



Photochemical degradation of crude oil: Comparison between direct irradiation, photocatalysis, and photocatalysis on zeolite

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ABSTRACT

Direct irradiation for 100 h of crude oil from Basilicata (Southern Italy) gave in the case of linear and branched alkanes a reduction of 9 and 5%, respectively. On the contrary, cyclic alkanes decreased for 54% while aromatic hydrocarbons showed a reduction of 37%. These results are in agreement with a prevalent electron transfer mechanism. Photocatalysis (100 h) gave extensive degradation of crude oil: linear alkanes were degraded for 98.66%, branched alkanes were reduced for 97.31%, cyclic alkanes for 96.04%, while aromatic compounds and alkenes were reduced for 99.54 and 98.38%, respectively. These results are in agreement with a prevalent hydrogen abstraction mechanism. When photocatalysis is performed in the presence of zeolite linear alkanes were degraded for 79.85%, branched alkanes were reduced for 45.38%, cyclic alkanes for 58.10%, while aromatic compounds were reduced for 91.85%. In this case, an increase of the relative amount of alkenes (42.05%) was observed.

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1. Introduction

Oil extraction represents one of the most important extractive industries in the world. Basilicata is a region in Southern Italy where recently an extraction activity has been started by ENI SpA, the most important extraction firm in Italy. The extraction of crude oil present in Basilicata can cover 10% of Italian needs in the energy production. The oil extraction was performed mainly in Val d'Agri, a valley in Basilicata where both an extensive agricultural activity and some environmental constraints with the presence of National Park of Val d'Agri are present.

Crude oil can escape into the environment. Extraction techniques, transportation and refinery treatments of crude oil can originate pollution phenomena due to dispersion of these compounds in the environment. Thus, terrestrial spills may soak into the ground, while spills at sea or on lake and rivers often disperse into the water column [1].

In this contest, oil spill can represent an immediate damage to the tourist image of the region and for its economy. Gas chromatography (GC) coupled with FID and with mass spectrometry (MS) has been used to determine and characterize crude oil [2–6]. Recently, we found that GC analysis in solution and headspace SPME-GC analysis of a sample of crude oil gave different results [7]. SPME

technique allowed the identification of a larger number of components than by using usual GC–MS.

Crude oil is subjected to some degradation processes. Biodegradation can be one of the most important processes in the environment. Photochemical degradation mediated by sunlight is an important pathway for transformation of crude oil in tropical seawater, especially when the oil is rich in aromatics. Since chromophores are abundant in crude oils, many of the transformations are the result of direct photochemical processes due to absorption of light in the UV region, or of photosensitized reactions due to the presence of compounds able to absorb light in the visible region.

In different studies of oil dispersed in seawater, it was found that the synchronous fluorescence decreased with irradiation [8–11]. Photochemical weathering of Brazilian petroleum was evaluated by using EPR spectroscopy showing a partial destruction of the asphaltenic fraction of the oil [12].

In recent works, GC–MS analysis of crude oil after irradiation showed that the alkanes are unaffected but the majority of the aromatic hydrocarbons have been converted to resins or polar molecules [13–16]. These results are not in agreement with the observed photooxidation of *n*-pentadecane [17] and with the observed mineralization of *n*-alkanes in photocatalytic conditions [18,19]. A GC–MS analysis of water-soluble fraction of crude oil showed that only the peaks with retention time between 8.46 and 12.36 min disappeared after 24 h under photolysis [20]. The rate constant for hydrogen abstraction in alkyl aromatics has been determined [21]. This result was in agreement with the observed

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preferential photooxidation of alkyl-substituted polycyclic aromatic hydrocarbons and heterocyclic aromatic in comparison to their unsubstituted parent compounds [17,22].

The fate of the crude oil under irradiation was studied by using both liquid injection and SPME methodologies [23]. After the UV irradiation, the fraction present in the highest percentage shifted from C8–C9 fraction to C13 one, in GC–MS analysis in solution. An increase of the relative amount of the C13–C25 fraction was observed, while a decrease in the relative amount of the C7–C12 fractions was present. In HS-SPME analysis, the C8–C10 fractions represented 53% of all the compounds detected. A decrease in the relative amount of the C8–C10 fractions was observed, while C11–C15 fractions increased. The irradiation with solar simulator of crude oil gave a mixture whose analysis using GC–MS in solution furnished the same type of results: the relative amounts of linear alkanes and aromatic compounds increased, while a sharp decrease of the relative amounts of branched and cyclic alkanes was observed. In the SPME analysis, a decreased relative amount of branched alkanes and alkenes and an increase of the relative amounts of cyclic alkanes and aromatic compounds were observed.

