

Photobleaching and mineralization of Orange II by oxone and metal-ions involving Fenton-like chemistry under visible light

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Abstract

Cu²⁺ and Fe³⁺ significantly improved the Orange II photobleaching and mineralization in the presence of oxone. In the presence of Cu²⁺ and Fe³⁺ the oxone needed for the photobleaching and total mineralization of the dye was determined along other solution parameters. In air, the photobleaching of Orange II in solution was observed to be complete within 60 min for Cu²⁺-ions and 30 min for Fe³⁺-ions showing a considerable faster kinetics with respect to other treatment systems reported until now. The transition metal-ions used seem to couple with oxone forming high oxidizing sulfate species. A reaction mechanism leading to Orange II photobleaching is suggested through a complex formation between the metal-ion and Orange II involves redox reactions activated by visible light.

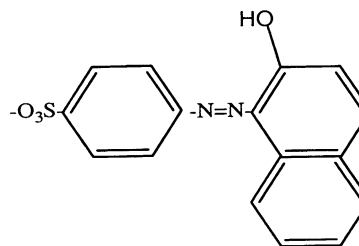
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Keywords: Orange II photobleaching; Orange II mineralization; Peroxymonosulfate; Oxone; Metal-cations; Photocatalysis

1. Introduction

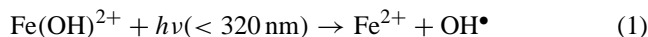
It is known that azo-dyes are bio-recalcitrant compounds existing in a wide concentration range in industrial effluents [1–4]. Apart from the various traditional methods of removing these azo-dyes: carbon adsorption, reduction by borohydride, membrane filtration, reverse osmosis and flocculation, new destructive oxidative processes for complete mineralization of azo-dyes leading to carbon dioxide and water have been gaining attention during the last decade. Studies on the toxicity of the breakdown products by chemical oxidation of the metabolites in chemical-biological treatment during the degradation processes become increasingly necessary. Advanced oxidation technologies (AOTs) involve light activation leading to the decomposition of the oxidant H₂O₂ in the presence of metal-ions in processes involving metal-ion peroxides [5–8].

In recent years it has been shown that molecular oxygen activated by solar simulated radiation was able to photobleach and degrade Orange II [9]. The Orange II molecule is:



Under visible light irradiation of Orange II in solutions saturated with O₂, photobleaching was found to occur within 4 h due to direct electron transfer from excited Orange II to O₂. The biological oxygen demand (BOD) values of the Orange II solutions pretreated by visible light irradiation in the presence of O₂ revealed the beneficial effect of photobleaching increasing the biodegradability of solutions compared to a pretreatment in the dark under the same experimental conditions [9].

Light activated Fenton reactions have shown to provide in diverse oxidative degradation processes OH• radicals due to the reaction (1) enhances the photo-assisted degradation of organic compounds [6,10]:



Reaction (1) presents a kinetics and an efficiency which are considerably higher with respect to the dark Fenton reaction due to the additional OH• radicals generated in solution

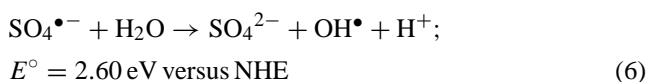
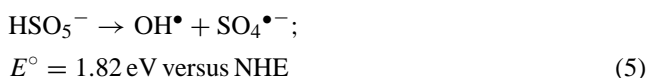
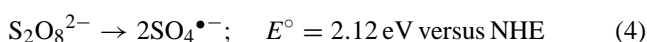
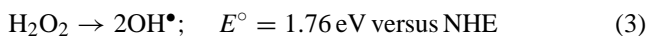
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under light):



Peroxymonosulfate, HOOSO_3^- (oxone) or more commonly noted as HSO_5^- , is a mono- SO_3^- substituted hydrogen peroxide (HOOH) and has been used in a restricted way as an oxidant in light induced processes. Unlike HOOH and peroxodisulfate ($\text{S}_2\text{O}_8^{2-}$), which are symmetrical peroxides, peroxymonosulfate is an unsymmetrical peroxide. It can liberate one sulfate radical anion ($\text{SO}_4^{\bullet-}$) and an hydroxyl radical and exhibit the properties of both $\text{S}_2\text{O}_8^{2-}$ and H_2O_2 as shown below. It can also undergo homolytic scission leading to oxidative radicals with the and produce sulfate redox radicals as shown in Eq. (6) below [11]:



The present study has investigated the photobleaching and mineralization of Orange II, taken as a model compound in the presence of the metal-ions, Mn^{2+} , Fe^{3+} or Cu^{2+} and oxone under solar simulated irradiation. The use of oxone is due to the fact that it has a higher oxidizing potential (1.82 V) than H_2O_2 (1.76 V) and in many cases intervenes in degradation processes in a more efficient way than peroxodisulfate ($\text{S}_2\text{O}_8^{2-}$) [12–14]. These two oxidants are frequently used in reactions involving advanced oxidation technologies for the mineralization of pollutants. Moreover, metal-ion catalyzed reactions of oxone have been reported to generate reactive oxidative radicals, $\text{SO}_4^{\bullet-}$, OH^\bullet and HSO_5^- involving chain oxidative processes leading to the mineralization of dyes [15,16]. The aim of our study is to show that metal-ions can accelerate the oxidation of Orange II taken as a model organic compound, since oxone has been used alone to oxidize recalcitrant pollutants but presents a kinetics that is too slow to be useful in practical applications.

