

COMPARISON BETWEEN IONIZING AND NON-IONIZING RADIATION TECHNOLOGIES FOR WASTEWATER REMEDIATION

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Abstract

A study on the decomposition of a surfactant (SDBS) and of four emerging pollutants (ofloxacin, carbamazepine, benzophenone-3, benzophenone-4) in a multicomponent system is presented. These pollutants are decomposed in water by a few types of Advanced Oxidation Processes. The remediation methods included UV and γ -rays, all running in atmospheric conditions. It is shown that UV degradation methods can be improved by adding a photocatalyst (TiO_2), or a radical mediator (H_2O_2). The processes were monitored step by step, by determining the concentration of pollutants by UV, HPLC and a specific surfactant selective kit, and measuring the total organic carbon content.

1. Objective of the research

Many efforts to remediate wastewater are nowadays dedicated to the development of Advanced Oxidation Processes (AOPs), having the objective to destroy more and more efficiently the organic pollutants rather than separate them through filtration. Methods are requested therefore to join effectiveness and speed. However, as cost increases with treatment speed, it is necessary to tailor remediation processes to the quality, amount and fate of water to reuse. Our objective is then to explore and optimize some AOPs like EB, γ -rays, photocatalytic oxidation, UV photolysis, ultrasound cavitation and possibly any hybridization among them to offer a response to different remediation needs.

2. Introduction

The ubiquitous nature of $\cdot\text{OH}$ associated with its high reactivity and oxidative power has consequences of various type on the aquatic system and atmosphere. Therefore its production for basic knowledge, industrial needs and environmental preservation is matter of a wide range of investigations by governmental groups and private companies. Given that $\cdot\text{OH}$ attack to organic molecules and the subsequent cascade of radical reactions demonstrated already to achieve the destruction of a plenty of pollutants, nowadays these efforts focus on methods which join the effectiveness of remediation with higher speed and cheaper treatments. However, as cost increases with treatment speed, it seems wise to develop other methods, flexible enough to suit specific application scales and reuse purposes. By far the most efficient $\cdot\text{OH}$ producing method is performed by hitting water with an electron beam. However, as EB treatment becomes economically appealing when the effluent volumes exceed $1000 \text{ m}^3/\text{day}^1$, we planned to explore and compare the remediation performances of a few Advanced Oxidation Processes like EB itself, γ -rays, photocatalytic oxidation, UV photolysis and ultrasound cavitation.

Working in the frame of a project supported by the Ministry of Development aiming to promote domestic eco-laundry machines, we developed a prototype reactor to rehabilitate washing water for reuse. As, in the case above, anionic surfactants represent a considerable part of the dissolved organic waste, we show here some results on the decomposition of a dual

system sulfonates (MIX-2), i.e. sodium dodecylbenzenesulfonate (SDBS), and benzophenone-4 (BP4), by means of TiO₂ photocatalysis.

Also our attention was attracted by the increasing use of new chemical compounds for agriculture, zootechnics and personal care products (pesticides, drugs, UV filters, cosmetics and so on) which show a relatively poor bio-degradability. Recent reports, in fact, pointed out the presence of ofloxacin (OFX) and carbamazepine (CBZ) in several rivers in Italy^{2,3} [2,3] and of benzophenone-3 (BP3) and the already mentioned (BP4) in sewage, surface and drinking water in Spain⁴ [4]. Therefore we decided to carry out an investigation on the mineralization of a multicomponent aqueous system, mixing all the four together (MIX-4), by UV methods and ionizing radiation. At the same time we tuned the TOC analysis in the presence of H₂O₂, as hydrogen peroxide went up to interfere with TOC measurements.