As reported above photocatalysis can be used to induce photooxidation of petroleum hydrocarbons. Photocatalysis has been extensively used in petroleum photodegradation [24,25]. The most important application is the photodegradation of crude oil dispersed in water [17,26–34]. This procedure has been used also on sand [35] and on zeolite [36] or bentonite [37].

In this paper, we want to compare the crude oil degradation performed by using direct irradiation, photocatalysis by using titanium dioxide, and photocatalysis by using titanium dioxide supported on NaY zeolite. The results of these experiments could furnish a practical way to destroy residual crude oil in contaminated vessels, for example; in particular, the eventual success of the photochemical degradation of crude oil by using photocatalysis within zeolite could give a way to destroy crude oil residues without dispersion of titanium dioxide in the environment.

2. Materials and methods

In this study, we used a sample of crude oil deriving from Centro Oli in Val D'Agri (Basilicata, Southern Italy). The sample showed in the elemental analysis the following composition: C, 85.13%; H, 12.31%; N, 0.00%; and S, 2.74%.

2.1. Irradiation of crude oil

Crude oil (0.1 g) was suspended in water (20 ml) in a sealed vial for SPME analysis. The mixture was irradiated with a 125 W high-pressure mercury arc (Helios Italquartz, Milan, Italy) for 100 h.

2.2. Photocatalytic degradation

Crude oil (degassed with nitrogen for 2 days in order to eliminate compounds with a high volatility, 0.1 g) was suspended in water (20 ml) in the presence of TiO₂ (1 g) in a sealed vial for SPME analysis. The mixture was irradiated with a 125 W high-pressure mercury arc (Helios Italquartz, Milan, Italy) for 100 h in the presence of bubbling oxygen (introduced through the silicone septum of the vial) and vigorous stirring.

2.3. Photocatalytic degradation in the presence of zeolite

TiO₂ (0.02 g) was stirred in the presence of NaY zeolite (1 g) in ethanol (20 ml) for 4 h. The solvent was evaporated and the residue was dried at 110 °C in an oven. Then, the product was calcinated at 400 °C for 6 h. Before the use the catalyst was maintained at 300 °C

for 4 h. Crude oil (degassed with nitrogen for 2 days in order to eliminate compounds with a high volatility, 0.1 g) was suspended in water (20 ml) in the presence of the catalyst (1 g) in a sealed vial for SPME analysis. The mixture was irradiated with a 125 W high-pressure mercury arc (Helios Italquartz, Milan, Italy) for 100 h in the presence of bubbling oxygen and vigorous stirring.

2.4. SPME analysis

An SPME fibre coated with 100 μm of nongrafted poly(dimethylsiloxane) (PDMS) phase (Supelco 57300-U, mounted on a Supelco 57330 support) was conditioned for 1 h at 250 °C in a stream of helium. A single fibre was used for the complete study. A blank run was performed after the analysis in order to confirm that no residual compound was polluting the fibre or the column. The headspace was generated from 10 ml samples placed in a 20 ml flask. The flask was sealed and heated for 20 min in an aluminium block maintained at 45 °C (40 °C in the flask). During this time, the fibre was maintained over the sample. The fibre was then introduced into the injection port of a HP6890 plus gas chromatograph equipped with a Phenomenex Zebron ZB-5 MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness). As detector we used a HP5973 mass selective detector (mass range 15–800 amu, scan rate 1.9 scans/s, and EM voltage 1435), helium at 0.8 ml/min was used as carrier gas. The injection port, equipped with glass insert (internal diameter 0.75 mm) was splitless at 250 °C. The desorption time of 1.0 min was used. Detector was maintained at 230 °C. Oven was maintained at 40 °C for 2 min, then the temperature increased until 250 °C (8 °C/min); finally, this temperature was maintained for 10 min. All the analyses were performed in triplicate (R.S.D. 0.03%). The chromatograms obtained from the total ion current (TIC) were integrated without any correction for coelutions and the results were expressed in arbitrary surface units (asu). All the peaks were identified from their mass spectra by comparison with spectra in Wiley6N and NIST98 libraries.

3. Results and discussion

In our experiments we used a crude oil sample from Basilicata (Southern Italy). The composition of this sample and the comparison of analytical data obtained by using HS-SPME or liquid injection were discussed elsewhere [7]. The chromatogram of crude oil before irradiation is shown in Fig. 1.