2. Experimental

2.1. Materials

Orange II solutions were prepared by dissolving Orange II sodium salt (Fluka No. 75370, Orange II sodium salt) in distilled water. The solutions of Fe^{3+} and Mn^{2+} were prepared from $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (p.a. from Fluka). Oxone[®] [$2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$] and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were obtained from Aldrich (Cat No. 22803-6).

2.2. Irradiation procedures

The solar simulated light irradiation was carried out on cylindrical Pyrex reactor vessels (40 ml) with appropriate solutions of the dye, metal-ion and oxone. The oxone was always added at the end of the preparation, to the solutions. Light irradiation was carried out by means of a Hanau Suntest lamp (AM1, tunable in light intensity) equipped with an IR filter to remove the infrared radiation. The radiant flux of the Suntest solar simulator was measured with a power-meter (YSI Corp. Colorado, USA). The short wavelength radiation ($\lambda < 320 \text{ nm}$) was removed by the walls of the reaction vessels. The Orange II photobleaching was followed in a Hewlett-Packard 38620 N diode array spectrophotometer by following the optical density (o.d.) at the maximum of Orange II absorption ($\lambda = 486 \text{ nm}$). The organic carbon (TOC) was measured with a Shimadzu 500 TOC analyzer. Sulfate concentration was followed using a Dionex DX-100 ion-chromatograph, provided with an Ionpac AS14 column. The eluent consisted of a solution containing sodium carbonate (3.5 mM) and sodium-bicarbonate (1 mM).

3. Results and discussion

3.1. Catalytic activities of Mn^{2+} , Cu^{2+} and Fe^{3+} on the discoloration and mineralization of Orange II under light

Control experiments showed that neither photobleaching nor mineralization of Orange II was possible in the presence of Mn^{2+} , Fe^{3+} or Cu^{2+} -ions alone (sulfate or nitrate salts) in the dark or under Suntest irradiation. These experiments also indicated that (a) no appreciable photobleaching or mineralization of Orange II was observed in the presence of oxone alone or (b) in presence of oxone and the metal-ions mentioned above in the dark.

But if chloride salts of Mn^{2+} , Fe^{3+} or Cu^{2+} are used instead of the sulfate or nitrate salts to photocatalyze Orange II mineralization in the presence of oxone, Orange II photobleaching was observed in the dark and also under Suntest light irradiation. This latter observation was attributed to the chloride-ions undergoing a thermal reaction with oxone leading to in situ chlorine generation. In our case, the chlorine produced in solution reacts with Orange II leading to photobleaching of the dye. The latter process was accelerated when the amounts of chloride salt and oxone were increased, as expected in oxidative processes employing a higher concentration of oxidants. The validity of this process was confirmed in separate experiments where chlorinated solutions reacted with Orange II almost instantaneously. Ghosh et al. have reported the use of chlorine for the color removal processes of dyes in solution [17]. Many dyes have been effectively pre-treated by using chlorine in the form of a liquid or gas or by chlorine-water. Subsequently, the pre-treated waste waters are amenable to a biological degradation in a

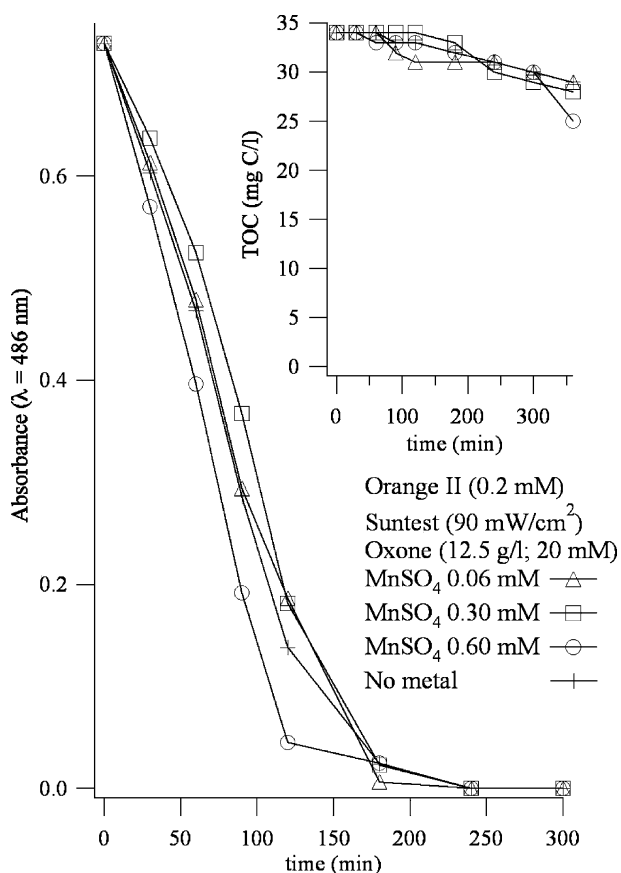


Fig. 1. Photobleaching of Orange II under visible light irradiation at pH 2 using oxone as an oxidant in the presence and in the absence of Mn²⁺-ions. For other experimental details see text. The insert shows the TOC reduction under the same experimental conditions.

municipal waste water treating station. However, the use of chlorine in oxidation processes for water detoxification is viewed with increasing disfavor since chlorine leads to the formation of chlorinated organic compounds in the presence of O₂ and light irradiation which are toxic and carcinogenic.

