0.004 mM).

of these solutions in the presence of the oxone/Co²⁺ catalyst decreases less than 10% as shown in Fig. 1D.

When oxone was added in the solution containing organic compound(s), the formation of peroxides (ROOH + H₂O₂) due

to radical chain processes has been widely reported [7–9]. This reaction is accelerated in the presence of oxone/Co²⁺. The simplified mechanism of organic peroxide decomposition generating the radicals necessary for the photobleaching of azo dyes

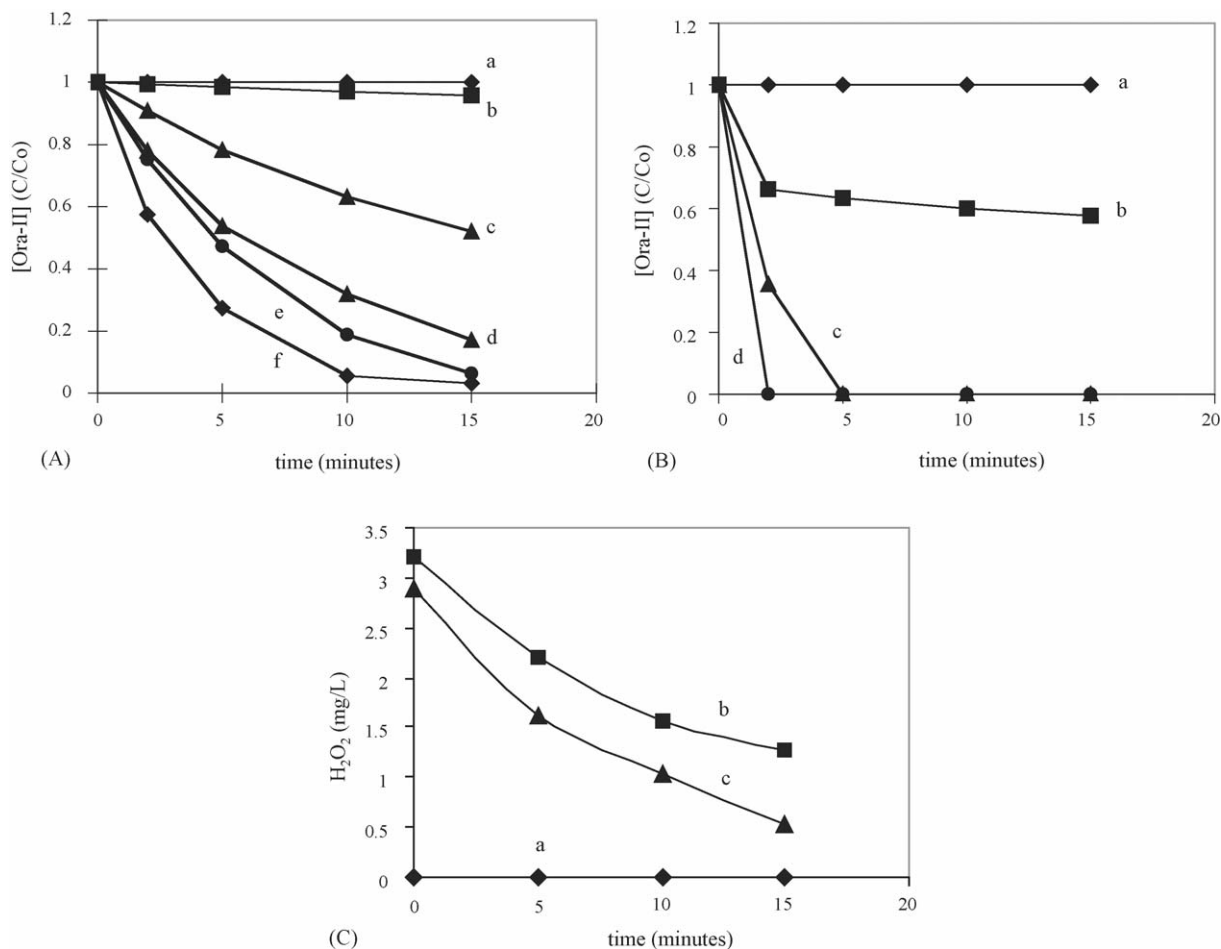


Fig. 2. (A) Bleaching of Orange II (0.01 mM) at pH 4.3 in the dark. (a) Orange II alone at pH 5.9, (b) Orange II (0.01 mM) + oxone (0.06 mM), (c) (b) + Co²⁺ (0.001 mM), (d) (b) + Co²⁺ (0.002 mM), (e) (b) + Co²⁺ (0.003 mM) and (f) (b) + Co²⁺ (0.004 mM). (B) Photobleaching (Suntest light, 70 mW/cm²) of Orange II (0.01 mM) at pH 4.3. (a) Orange II alone at pH 5.9, (b) Orange-II + oxone (0.06 mM), (c) Orange-II + oxone (0.06 mM) + Co²⁺ (0.001 mM) at pH 4.3 and (d) Orange II + oxone (0.06 mM) + Co²⁺ (0.004 mM). (C) Decrease of H₂O₂ produced in solution containing Orange II (0.01 mM) at pH 4.3 (Suntest light, 70 mW/cm²). (a) Orange II alone at pH 5.9, (b) Orange II + oxone (0.06 mM) + Co²⁺ (0.001 mM) at pH 4.3 and (c) Orange II + oxone (0.06 mM) + Co²⁺ (0.004 mM).

has been reported recently [15]:

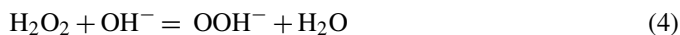


The consumption of H₂O₂ generated almost instantly was tested and the experimental data is shown in Fig. 1E. Runs in the absence of light showed a negligible formation of H₂O₂ confirming that the generation of peroxides is a light activated process [9,15]. H₂O₂ values reported in Fig. 1C are on the basis of I₃⁻ and the stoichiometry noted above in Eq. (1).

