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Photocatalytic decomposition of seawater-soluble crude-oil fractions using high surface area colloid nanoparticles of TiO_2

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Abstract

Photocatalytic destruction of the water-soluble crude oil fraction, WSF, was conducted using TiO_2/UV–VIS. Infrared studies were carried out to investigate the transformations of crude oil compounds during the photolytic and heterogeneous photocatalytic processes. Although no mineralization occurred due to photolysis, important chemical changes were verified. However, when in the presence of TiO_2, degradation reached 90% (measured as dissolved organic carbon, DOC) in waters containing 9–45 mg C l^{-1} of seawater-soluble crude oil compounds after 7 days of artificial light exposure. Inorganic peroxides were photo-generated in a concentration of up to 8.0 μmol l^{-1} upon illumination, but total destruction of these peroxides occurred during heterogeneous photocatalysis. Toxicity studies before and after irradiation of the WSF using the *Vibrio fischeri* (Microtox®) were performed. During light exposure of the WSF, transient intermediates which showed higher toxicity than the initial compounds were observed, but were subsequently destroyed. Heterogeneous photocatalysis using TiO_2 was shown to be a promising process to minimize the impact of crude oil compounds on contaminated waters. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Crude oil; TiO_2; Water-soluble fraction (WSF); Heterogeneous photocatalysis; Microtox®

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1. Introduction

The problem with crude oil pollution in the coastal zone has been mainly associated with tanker accidents. However, the major petroleum contamination source in these waters is related to human activities such as shipping operations, accidental spills, and corrosion of equipment. In addition, refinery wastewater is another important contamination source, principally when petrochemical complexes are located in coastal zones. Wastewater is usually rich in dissolved organic carbon (DOC) from crude oils, the so-called soluble crude oil fraction, WSF. This continuous input of organic load is the main source for chronic toxicity in coastal ecosystems, providing compounds that are potentially available for uptake and bioacumulation by aquatic organisms. Conventional technologies, such as biological treatment and carbon adsorption and coagulation are usually used to remove these soluble organic compounds from water before final disposal. However, these end-of-pipe controls and emission standards are limited in their application, since they are not preventive. Regulatory agencies are supporting on-line changes and modifications to further reduce emissions, meantime, conventional technologies will continue to be used in conjunction with innovative technologies aimed towards environmental compliance. The EPA Science Advisory Board (US EPA 1990) recommends pollution prevention in replacement of the traditional pollution control approaches to environment, health, and safety issues. As a result, new technologies have emerged for controlling environmental contamination and wastewater toxicity.

In recent years, there has been remarkable progress in advanced oxidation technologies (AOT), based on the generation (by whatever means) of highly reactive intermediates (e.g. hydroxyl radicals) that initiate a sequence of reactions resulting in the destruction of organic pollutants in water and air. Among the AOT, heterogeneous photocatalysis using semiconductors as catalysts (UV/TiO_2) is an important technology for accelerating the oxidation and destruction of a wide range of organic contaminants in polluted waters. It is interesting to note that many laboratory studies

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have demonstrated the feasibility of the photocatalytic detoxification for almost all classes of hazardous compounds [1–3]. In addition, natural sunlight can provide photons with enough energy to excite some photocatalysts (TiO_2) as the first step in the cyclic mechanism [4] for the photodegradation of organic compounds with high efficiency and low costs.

The disappearance of a target compound present in the wastewater stream does not necessarily mean toxicity removal and, in this case, the biological response needs to be assessed. Several methods (and organisms) can be used to determine acute toxicity in industrial effluents, including the Microtox®. This toxicity test uses a luminescent marine bacteria (*V. fischeri*) [5]. In this work, heterogeneous photocatalysis using TiO_2/UV–VIS was evaluated as an alternative process to destroy the seawater-soluble crude oil hydrocarbons, taking into consideration not only the removal rates obtained in the dissolved carbon content, but also the toxicity of the water samples prior to and after the photocatalytic treatment.

2. Experimental

2.1. Crude oil samples and seawater

Brazilian crude oil samples (named A and B for simplicity) came from the Campos Basin on the continental shelf of Rio de Janeiro State, Brazil. The Campos Basin exploration and production region, with water depths reaching down to 3500 m (11,500 ft), and reserves of 13.9 billion, the country's largest offshore basin, is located in the South Atlantic, off the southeastern coast of Brazil, being responsible for producing almost 1 million barrels of crude oil per day (80% of total national production). A detailed description of these oils has been published [6,7] and a brief summary can be found in Table 1.