Figs. 1–3 show the catalytic activities of Mn²⁺, Cu²⁺ and Fe³⁺ in the presence of oxone. Photobleaching and mineralization of Orange II under Suntest light irradiation was observed. In a solution containing oxone (20 mM) and Orange II (0.20 mM), increased the photobleaching and mineralization of the dye solutions were observed in the order Fe > Cu > Mn (Fig. 4). The pH of the solutions at the beginning and at the end is around 2 as shown in Figs. 1–3. The photobleaching was measured by the decrease in the absorbance of the dye at λ = 486 nm. In all cases the photobleaching and mineralization of Orange II was seen to be accelerated with higher concentrations of metal-ions in solution. When using the highest concentration of the metal-ions [0.60 mM], the complete photobleaching was attained in about 240 min for Mn²⁺ in about 120 min for Cu²⁺ and in about 65 min for Fe²⁺. By inspecting of Figs. 1–3, two observations are noteworthy (a) the mineralization process starts or becomes important after the photobleaching process has been almost

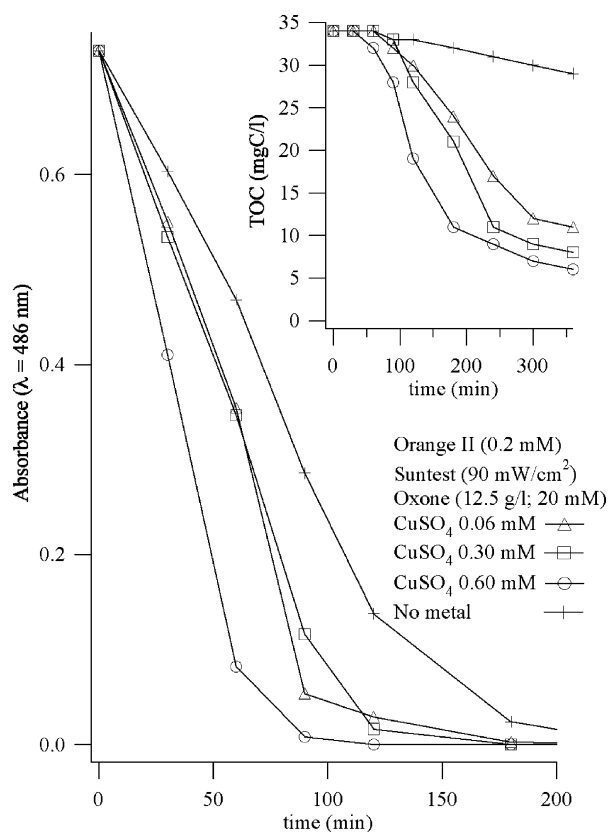


Fig. 2. Photobleaching of Orange II solutions under visible light irradiation at pH 2 using oxone as an oxidant in the presence and in the absence of Cu²⁺-ions. For other experimental details see text. The insert shows the TOC reduction under the same experimental conditions.

completed and (b) the TOC reduction within 300 min in the case of Mn²⁺ is only 12%, which is in the range of the results obtained in the absence Mn²⁺. Figs. 2 and 3 show that with 360 min of irradiation, the TOC decrease is 82% in the case of Cu²⁺ and 100% with Fe³⁺, respectively.

3.2. Photobleaching/degradation of Orange II solutions as a function of oxone concentration with a low fixed concentration of metal-ion

Figs. 5 and 6 show the effect of oxone concentration on the photobleaching and mineralization of Orange II when a low concentration (0.06 mM) of Cu²⁺ or Fe²⁺ was used. Figs. 5 and 6 show that the photobleaching/mineralization of Orange II (0.2 mM) solutions is strongly dependent on the concentration of added oxone in the range between 1.35 and 20 mM at a low concentration of Cu²⁺ or Fe³⁺. Figs. 5 and 6 show a strong concentration effect from the catalytic activities of both Cu²⁺ and Fe³⁺-ions towards Orange II photobleaching and TOC decrease in solution under light irradiation.

In the case of Cu²⁺ (0.06 mM) within 30 min of irradiation, the decrease of the dye optical absorption with respect to the initial concentrations of oxone follows the