The decrease in the bleaching kinetics observed in Fig. 1B at pH 10.5 was due to decomposition of H₂O₂ at higher pH (see reaction (1)) since H₂O₂ has a pK_a of 11.63:



At more basic pH values, H₂O₂ also reacts with OH⁻ to form perhydroxyl anion OOH⁻ [12]:



The perhydroxyl anion reacts further with H₂O₂. This reaction is responsible for the instability observed for H₂O₂ in basic media

releasing with the concomitant release O₂:



3.2. Effect of Co²⁺ and oxone concentration on the bleaching and photobleaching of Orange II

Fig. 2A shows that the kinetics and efficiency of the bleaching of Orange II is very similar to the one reported in Fig. 1A for Methyl Orange under the same conditions. The initial pH of 4.3 of Orange II (Fig. 2A) did not change during the course of the reaction and this observation was valid also for initial pH values up to 10.4. This means that addition of oxone to dilute dye solutions as usually found in lakes and water reservoirs in Europe, Africa and India allows the bleaching by the oxone/Co²⁺ reagent without a significant drop in pH. A significant drop in pH was observed only when higher concentrations of oxone were added to more concentrated solutions of Orange II (~20 mM) [7–9] as stated above. The addition of (Fe³⁺, Mn²⁺, Cu²⁺) [8] or Co²⁺ [7,9] in concentrations ~1 mM to dye solutions were shown to mediate oxone decomposition

in the concentration range 6–25 mM leading to effective dye photobleaching.