Seawater (salinity 33‰, pH 8.4) used in all experiments was collected at São Sebastião (São Paulo State), along the coast line of the Ilha Bela Channel, for practical geographical localization and because in this channel, there are strong water currents that continuously remove every possible oil residue from the area. Besides the initial DOC concentration, depth, conductivity, dissolved oxygen, wind direction, sky conditions and visibility (about 9 m, with Sechi disk), were also monitored during the collection of the seawater in order to maintain a standard of the seawater among the experiments. Blanks were performed using the seawater sample.

Table 1
Features of the crude oils

Crude oil	API gravity	Asphaltenes (wt.%)	Sulfur (wt.%)
A	16.5	3.8	0.83
B	24.7	1.0	0.49

2.2. Photocatalysis

Titanium dioxide (Degussa P-25, predominantly anatase, specific area of $50\,m^2\,g^{-1}$, non-porous), 70:30 anatase form, BET surface area $50\,m^2\,g^{-1}$, 30 nm average particle size was used as photocatalyst. All the experiments were carried out in an aqueous suspension of TiO_2, at a concentration of 0.1% w/v. After each experiment, the suspension was filtered and the filtrate was subjected to analysis.

2.3. Obtaining the WSF

For each tested oil sample, a 2.0 l Pyrex glass with a Teflon drain at the bottom filled with 1.5 l of seawater was used. Crude oil was added in the ratio 1:20 v/v, and the solution was magnetically stirred for 30 min. Flasks were left to equilibrate for up to 15 days in the dark at the room temperature, remaining closed for the entire period until the tap was opened to obtain the WSF for the experiments. The WSF (about 1200 ml) was drained without disturbing the oil/seawater surface. This procedure is in accordance with Ziolli and Jardim [7], who pointed out operational problems related to the production of WSF of crude oils.

2.4. Irradiation experiments

Samples (1200 ml) were irradiated in a Pyrex® reactor (80 mm × 210 mm) in batch experiments as shown in Fig. 1, using as the radiation source, a 125 W high-pressure mercury lamp (Philips, HPL-N) with the maximum wavelength at 366 nm, for up to 7 days of exposure. Cooling water was circulated through a quartz inner sleeve to control the temperature. In the photocatalytic experiments carried out in the presence of TiO_2, the aqueous suspension was kept

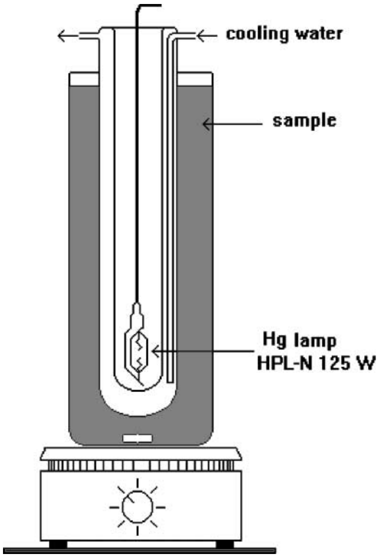

Fig. 1. Scheme of the photocatalytic reactor.

homogeneous in the reactor vessel with the help of a magnetic stirrer.

2.5. DOC analysis

The amount of DOC present in the aqueous phase was measured using a Shimadzu TOC 5000 total organic carbon analyzer. Samples from the photocatalysis experiment had TiO_2 particles removed by filtration through a 0.45 μm cellulose acetate Whatman filter.

2.6. Infrared analysis

A Perkin-Elmer 1600 series FTIR infrared spectrophotometer was used in the analysis of WSF content after extraction with dichloromethane. The extracts were concentrated under vacuum and the spectra were recorded between 4000 and 500 cm^{-1} using a film on NaCl. A blank (seawater sample) was prepared following the same treatment and used as a reference.

2.7. Determination of hydrogen peroxide

Photoproduction of hydrogen peroxide was investigated during irradiation of the WSF in the presence and in the absence of TiO_2. Samples (~20 ml) were collected during radiation exposure and the determination, including the speciation of organic and inorganic peroxide, was carried out using the photometric method based in the peroxidase catalyzed oxidation of *N*,*N*-diethyl-*p*-phenylenediamine (DPD) [8].