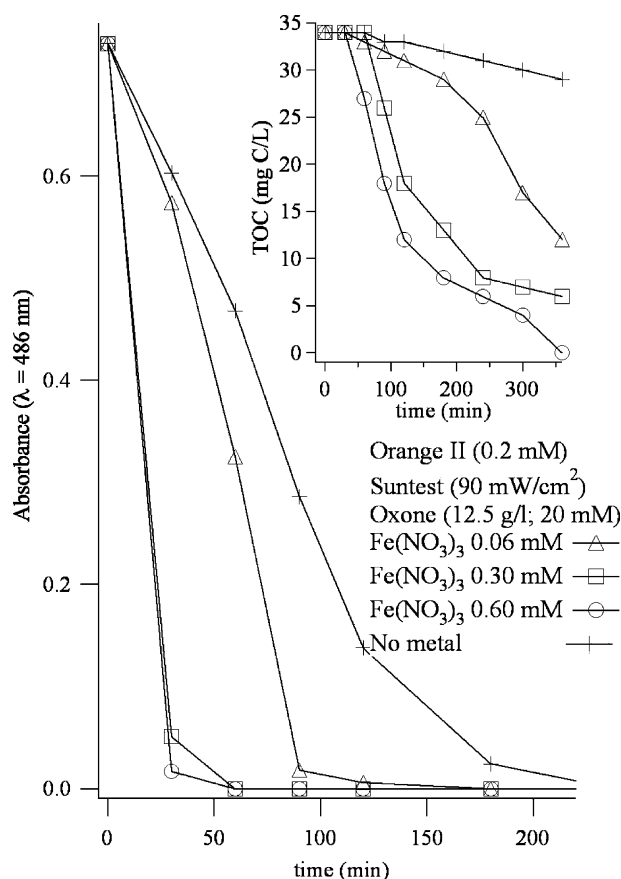
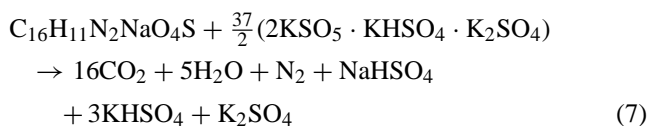


Fig. 3. Photobleaching of Orange II solutions under visible light irradiation at pH 2 using oxone as oxidant in the presence and in the absence of Fe^{3+} -ions. For other experimental details see text. The insert shows the TOC reduction under the same experimental conditions.

trend $5.4 \text{ mM} > 1.35 \text{ mM} > 20 \text{ mM} \sim 2.7 \text{ mM} > 10 \text{ mM}$. But after 60 min irradiation, the trend changed somewhat to $5.4 \text{ mM} \sim 2.7 \text{ mM} > 1.35 \text{ mM} > 10 \text{ mM} \sim 20 \text{ mM}$ indicating that the optimum oxone concentration for Orange II photobleaching was in the range 2.7–5.4 mM. For the reduction of TOC at 120 min the observed trend was $2.7 \text{ mM} \sim 5.4 \text{ mM} > 10 \text{ mM} > 20 \text{ mM} > 1.35 \text{ mM}$.

The approximate stoichiometry of Orange II decomposition in the presence of oxone under light irradiation can be noted as:



The stoichiometric amount of oxone needed to mineralize 0.2 mmol of Orange II is 3.7 mmol. This is within the range of the experimental results reported in Fig. 6. With an oxone concentration of 2.7 mM it was possible to reduce the TOC of Orange II from 35 to $\sim 3 \text{ mg C l}^{-1}$. However, after 360 min of irradiation, a maximum TOC decrease of $\sim 91\%$ was observed for oxone concentrations of 5.4–10 mM, but with an oxone concentration of 20 mM, the decrease of TOC

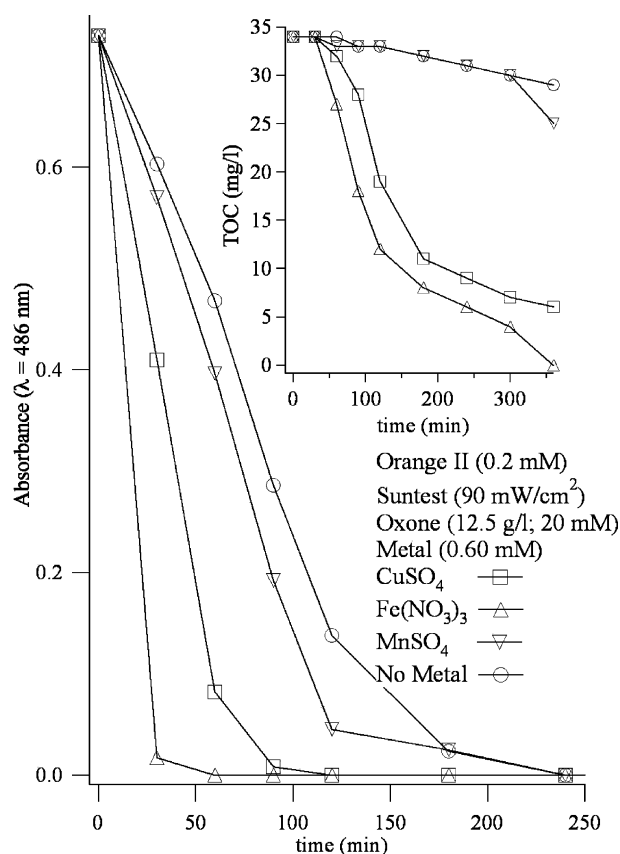


Fig. 4. Optimal results obtained for the photobleaching and mineralization of Orange II with no metal addition and in the presence of Mn, Cu and Fe-ions under visible light irradiation in oxone solutions. For other experimental details see text.

was $\sim 82\%$. This higher amount of oxone added seems to scavenge the highly oxidative radical $\text{SO}_4^{\bullet -}$ available in the solution.