The relative photonic efficiency relates the reactant disappearance (Orange II) to the incident photon flux on the reactor cell walls in a defined time interval. This number allows the standardization of photochemical processes when using different experimental conditions in different laboratories. In Fig. 1a, the photonic efficiency (PE) for the photobleaching of Orange II is calculated from the relation:

$$\text{photonic efficiency} = \frac{\text{molecules of Orange II reacted}}{\text{quanta reaching reactor wall}} \quad (6)$$

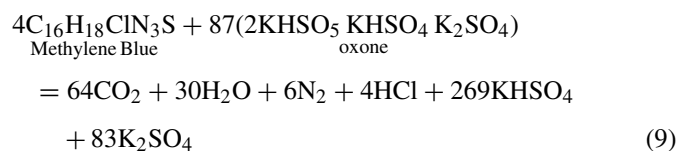
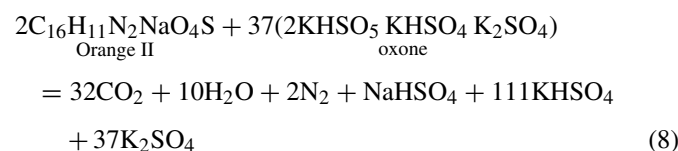
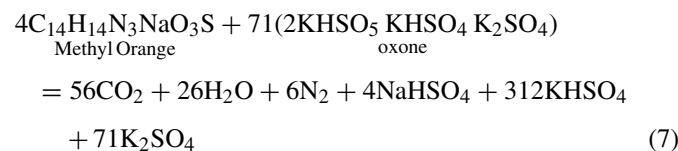
Taking the Suntest light flux as $1.6 \text{ photons/s} \times \text{cm}^2$, the solution volume in the reactor as $\sim 50 \text{ ml}$ and a cell wall surface of 48.8 cm^2 , the photobleaching of Orange II (0.01 mM) within 10–15 min proceeds with a photonic efficiency of ~ 0.24 (Fig. 2a).

Fig. 2B shows the photobleaching of diluted Orange II (0.01 mM) under Suntest irradiation increases as a function of Co^{2+} -ion concentration in the presence of oxone. Comparing Fig. 2B with Fig. 2A, it is found that photobleaching accelerates the decomposition of Orange II. The consumption of H_2O_2 that occurs concomitantly to Orange II decomposition was tested and the experimental data is shown in Fig. 2C.

The bleaching and photobleaching of Methylene Blue (MB) were also tested with the oxone/ Co^{2+} reagent used in Figs. 1 and 2. The experimental data shows the same trend and efficiency as the bleaching and photobleaching of Methyl Orange and Orange II. Therefore, the oxone/ Co^{2+} reagent can be applied in the decomposition of a variety of dyes in the dark or under Suntest light.

3.3. Overall stoichiometry observed during dyes decomposition

The overall oxidation mechanism of azo dyes upon the addition of oxone and transition metals has recently been reported and will not be discussed further in this study [4–9,16]. The stoichiometry for the decomposition of dilute solutions of Methyl Orange, Orange II and Methylene Blue is described by Eqs. (7)–(9). Eqs. (7)–(9) show that the ratio between dye and oxone for Methyl Orange, Orange II and Methylene Blue is 1:17.75; 1:18.5; 1:21.75, respectively. Co^{2+} -ions were observed in all cases to accelerate considerably the dye decomposition due to the generation of the oxidizing radicals produced by oxone in the dark and under light irradiation [9].



3.4. Photobleaching of orange II by the oxone/ Co^{2+} reagent at biocompatible pH-values in the dark and under light

Fig. 3 shows the photobleaching of Orange II in the presence of oxone/ Co^{2+} reagent starting at pH ~ 8 . By inspection of Fig. 3, it is readily seen that in the dark (trace a), that after 2 min the pH decreases from 8.05 to 6.71 (see trace a). Under light irradiation of 20 mW/cm^2 , the Orange II photobleaching kinetics become more efficient and the final pH decreased to 6.01 (see trace b). When the intensity of the Suntest irradiator was increased to 90 mW/cm^2 , the photobleaching of Orange II is further enhanced and the final pH attains 4.96 as seen in Fig. 5, trace c). Using the Aberchrome 540 actinometry [17] a value of $0.4 \times 10^{16} \text{ photons/s} \times \text{cm}^2$ was found when the Suntest irradiator was set at 20 mW/cm^2 . Fig. 3, trace b shows that the discoloration of Orange II is 80% after 2 min. Under these circumstances it is interesting to see if applying a light intensity of 90 mW/cm^2 , saturation is attained for the absorption of photons by this solution. But applying this higher light intensity of 90 mW/cm^2 , the discoloration kinetics did not improve considerably over the kinetics observed when applying 20 mW/cm^2 . Taking in Fig. 3 Orange II (0.01 mM) concentration, we estimate a $6 \times 10^{16} \text{ molecules/ml}$ of Orange II in the 50 ml reactor with a cell wall surface of 48.8 cm^2 . Since the incident photonic density at 90 mW/cm^2 is $1.6 \times 10^{16} \text{ photons/s} \times \text{cm}^2$, the concentration of Orange II molecules/ cm^2 close to the reactor walls is still ~ 4 times above the photonic density of the incident light. Other factors like reaction mechanism, long-lived intermediates and activation energies will then be more important