3. Materials and methods

Instrumentation and sample preparation

UV irradiation was performed by a Rayonet irradiator, equipped with 16 UV lamps (8W, 253.7 nm, Hg low pressure, Sylvania). A quartz reactor flask was placed in the center of the irradiation chamber. The flask was equipped with a condenser. γ -irradiation was done in a Nordion 220 gamma-cell. A dose rate of 4.5 Gy/min was measured with the Fricke dosimeter in the reaction cells. For radiolysis in the presence of H₂O₂ 10 mM a G(OH) = 0.52 $\mu\text{mol J}^{-1}$ was taken⁵. Air bubbling was provided during all treatments throughout irradiation. To reach a complete dissolution of compounds in MIX-2 and MIX-4, mother solutions were kept under magnetic stirring for 16 h in the dark at 25°C. The progress of degradation was checked as reported in the text; analyses were performed immediately or on samples stored in the fridge, if analyzed afterward (max. 48 h). As for TiO₂, Evonik VP aeroperls P25/20 $\phi=20$ mm were used. An Agilent 1260 HPLC instrument equipped with a diode array detector was used to follow the disappearance of the selected compounds. 0.5 mL samples were used as sources for the automated injection of 40 μL of each chromatographic run performed on a reverse phase C-8 poroshell (Agilent) 120, 2.1 \times 50 mm 2.7 μm , with a linear gradient from 0.1% trifluoroacetic acid in water to 100% acetonitrile in 5 min, then isocratic up to 10 min; flow rate of 0.5 mL/min. The total organic carbon (TOC) and the anionic surfactants (AS) concentrations were measured by means of the Hach-Lange kits: LCK-385 for TOC and LCK332 for AS. Their performances were validated against standard solutions: the TOC kit showed an experimental error of $\pm 15\%$ in the 3-30 mg/L range. Its Limit-of-Detection (LOD) is 3 mg/L. A linear overestimation of about 50% of the AS kit was found and considered.

4. Results and discussion

MIX-2

SDBS (20 mg/L) and BP4 (5 mg/L) were mixed and dissolved in water under continuous stirring for 16 hours. After adding TiO₂ pearls, the solution was air saturated by bubbling the gas for 5' before and throughout the treatment. Irradiation by UV light (254 nm) was carried out for 4 hours. The temperature of samples reached a maximum of 56°C. The pH remained almost neutral (7.3-7.5). The destruction of pollutants has been monitored in the intermediate and final samples by comparing the UV-vis absorption bands (Figure 1), and by measuring the relative areas of HPLC chromatograms.

The progressive spectral bleaching shown in figure 1 clearly evidences the full destruction of BP4, but nothing can say on SDBS fate. The absorption of SDBS is, in fact, too low to be distinguished from the stronger absorbance of BP4. Fortunately, the destruction of SDBS can be revealed by the progressive extinction of its fluorescence after HPLC separation.

Therefore, by matching UV-vis spectroscopy and HPLC information, it can be observed that BP4 is consumed after 240 minutes. More efficient is the destruction of SDBS, as a 93.5% of it disappeared just after 30 minutes. Interesting, the destruction of the surfactant properties does not match the disappearance of SDBS. In fact, inspecting the concentrations after 30 min in Figure 2, one can notice that 1.3 mg/L (6.5%) of SDBS is left, but the samples contain 7.0 mg/L of AS. It may mean that the intermediates formed during the degradation of SDBS still maintain a surfactant character. To this purpose, any interference of BP4 on AS content evaluation was ruled out by checking the method against BP4 solutions at various concentrations.

The extent of mineralization was controlled by measuring the TOC of the same samples above. The TOC dropped down regularly with time from 13.9 mg/L to a value below the limit of detection (LOD), 3 mg/L (Figure 3).