Fig. 6 shows that in the case of Fe^{3+} discoloration of the dye takes place within 30 min and this process is independent of the oxone concentrations used. The minimum concentration needed for discoloration, with acceptable kinetics, was 1.35 mM. A 100% reduction of the Orange II TOC values within 369 min is observed in Fig. 6 using an oxone concentration of 20 mM. In Fig. 6 it is also seen that the most efficient reduction of the initial TOC values with respect to the oxone concentration takes place in the 2.7–5.4 mM region.

3.3. Effect of O_2 purging on the discoloration/mineralization of Orange II solutions

The effect of oxygen on Orange II solutions in the presence of Cu^{2+} and Fe^{3+} -ions is shown in Figs. 7 and 8. The effect of oxygen in the presence of light irradiation is not important during the photobleaching of Orange II solutions as shown in Figs. 7 and 8. The photobleaching of Orange II in the presence of Fe-ions is seen to be four times faster than in the presence of Cu-ions.

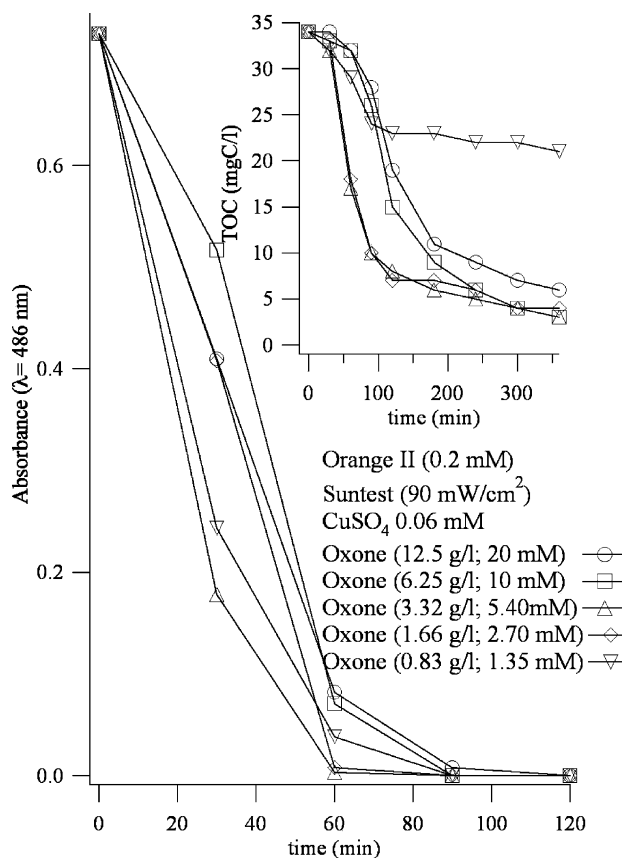


Fig. 5. Photobleaching of Orange II solutions under visible light irradiation in the presence of different concentrations of oxone and a fixed concentration of Cu-ions. For other experimental details see text. The insert shows Orange II mineralization under the same experimental conditions.

Figs. 9 and 10 show that within 90 min, Orange mineralization is complete with Cu^{2+} and in 60 min it is about complete with Fe^{2+} . The stoichiometric ratios of oxone to Orange II were 1:1 and 1:0.5 as noted in Figs. 9 and 10. The times for the TOC reduction are close to the photobleaching times previously shown in Fig. 7 for Cu^{2+} . But in the case of Fe-ions added to the solution (Fig. 10) the TOC reduction is a much longer process than the photobleaching presented in Fig. 8. Long-lived intermediates generated in the solution seem to need a much longer reaction time to be destroyed and allow the mineralization to proceed in the latter case.

3.4. Mechanistic considerations and suggested reaction scheme

As indicated by the results from the control experiments, no thermal reaction takes place between the metal-ions and oxone (see Figs. 1–6) and none was also observed between oxone and Orange II. The metal-ions used throughout this work do not absorb the Suntest radiation in the visible region as is the case with oxone with absorption at wavelengths below 300 nm. Hence, the only absorbing species is

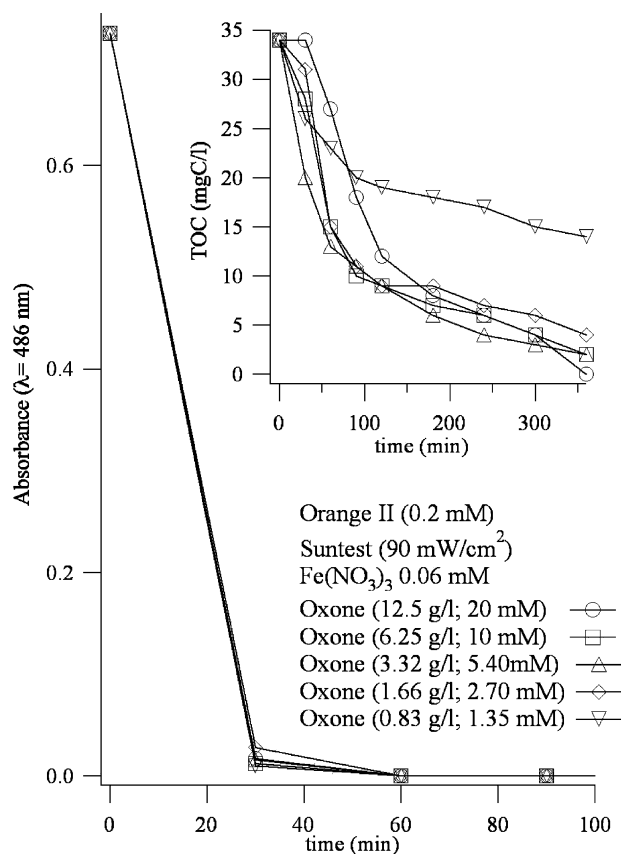
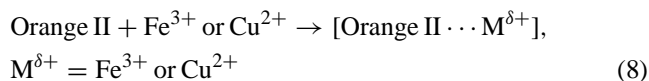