2.8. Toxicity test (Microtox®)

The relative acute toxicity of the water-soluble fraction (WSF) was determined by conducting the Microtox® bacterial bioluminescence assay on the deionized water extract of the WSF. The Microtox® [9,10] system utilizes a suspension of marine luminescent bacteria (*V. fischeri*) as a test organism for measuring acute toxicity in aqueous samples. Suspensions with approximately 10^6 organisms were exposed to serial dilutions of the WSF. The Microtox is used to measure the light output of the organisms before and after they are exposed to the stressing agent. A reduction of light output reflects deterioration in the state of health of the organisms as physiological inhibition, thereby indicating the presence of toxic constituents in the sample. The results are expressed as toxic units (TU), where $TU > 1$ means that the sample shows acute toxicity.

3. Results and discussion

3.1. Photo-oxidation experiments

The results obtained in the photo-oxidation experiments of the WSF are presented in Fig. 2 for the crude oil A and in Fig. 3 for the crude oil B. The time of exposure was 7 days under artificial irradiation. The amount c/c_0 refers to the concentration ratio of the DOC in the aqueous phase measured at any time, compared to the initial concentration. As pointed out by Ziolli and Jardim [7], the WSF are very dependent on the nature of the oil, and the two crude oils used in this work yielded aqueous phases saturated with very distinctive amounts of organic compounds: 45 mg C l^{-1} for the crude oil A and 9 mg C l^{-1} for the crude oil B. Since crude oil B is more paraffinic (24.7° API gravity) than crude oil A (16.5° API gravity), one should expect the WSF obtained from crude A to be more rich in organic compounds.

When the WSF was kept in the dark and in the absence of the catalyst, no change in the DOC concentration was

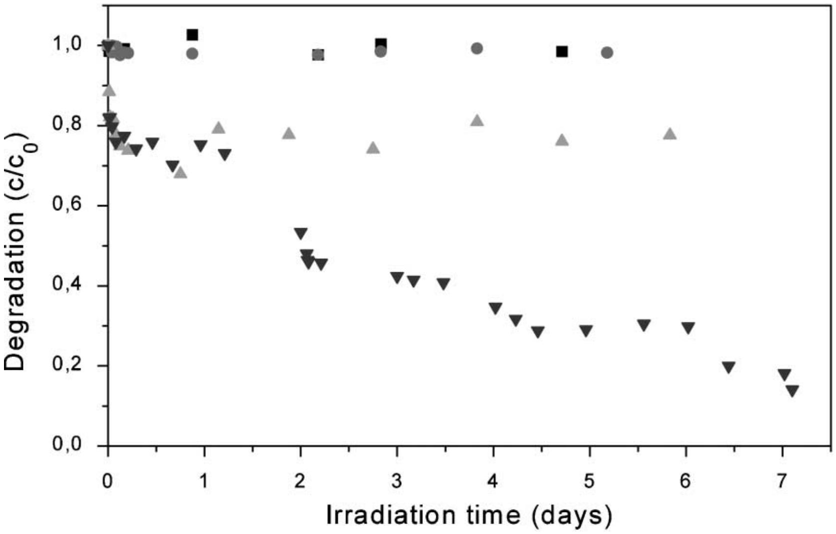

Fig. 2. WSF of A-Brazilian crude oil in seawater (■) Only WSF-A (control); (▲) WSF-A with TiO_2 in dark; (●) WSF-A during exposure to UV–VIS irradiation without TiO_2;(▼) WSF-A with TiO_2 during exposure to UV–VIS irradiation.