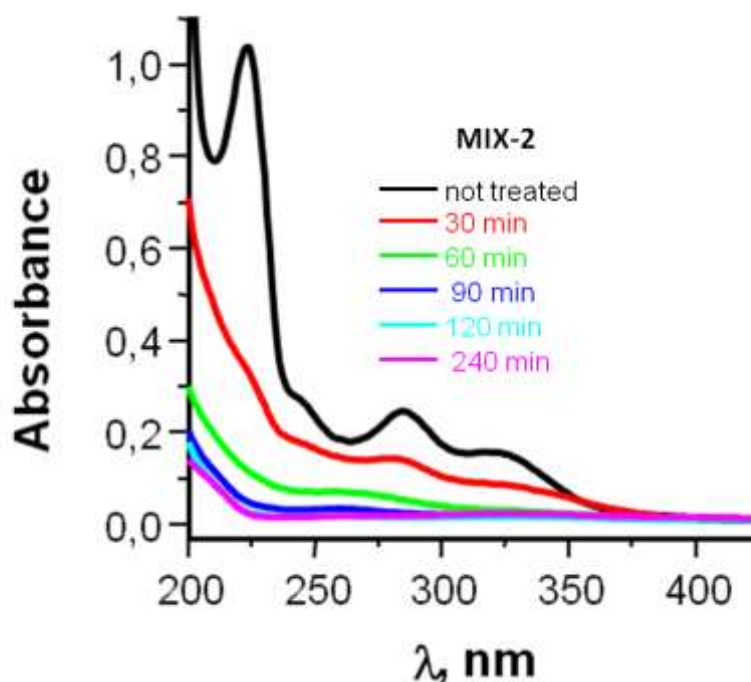


Fig. 5. UV-vis spectra of an aqueous solution of SDBS & BP4 (MIX-2) under heterogeneous photocatalysis induced by UV light and TiO₂.

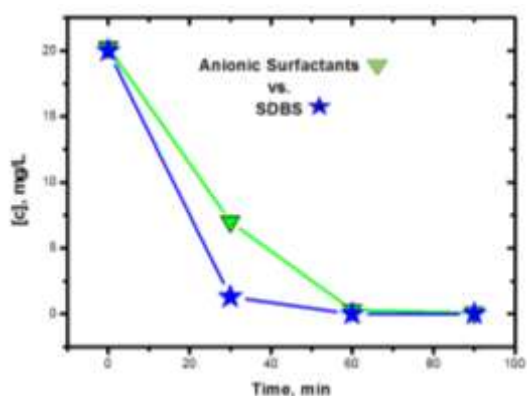


Fig. 2. Initial and intermediate concentrations of Anionic Surfactants AS (LCK332 kit) and SDBS (HPLC) in MIX-2 treated by UV light and TiO_2

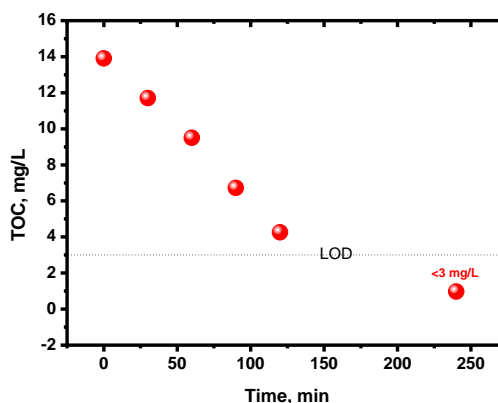


Fig. 3. Decrease of TOC during the photocatalysis of MIX-2. LOD is the limit of detection = 3 mg/L

MIX-4

Regarding the degradation of a complex system containing OFX (0.013 mM), CBZ (0.021 mM), BP3 (0.023 mM), and BP4 (0.016 mM) in water solution, the following methods were used: (A) UV irradiation alone, (B) UV in the presence of TiO_2 particles, (C) and (D) UV with addition of H_2O_2 , (E) γ -rays in the presence of H_2O_2 . All degradations were carried out under constant air bubbling.

UV irradiation

Method (A) is obviously the simplest but it cannot be considered a proper AOP, being mostly a photochemical process. It is however of interest because it can be related to the natural degradation under solar radiation. Methods (C) and (D) are well known AOPs^{6,7} being hydrogen peroxide easily photolyzed to hydroxyl radicals. They differ only with respect to H_2O_2 concentration: $[\text{H}_2\text{O}_2]$ was 0.6 mM in (C) and 10 mM in (D). Method (B) is the same heterogeneous process used for MIX-2, usually depending on complex parameters^{8,9,10}.

As OFX, BP4, CBZ and BP3 are consumed in a competition kinetics for $\cdot\text{OH}$, two wavelengths, 285 and 294 nm (294 nm specifically for OFX) have been carefully selected to distinguish the four HPLC analytes each other. Their concentrations were quantified calculating the ratio of each peak area with that of the initial sample.