The irradiation of crude oil with a high-pressure mercury arc for 100 h gave the results depicted in Fig. 1 (the chromatogram after irradiation) and Fig. 2. After irradiation, we observed a decrease (22%) of the total amount of the identified compounds. The SPME analysis of the same sample showed that all the classes of compounds decreased but linear alkanes and branched alkanes showed a light reduction, while we observed a sharp decrease in the relative amounts of both cyclic alkanes and aromatic compounds (Table 1). In this case, we determined the presence of alkenes and we observed a reduction of the relative amount after irradiation (65%). In particular, in the case of linear and branched alkanes we observed a reduction of 9 and 5%, respectively. On the contrary, cyclic alkanes decreased for 54% while aromatic hydrocarbons showed a reduction of 37%.

On the basis of these results, we can conclude that linear alkanes showed a low susceptibility to degradation while the most sensible fractions were those of the aromatic compounds and of cyclic alkanes. Aromatic compounds are involved in photodegradation: they represent the sole class of compounds able to absorb light in the crude oil and the formation of excited states of these compounds can induce the formation of condensation compounds with

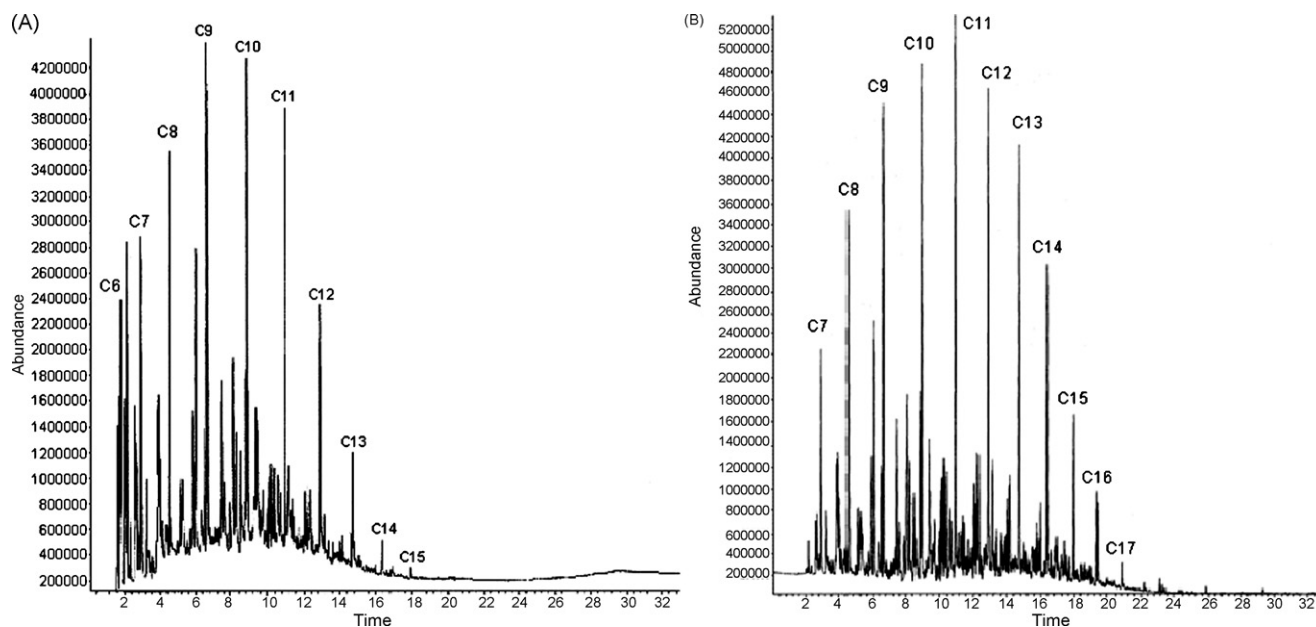


Fig. 1. Chromatograms of crude oil before (A) and after (B) irradiation.

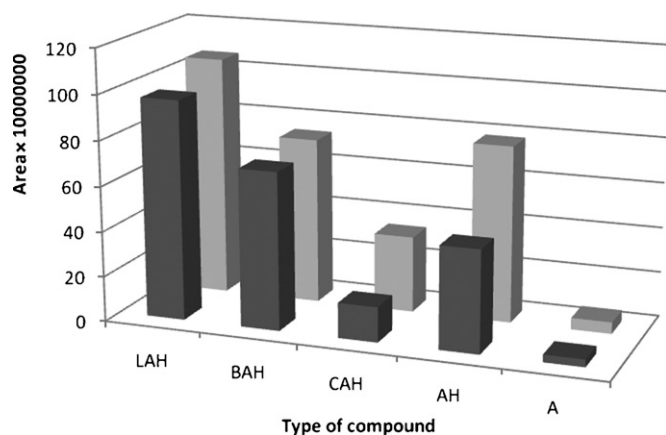
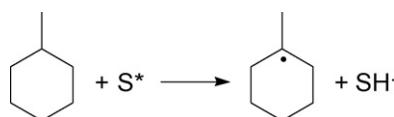