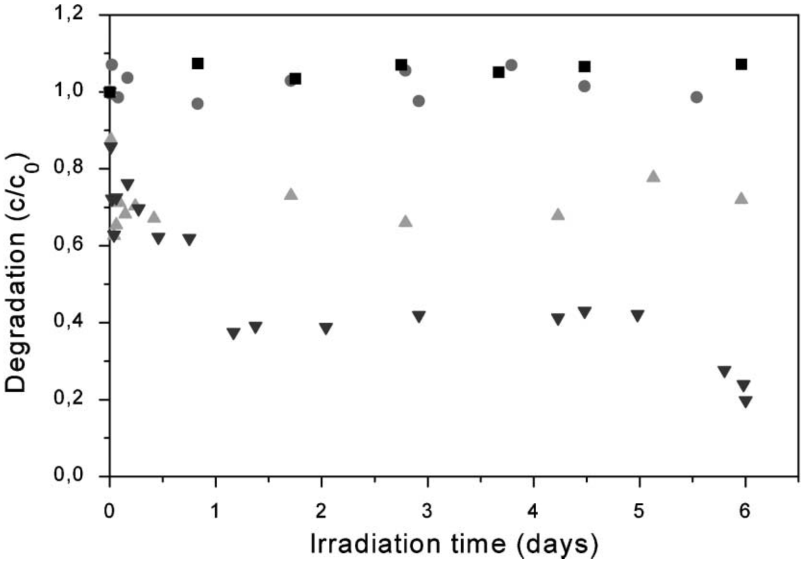

Fig. 3. WSF of B-Brazilian crude oil in seawater (■) Only WSF-B (control); (▲) WSF-B with TiO_2 in dark; (●) WSF-B during exposure to UV–VIS irradiation without TiO_2;(▼) WSF-AB with TiO_2 during exposure to UV–VIS irradiation.

observed (Figs. 2 and 3). This same behavior occurred in the samples exposed to irradiation without catalyst (photolysis process), indicating that photolysis plays a minor role in the mineralization of the DOC. It is interesting to note in the experiments of WSF with TiO_2 in the dark that there is adsorption of some dissolved organic compounds onto the catalyst surface. This adsorption process was responsible for the reduction of about 25% of the initial concentration of DOC in the first 12 h, until it reaches an equilibrium concentration. However, when the WSF with TiO_2 in suspension was irradiated, a sharp decrease in the ratio c/c_0 was observed, especially in the first 2 days of irradiation, in a clear indication that TiO_2 assisted photo-oxidation is the major process in the removal of about 90% of the pool of DOC. In fact, up to first 24 h, the adsorption process predominates over photocalytic degradation. Figs. 2 and 3 show a similar pattern of WSF photodegradation in the presence of TiO_2 for both crude oils. The behavior observed in the disappearance of the DOC, together with the IR data indicates the presence of numerous intermediates before the generation of CO_2. Hydrocarbons are initially degraded to a complex mixture that appear to be extremely recalcitrant to further degradation (although even these compounds were later degraded by the heterogeneous photocatalysis). In addition, a saturation of the catalyst surface results in a decrease of active sites available for adsorption and reaction with the organic compounds, and this mechanism is assumed to be the major one responsible for the kinetics of degradation.

Although, the mechanism of heterogeneous photocatalysis is not yet fully understood, the following are expected to occur: (i) direct mechanism, where the oxidation of organic compounds occurs directly at the holes in the valence band of the semiconductor (oxidation site); or (ii) indirect mechanism, when water molecules adsorbed on valence band holes of the semiconductor oxide form hydroxyl radical, $^\bullet$OH, and subsequently attack the organic compounds adsorbed onto the catalyst or in the vicinity of the interface [4]. The slow kinetics of the intermediate products showed in the Figs. 2 and 3 may inhibit a faster adsorption process on the catalyst sites, supporting the hypothesis that the rate-limiting step is the formation of the active species ($^\bullet$OH) through reactions on the surface of the TiO_2.

Previous studies on heterogeneous photocatalysis using simple model samples have focused on degradation of individual pure compounds, with few references to hydrocarbons mixtures or to real samples of crude oils. In most of these cases, complete oxidation in achieved in a few hours. In this work, using a very complex (and real) mixture of hydrocarbons, total degradation requires a much longer time. The results indicate that the efficiency of the photocatalytic process is drastically affected when the complexity of the sample is increased.

3.2. Infrared analysis

The Fig. 4 shows the infrared spectra of the WSF of crude oil A (A spectra), WSF of crude oil A after exposure to UV–VIS irradiation (B spectra), WSF of crude oil A with TiO_2 after exposure to UV–VIS irradiation (C spectra), and only seawater (blank) (D spectra). After 5 h of photolysis, the IR spectrum of the WSF-B reveals that the important changes occurred during illumination, such as the appearance of the new bands (mainly 877.1, 1117, 1656.1, 2927 cm^{-1}) when taking into consideration the sample prior to irradiation (spectrum A). These bands were attributed to alcohol and ether (1300–900 cm^{-1}), to carbonyl (at 1720