A severe disappearance of the analytes before reaching a substantial reduction of TOC has been observed. For an immediate appreciation of the trend of the mineralization process, the TOC values in mg/L units are reported in Figure 4 in percentage units, beside the remaining pollutants. The temperature of solutions increases of about 40°C for all methods excluding different thermal effects on the processes. On the other hand, the pH decreases at values between 4 and 5, indicating the formation of organic acids and CO_2 .

These observations are coherent with the general view that advanced oxidations proceed through a complex process consisting primarily in the fragmentation of pollutants

(destruction), followed by the transformation into CO₂ and carbonates (mineralization) in a second phase. It has yet to be verified whether non-homogeneous processes obey the same behaviour. A detailed comparison between photocatalyzed (heterogeneous), on one side, and UV and γ (homogeneous), on the other, might help to solve the problem.

In (D) the concentration of H₂O₂ was increased to 10 mM: the purpose was to study the effect of H₂O₂ on the photodecomposition rates and compare the efficiencies between UV- and γ -treatments. Fundamentally, with H₂O₂ 10 mM the photomineralization rate can be estimated as having a $t_{1/2} < 5$ min, while with H₂O₂ 0.6 mM the rate is almost 4 times slower ($t_{1/2}$ ca. 20 min). The following section allows the comparison between UV/ H₂O₂ and γ /H₂O₂.

γ -irradiation

Mix-4, containing H₂O₂ 10 mM, was also exposed to γ -rays under continuous air bubbling. Figure 5 shows the concentration changes for each component during the treatment as obtained by HPLC measurements. Their overall decomposition follows similar dose profiles, as \cdot OH reactions occur almost with the same rate constants (ca. $10^9 \text{ M}^{-1}\text{s}^{-1}$) with any of them. BP3 may be decomposed through more complex pathways than the others. After irradiation the solution became slightly acidic, similarly to UV degradation: i.e. pH changed from 8 to 4.

TOC measurements could be accurate only in the absence of H₂O₂. Actually, it turned out that H₂O₂ interferes on TOC measurements at concentration > 1 mM. At 10 mM for example the initial TOC was underestimated of 50%, while in the absence of H₂O₂, the underestimation was $< 8\%$. It meant that TOC data during the initial and core stages of degradation are meaningless. However mineralization is indeed produced at a very large extent, as it can be ascertained when H₂O₂ concentration is reduced below 1 mM. This occurs after the application of ca. 20 kGy: at this stage, in fact, the TOC value drops down at 3 mg/L (LOD) from an original 12.6 mg/L (Figure 5, inset).