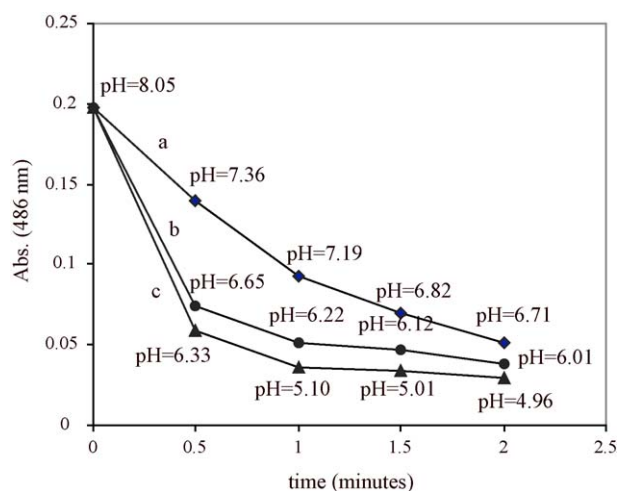


Fig. 3. Photobleaching of Orange II (0.01 mM) in the presence of oxone (0.06 mM) and Co^{2+} (0.004 mM) in the dark and as a function of light intensity. Traces: (a) dark run, (b) run under Suntest irradiation (20 mW/cm^2) and (c) run under Suntest irradiation (90 mW/cm^2).

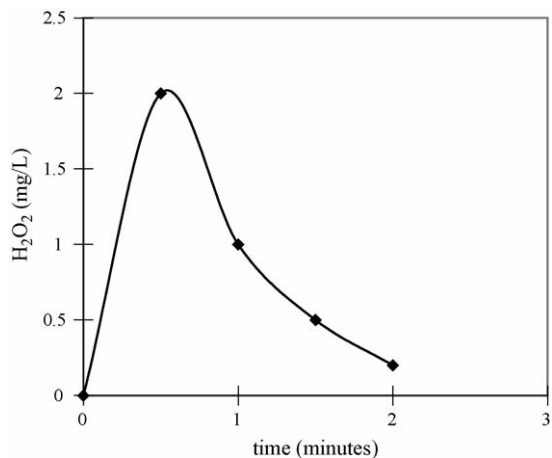


Fig. 4. Evolution of the H₂O₂ concentration for a solution of Orange II (0.01 mM) in the presence of oxone (0.06 mM) and Co²⁺ (0.004 mM) under Suntest irradiation (20 mW/cm²). Initial solution pH 8.05.

determining the photobleaching kinetics of Orange II shown in Fig. 3.

Fig. 4 shows the H₂O₂ concentration in solution during photobleaching of Orange II solution in the presence of the oxone/Co²⁺ reagent. It is readily seen that the concentration of H₂O₂ initially increases and then decrease as H₂O₂ is consumed during the dye photobleaching process. At times ≤0.5 min, the orange color of the Orange II was still observed in solution. The peroxide formation stopped after 0.5 min when Orange II azo-dye was used up and the color in the solution disappears. Fig. 4 shows that the intermediates of Orange II degradation were not able to participate in the photogeneration of H₂O₂. After half-minute, the H₂O₂ produced either decomposes or reacts with the long-lived intermediates left in the solution [15]. In the dark no formation of H₂O₂ was observed in solution (Fig. 4).