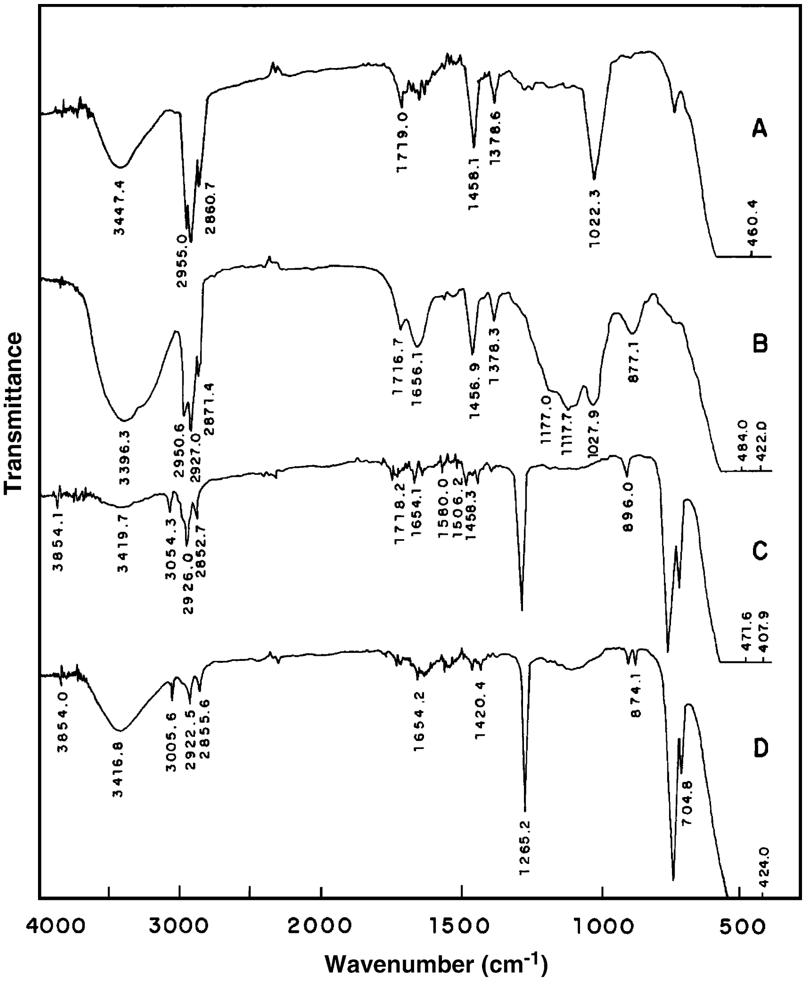

Fig. 4. FTIR spectra of (A) WSF of Brazilian crude oil in seawater; (B) WSF after exposure to UV–VIS irradiation; (C) WSF with TiO_2 after exposure to UV–VIS irradiation and (D) only seawater (blank).

and 1650 cm^{-1}), and alkenes (C=C) at 1650 cm^{-1}. The comparison of the infrared spectrum from WSF before irradiation (A) and WSF irradiated for 5 h (B) indicates a transformation of the initial compounds, although no mineralization occurs without TiO_2. However, the most important result was observed after 7 days (C) in the sample containing the photocatalyst that was exposed to light, when the disappearance of the vast majority of absorption bands as well the decrease in the remaining ones was observed. These results clearly indicate that the vast majority of organic compounds present in this WSF were almost completely destroyed, resulting in an infrared spectrum that closely resembles the blank (D).

In the photolysis experiments, the detection of more oxygenated compounds in the final reaction products than in the initial ones present in the WSF may be used as a surrogate to predict the formation of highly reactive compounds when crude oil wastewater is spilled to seawater under sunlight (typical situation in tropical regions). Under these conditions, an increase (but barely computed) in the environmental impact associated to oils spills in tropical regions would be expected, since these oxidized intermediates can be more toxic to marine organisms than the initial compounds present in the WSF, strengthening the need for effective removal of water-soluble crude oil compounds before disposal. On the other hand, it is feasible to assume that these oxidized intermediates can undergo a wide range of abiotic reactions, considering the variety of organic compounds naturally occurring in seawater, such as dissolved and colloidal humic material [11–13], riboflavin [14], pteridines [15], and additional uncharacterized material [16], algae pigments, cyanocobalamine, thiamin, and biotin [17], all of which are natural photosensitizers. However, natural conditions may not provide all the suitable conditions needed to assist in complete oxidation or to yield a less toxic form of these partially oxidized compounds. Besides these transient species, one also has to consider the formation of highly reactive OH radicals as well as dissolved organic material derived peroxy radicals, for which the WSF may act as a precursor.