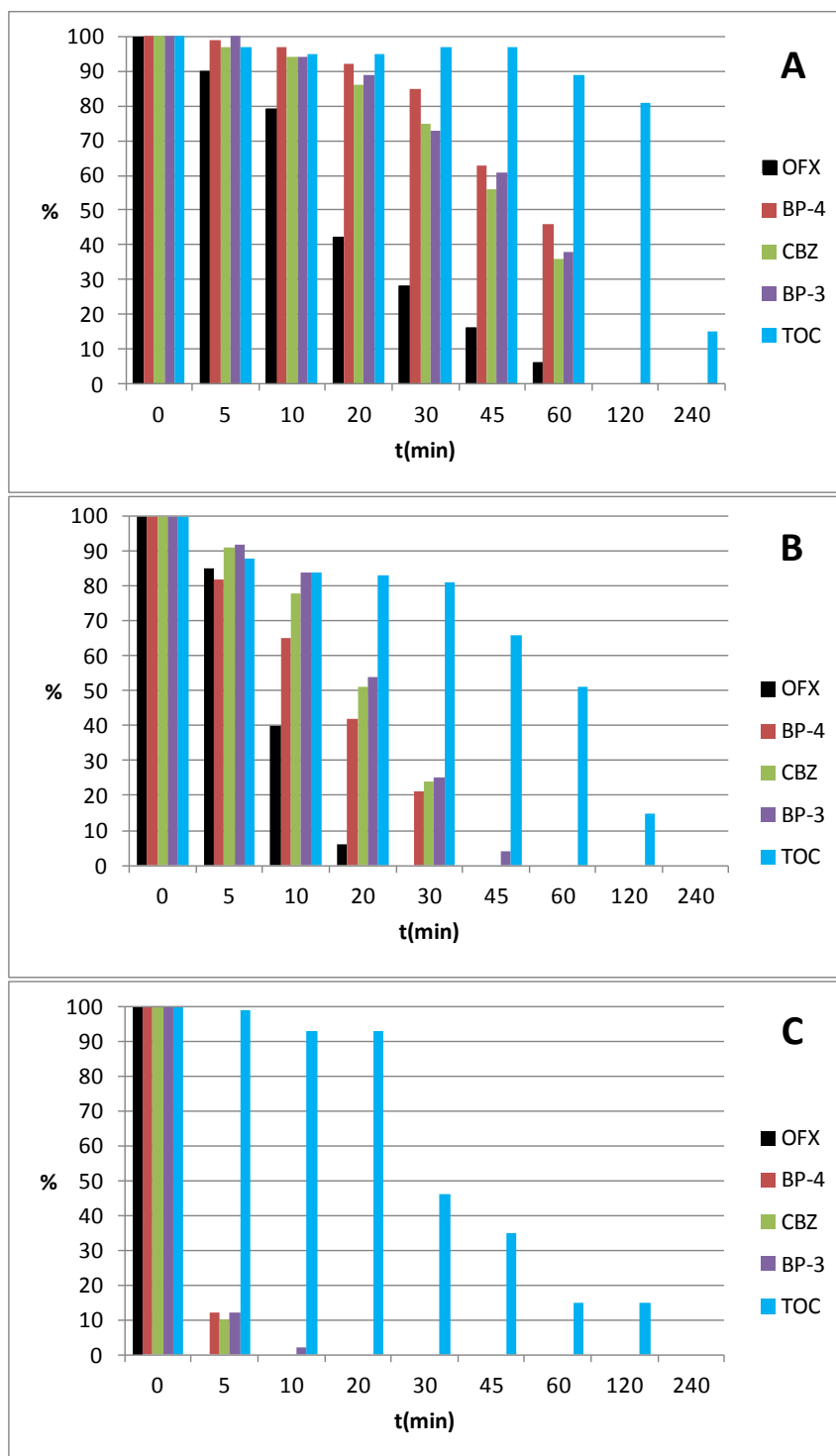


Fig. 4. Relative concentrations of pollutants and relative TOC values for methods (A),(B), and (C), quantified by HPLC at 285 and 294 nm. TOC readings under the limit of detection (3 mg/L) were conventionally plotted at 15% height, corresponding to the uncertainty of the method.