Fig. 6. Photobleaching of Orange II solutions under visible light irradiation in the presence of different concentrations of oxone and a fixed concentration of Fe-ions. For other experimental details see text. The insert shows mineralization under the same experimental conditions.

the dye. Bandara and Kiwi [9] have recently reported that the light absorption of Orange II in the presence of oxygen generates $(\text{Orange II})^{\bullet+}$ and $\text{O}_2^{\bullet-}$, the species responsible for photobleaching which is detected by fast kinetic laser spectroscopy. They have also determined the redox potential of the couple $\text{Orange II}^*/\text{Orange II}^{\bullet+}$ as -1.54 V (NHE). The very low catalytic reactivity of Mn^{2+} in the presence of oxone and the dye in the dark and under Suntest light irradiation shows that even though the redox potential of oxone is higher than the couple $\text{Mn}^{3+}/\text{Mn}^{2+}$ (1.51 V), the thermal reaction between oxone and Mn^{2+} seems to be kinetically inhibited. The catalytic activity of a $\text{Mn}^{2+}/\text{oxone}$ mixture was very close to the one observed during the photobleaching and mineralization of Orange II in the absence of the Mn^{2+} . Hence no reactive intermediate is formed through the thermal reaction between Mn^{2+} and oxone or Mn^{2+} and Orange II^* . With the other two metal-ions, Cu^{2+} and Fe^{3+} , the following reaction mechanism may be suggested for the mineralization mechanism of Orange II under Suntest visible light irradiation.



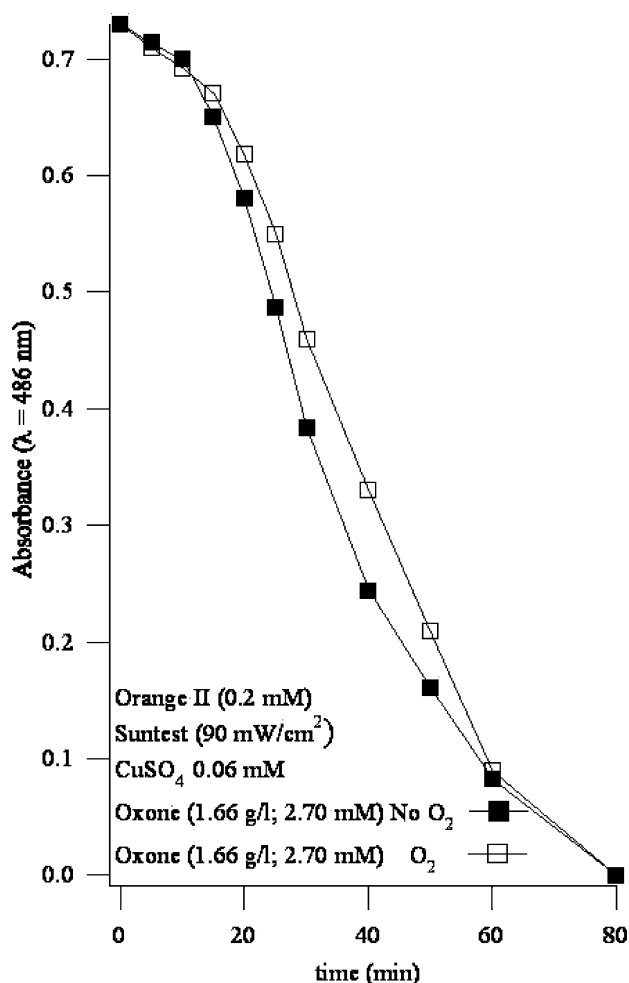


Fig. 7. Photobleaching of Orange II under visible light irradiation in solutions with oxone and Cu-ions in oxygen free and oxygen saturated solutions. For other experimental details see text.