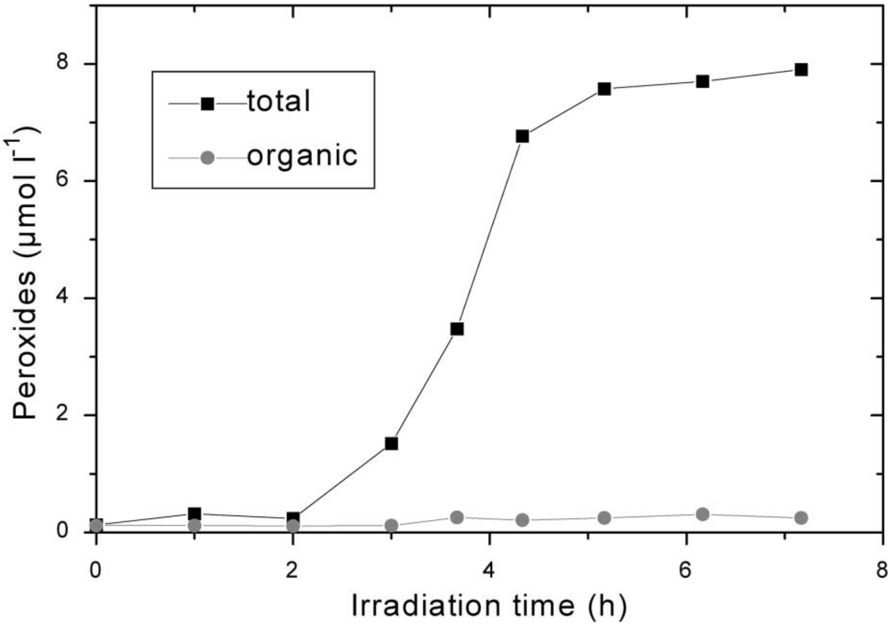

Fig. 5. Photochemical formation of hydrogen peroxide in the WSF during UV–VIS irradiation. It was used catalase enzyme to distinguish inorganic and organic peroxides.

3.3. Photoproduction of hydrogen peroxide

Photoproduction of hydrogen peroxide in the WSF was investigated both during photolysis experiments (Fig. 5) and during heterogeneous photocatalysis (Fig. 6) using crude oil A. Since the catalase enzyme is able to destroy inorganic peroxide, it was used in order to separate inorganic and organic peroxides. Fig. 5 shows that the formation of peroxide during photolysis results in the inorganic form (H_2O_2), since no organic peroxide was detected. However, when in the presence of TiO_2 (Fig. 6) inorganic peroxide is completely decomposed during the first few hours of irradiation.

The photochemical formation of peroxides occurs in the presence of oxygen in an aqueous medium and it acts as a precursor of many reactive species in light-driven reactions. The possibility that this H_2O_2 assists in the destruction of WSF cannot not be ruled out, since this reagent is used as a coadjutant in many oxidative processes. On the other hand, one has to consider that this compound undergoes dismutation during heterogeneous photocatalysis generating the

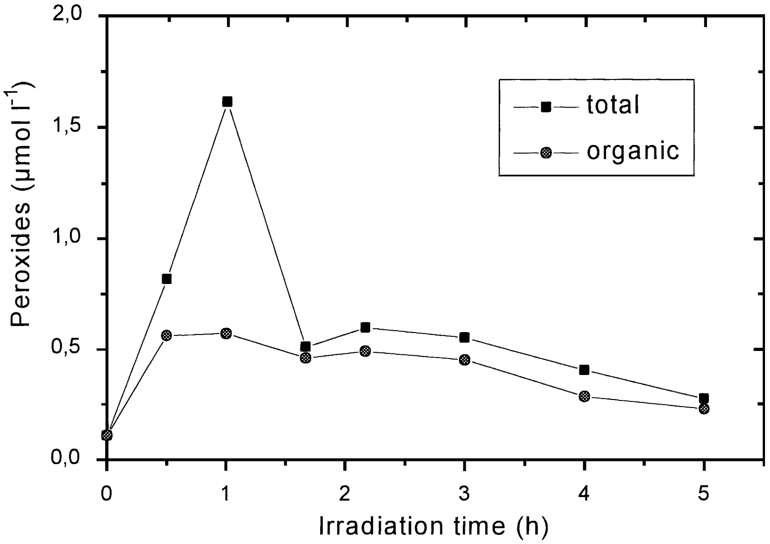

Fig. 6. Degradation of hydrogen peroxide in the WSF during TiO_2/UV–VIS irradiation. It was used catalase enzyme to distinguish inorganic and organic peroxides.