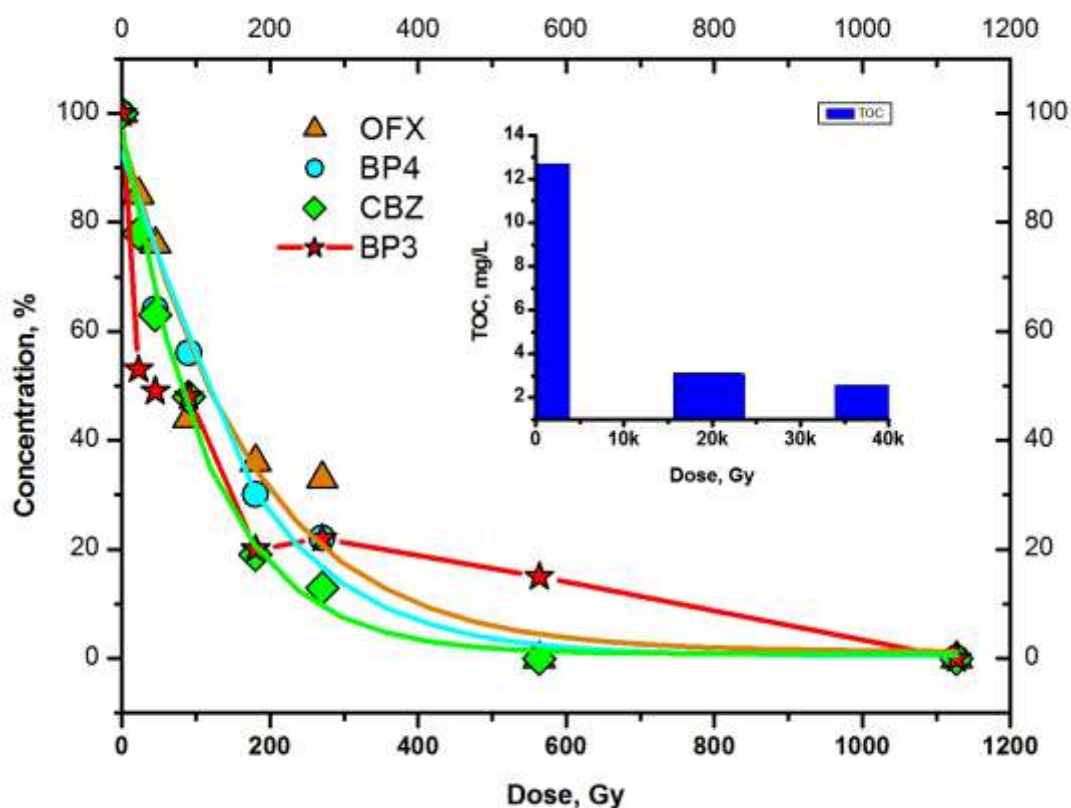


Fig. 5. Relative concentrations of OFX, BP4, CBZ, and BP3 measured by HPLC during γ -irradiation of MIX-4 the presence of 10 mM H_2O_2 . In the inset: TOC decreases below 3 mg/L after a dose of 20 kGy.

Conceiving a comparison between γ and UV methods, only specific considerations can be made, valid for our experimental conditions. The TOC limit of detection, constituted by 3 mg/L, is reached after 30 min by UV method (D), while γ -treatment requires almost 3 days (4400 min) of irradiation at a dose rate of 4.5 Gy/min. Generally speaking, this data evidences that the mineralization rate is related to the $\cdot OH$ production rate from H_2O_2 in the systems.

5. Provisional conclusions

MIX-2 and MIX-4 treated by UV/TiO₂, UV/H₂O₂, and γ /H₂O₂ under aerated conditions showed an efficient conversion of the organic carbon to inorganic one. In the UV treatments, the progress of mineralization has been evidenced since the very early times of irradiation, although some AOPs with a low $\cdot OH$ production rate (i.e. photocatalysis) show a longer induction period. The induction period represents the destructurement of the molecules, as proved by HPLC and spectrophotometric analyses.

Aqueous photolysis, alone, activates different and slower mechanistic routes than hydroxylation does. Photolysis is, however, capable to decompose all the chemicals of MIX-4 and to lead to mineralization as well.

The most efficient degradation of the chemicals was achieved in the presence of hydrogen peroxide. A 10 mM H_2O_2 has to be used to achieve the best efficiency of γ -treatment, while

the optimal value for UV/H₂O₂, under our experimental set up can be lower than that; the definition of this value is under course. HPLC analyses do not reveal significant formations of by-products absorbing in the 190-400 nm range.

In the absence of H₂O₂ (methods A and B), OFX was the fastest molecule to disappear, possibly due to its photolability. Instead, in the presence of H₂O₂, the compounds degrade almost in the same time domain (methods C, D, and E). This may be attributed to the fact that their rate constants with ·OH are very similar, although BP3 seems to decompose through a more complex kinetics.

In the whole any AOP succeeds in reducing the TOC below 3 mg/L, i.e. the detection limit of the method (see experimental section). Therefore, the starting TOC value (ca. 12-13 mg/L), can be followed since its abatement reaches the 75-76%. It appears however likely that mineralization proceeds to completion.

As photocatalysis with TiO₂ promptly destroys most surfactants, the method is proposed as a valuable choice for the remediation and reuse of water wasted during domestic washing cycles. Despite its complexity, TiO₂ photocatalysis is appealing due to the facts that TiO₂ is a natural, cheap, and non toxic compound. Its efficiency strongly depends on the adsorption of the target pollutants at the metal oxide surface/water interface and on the efficiency of the UV-activation of the complex. For these reasons, work is in progress to build up a prototype reactor using TiO₂ supported on glass, plastic or alloys.

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