3.5. Evolution of the toxicity of Orange II due to the photocatalytic pre-treatment

Fig. 5 shows the evolution of the toxicity when an Orange II solution was irradiated in the Suntest cavity in the presence of the oxone/Co²⁺ reagent with an initial solution pH of 8.05.

The points a, b, c, d and e in Fig. 5 refer to Orange II pre-treatment times of 0, 0.5, 1, 1.5 and 2 min. Each of these points is the result of an independent experiment and not the result of the toxicological determination of one single run sampled at different times. The highest value of the toxic unit in the ordinate (Fig. 5) is 2.3 at time zero. The reduction of the toxicity of the solution in Fig. 5 due to the photocatalytic pre-treatment is of the order of 35% when pre-treating with the oxone/Co²⁺ reagent. The toxicity value at time zero for the Orange II solution in Fig. 5 is relatively low with a value of UT₅₀ ≤ 3 [18,19]. Due to the pre-treatment used, this value can be further decreased but not in a significant way. The oxone/Co²⁺ reagent seems to be within the norms of the European Economic Community (EEC) since the concentration of Co²⁺ necessary was 0.004 mM or 0.2 mg/l. This value is only slightly above the limits allowed for other toxic metal-ions in drinking water. In this case, the oxone/Co²⁺

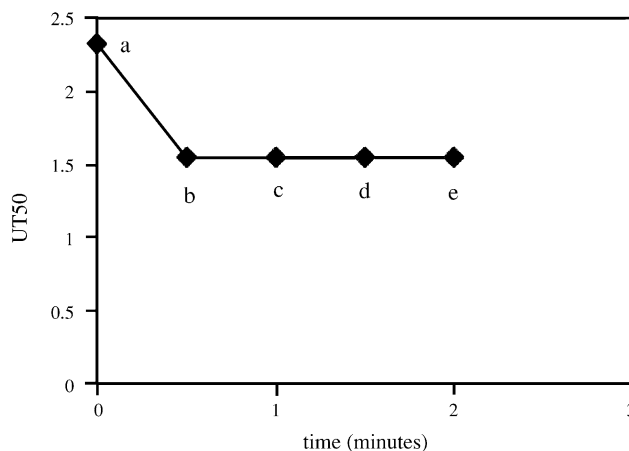


Fig. 5. Changes in acute toxicity as measured by the *Vibrio fischeri* bioassay for five different samples as a, b, c, d and e of Orange II (0.01 mM) irradiated at 90 mW/cm² (Suntest) in the presence of the oxone (0.06 mM)/Co²⁺ (0.004 mM) reagent. The toxicology units are shown in the ordinate. For other details see text.

reagent could be used for waste water recycling and reuse [20]. The remaining Co²⁺-ions could be precipitated at pH-values between 6.8 and 8.5 to scavenge the Co²⁺-ions in the treated solutions.

4. Conclusions

In the dark or under irradiation, the oxone/Co²⁺ reagent accelerates the bleaching and photobleaching of diluted dye solutions in acidic, neutral and alkaline solution. Small amounts of cobalt-ions show a striking effect. The bleaching and photobleaching of dye within the photocatalysis time depend on the solution pH, oxone and cobalt concentration and structure of the model dye used. The use of the oxone/Co²⁺ reagent is possible with no pH adjustment after the pre-treatment at biocompatible pH-values. This is an important aspect considering that water pre-treatment is followed generally by the lower cost secondary biological treatment in municipal wastewater station that functions only at biocompatible pH-values. The initial toxicity of the dye is decreased 35% using the oxone/Co²⁺ reagent under Suntest irradiation. The oxone/Co²⁺ reagent might be an attractive alternative remediation technology since the concentration of Co²⁺ used is in the μg/l range, the limit allowed for other toxic metals-ion.

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