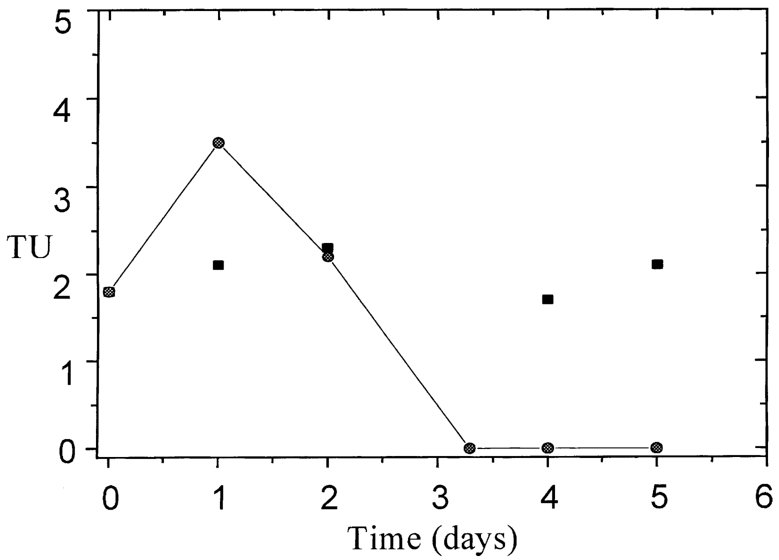

Fig. 7. Effect of WSF of A and B crude oil on the marine luminescent bacteria (*V. fischeri*) as test organism (Microtox® test). (■) during photolysis (UV–VIS irradiation) and (●) during heterogeneous photocatalysis (TiO_2/UV–VIS irradiation).

superoxide radical ion ($O_2^{\bullet -}$). This species is an important source of hydroxyl radical and avoids the recombination of the electron/hole pair in the catalyst, thus enhancing the redox process. As a result, the decomposition of H_2O_2 observed in the presence of TiO_2, can be seen as an additional source of OH radical species, thus increasing its efficiency in the destruction of organic compounds present in the WSF.

3.4. *Toxicity test*

The toxicity associated with the WSF before and after irradiation was evaluated in order to assess possible enhancement of toxicity due to intermediates generated during photocatalysis. Recently, Jardim et al. [18] pointed out that the use of TiO_2/UV in the destruction of some aromatic chlorinated compounds could produce intermediates with much higher toxicity than the mother compound used. Fig. 7 shows the toxicity results obtained for the WSF from crude oil A before ($t = 0$) and after irradiation (up to 5 days of irradiation) in presence and absence of the photocatalyst. A sample is considered to exhibit acute toxicity when the toxicity unit (TU) values equal to or above one. The WSF of crude oil A, showed the value of 1.8 TU before irradiation which remained almost constant during the photolysis process. However, the most interesting result in toxicity behavior refers to the heterogeneous photocatalysis. When the crude oil A sample was submitted to irradiation in the presence of TiO_2, the acute toxicity increased markedly in the first 24 h of irradiation, then disappeared after 3 days of light exposure, indicating that the initial toxic compounds as well as the toxic intermediates, were destroyed or converted to compounds which were not toxic to the test organism.

4. Conclusion

Photocatalytic processes using TiO_2/UV–VIS were shown to be quantitatively efficient in the destruction of the water-soluble crude oil fraction, reaching values around 90% of degradation for carbon concentrations which ranged between 9 and 45 ppm. The total destruction of water-soluble compounds originating from oil residues indicates that the photocatalysis is an extremely attractive potential process that could be employed for water treatment (petrochemical wastewater, for example). Ollis [19] has shown that photocatalysis can be economically comparable to UV-ozone treatment or even to other more traditional methods that employ absorbent materials such as activated charcoal.

Despite the fact that mineralization reaches values as high as 90% during photocatalysis, the generation of transient toxic species has been observed, what will demand special care when planning to use this technology in water remediation.

Considering all the aspects discussed in this paper, and assuming the continuos growth in the petrochemical industry with concomitant production and discharge, heterogeneous photocatalysis using the semiconductor TiO_2 has to be looked upon as an emerging technology attractive not only in terms of efficiency but also under the cost/benefit aspect in protecting coastal seawater.

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