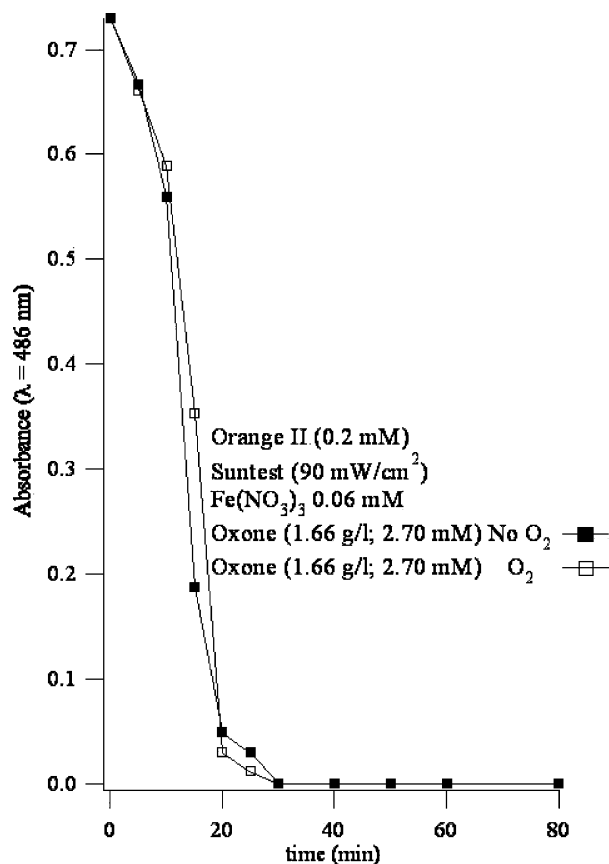
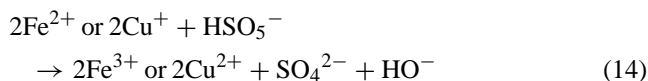
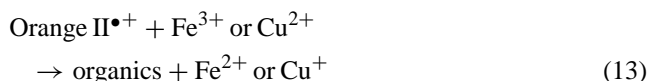
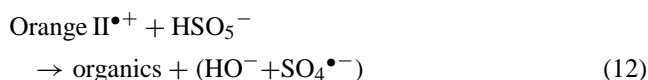
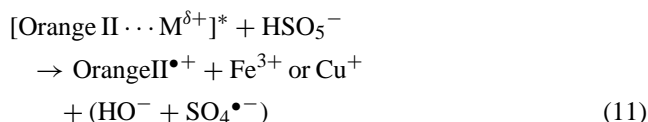
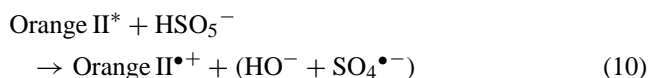
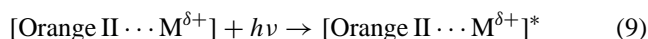
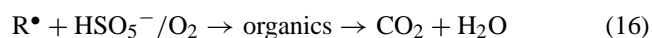
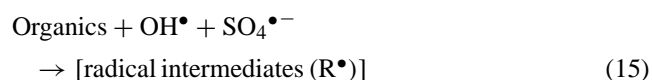
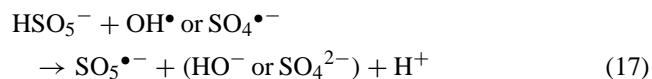


Fig. 8. Photobleaching of Orange II under visible light irradiation in solutions with oxone and Fe-ions in oxygen free and oxygen saturated solutions. For other experimental details see text.



and the possible side reactions



In the above mechanism, the formation of metal complexes (see reactions (8, 9 and 11) has been reported [8]. The reactions (10) and (11) involve one electron reduction of HSO_5^- (oxone) leading to the formation of OH^{\bullet} radicals [18,19]. The Fe^{3+} and Cu^{2+} in reactions (13) and (14) help to enhance the formation of the oxidative degradation products along with oxone. But it is not possible to ignore the formation of complexes between the oxidative degradation products formed and Fe^{3+} or Cu^{2+} reacting further with oxone [9]. Reactions (15) and (17) show chain oxidative reactions due to radical intermediates. Reaction (17) involves the destruction of OH^{\bullet} , $\text{SO}_4^{\bullet-}$ along oxone to form

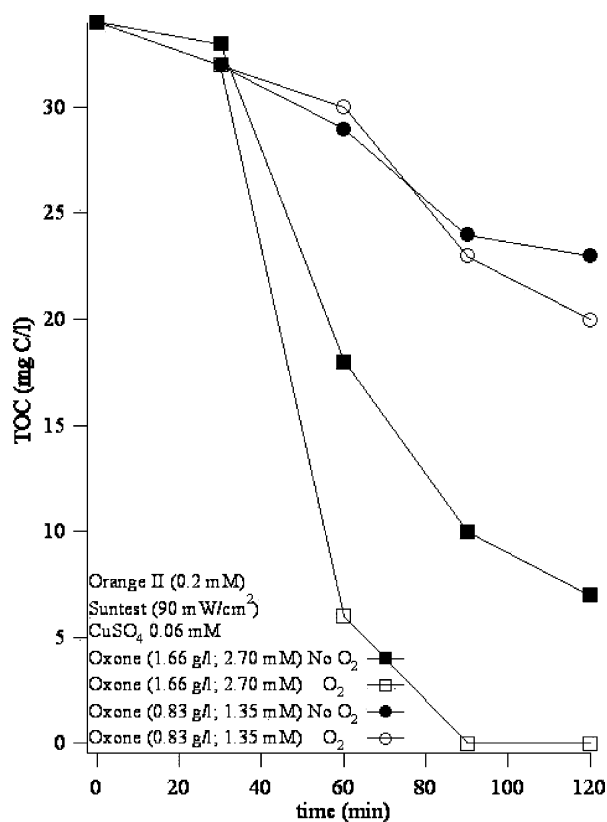


Fig. 9. Mineralization of Orange II under visible light irradiation in solutions with oxone and Cu-ions in oxygen free and oxygen saturated solutions. For other experimental details see text.

the less reactive radical, $\text{SO}_5^{\bullet-}$ (k_2 for OH^\bullet and $\text{SO}_4^{\bullet-}$ reactions with HSO_5^- are 1.7×10^7 and $\sim 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, respectively) [19]. This shows the effect of oxone concentration on the TOC reduction with a constant concentration of Orange II and metal-ions. For example in the case of Cu^{2+} (Fig. 5), using the optimum concentration range of oxone (2.7–5.4 mM) a further increase of oxone concentration (10–20 mM) makes the reaction (17) predominant in comparison to the TOC reduction. Similar results were observed with Fe^{3+} and reported in Fig. 6. Reaction (18) involving a radical (R^\bullet) becomes more important in the presence of oxygen. Almost all the reactions involving photocatalytic mineralization are carried out in the open atmosphere and the dissolved oxygen leads to peroxy radicals, ROO^\bullet ($\text{R} = \text{H}$, alkyl, aryl). These peroxy radicals are important and react with rate constants of $10^9 \text{ M}^{-1} \text{ s}^{-1}$ close to the diffusion control limit in aqueous solutions as it is the case of reaction (18) [22]. These peroxy radicals serve as chain propagators and oxidize organic materials either by hydrogen abstraction or by electron transfer processes [20,21]. In this investigation, all the experiments were carried out in the presence of atmospheric oxygen, this being available in a dilute aqueous solution with a concentration of 0.5 mM.

From the results presented for the light activated oxidation of Orange II mediated by Cu^{2+} , Fe^{3+} and Mn^{2+} -ions we

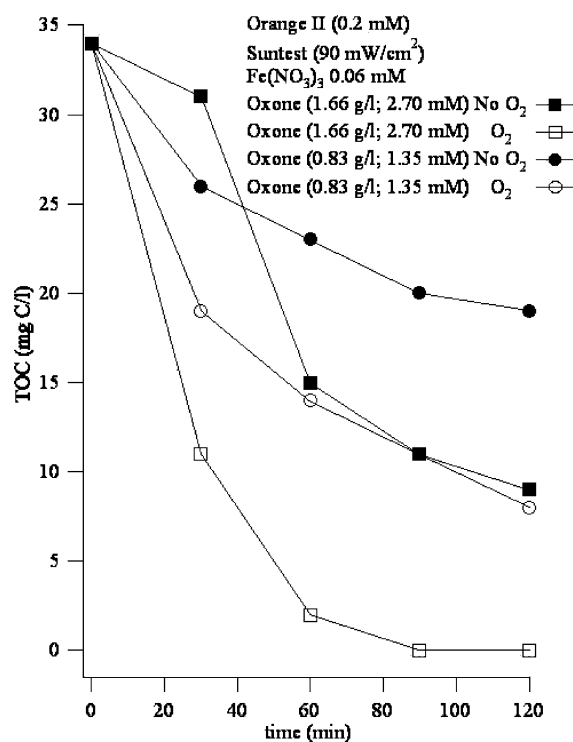


Fig. 10. Mineralization of Orange II under visible light irradiation in solutions with oxone and Fe-ions in oxygen free and oxygen saturated solutions. For other experimental details see text.

suggest that the thermodynamic values of the metal cations like the redox potentials do not account for the results obtained in this study. Many other factors seem to be playing an important role such as: ionic strength, concentration, temperature, hydration energies, size of the solvation shell, electronic transfer factors and stereoisomerism. The latter factors seem to play a controlling role in the observed photocatalysis.

4. Conclusions

This study introduces a novel approach based on advanced oxidation technologies for the photobleaching and mineralization of non-biodegradable persistent azo-dyes. The present approach is based on the generation of sulfate radicals similar to the OH^\bullet radicals to degrade organics in solution through the coupling of the oxidant with a selected transition metal.

Suntest solar simulated irradiation of Orange II in presence of oxone and the metal-ions, Cu^{2+} or Fe^{3+} is found to be an efficient process for the photobleaching and mineralization of Orange II. The photobleaching kinetics of Orange II was considerably improved with respect to: (a) oxone being used alone as an oxidant in the absence of the latter metal-ions and (b) TiO_2 under UV-Vis light irradiation needing a much longer time to photobleach/abate the

model dye. A photodegradation mechanism is suggested involving a dye-sensitized process with the formation of intermediate metal azo-dye complexes that are short lived and could not be detected by UV-Vis spectrophotometry. For a stoichiometric mixture of Orange II and oxone 1:1 in oxygen saturated solutions, Orange II photobleaching took place within 30 min for Cu^{2+} and 10 min for Fe^{3+} . The TOC reduction (mineralization) attained 100% within 90 and 60 min, respectively for Cu^{2+} and Fe^{3+} . These were the shortest times attained in this study and compare favorably with bleaching times reported for azo-dyes by other treatment methods [1–4].

Acknowledgements

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