Fig. 2. SPME analysis of crude oil before (light grey) and after UV irradiation (dark grey). LAH: linear aliphatic hydrocarbons; BAH: branched aliphatic hydrocarbons; CAH: cyclic aliphatic hydrocarbons; AH: aromatic hydrocarbons; A: alkenes.

a high molecular weight, with the result that they cannot be detected in a GC–MS analysis. To confirm this hypothesis we determined the asphaltene content in crude oil before and after irradiation [38] by filtration of crude oil dissolved in *n*-heptane. We observed an increase from 0.4345 to 0.5087%. It is unclear in this context the difference observed between branched and cyclic alkanes. Their degradation probably occurs through the formation of radical species obtained via hydrogen abstraction in a sensitized reaction (Scheme 1). Both branched and cyclic alkanes are able to give stable tertiary radicals and then, we waited for a similar photochemical behaviour. In order to understand this behaviour we performed some calculations of the energy required to form a radical from

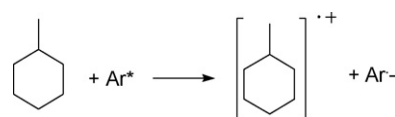


Scheme 1. Sensitized hydrogen abstraction from a branched cyclic alkane.

methylcyclohexane and from 3-methylhexane. We performed DFT calculations by using DFT/B3LYP/6-31G+(d,p) method on Gaussian03 [39]. The results are reported in Table 2. Clearly, the radical on 3-methylhexane is more stable than that formed on methylcyclohexane by 4.9 kcal/mol. This difference cannot explain the observed behaviour. However, calculated ionization potentials of hydrocarbons seem to be in agreement with the above reported results [40]. In this case, the ionization potential of branched alkanes is generally higher than that of cyclic alkanes. This evidence is in agreement with an electron transfer mechanism from the aromatic compounds (the only compounds able to absorb light) to the alkanes (Scheme 2).

We performed irradiation of the crude oil also in the presence of titanium dioxide and oxygen. The reaction of titanium dioxide with oxygen in the presence of water is a way to obtain a lot of oxidizing species, such as superoxide oxygen, hydroperoxyl radical, and hydroxyl radical. The irradiation was performed with a high-pressure mercury arc for 100 h. The chromatograms of the crude oil before and after photocatalysis are reported in Fig. 3. The results are reported in Fig. 4. After 100 h irradiation the sample was almost quantitatively degraded: linear alkanes were degraded for 98.66%, branched alkanes were reduced for 97.31%, cyclic alkanes for 96.04%, while aromatic compounds and alkenes were reduced for 99.54 and 98.38%, respectively. In this case, cyclic alkanes were photooxidized with a lower efficiency than branched alkanes, in agreement with the above reported calculations. In this case, the reaction seems to occur through hydrogen abstraction by one of the oxidizing species generated in the reaction and the hydrocarbon mixture.

Finally, we used zeolite (NaY) as absorbing phase during photocatalysis. Zeolites are microporous crystalline aluminosilicates with structural features that make them attractive hosts



Scheme 2. Sensitized electron transfer in a branched cyclic alkane.

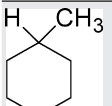
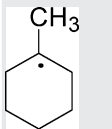
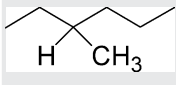
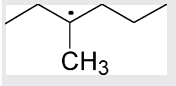
Table 1
Compounds used for the evaluation of irradiation on the composition of crude oil

Linear alkanes	Branched alkanes	Cyclic alkanes	Aromatic compounds	Alkenes
Propane	2-Methylbutane	Methylcyclopentane	Toluene	1-Hexene
Butane	2-Methylpentane	Methylcyclohexane	<i>p</i> -Xylene	1-Octene
Pentane	3-Methylpentane	<i>cis</i> -1,2-Dimethylcyclopentane	<i>m</i> -Xylene	1-Nonene
Hexane	2-Methylhexane	Ethylcyclopentane	1-Ethyl-2-methylbenzene	3,4,4-Trimethyl-1-hexene
Heptane	3-Methylhexane	1,2,4-Trimethylcyclopentane	1,2,4-Trimethylbenzene	1-Heptene
Octane	2,4-Dimethylpentane	1,2,3-Trimethylcyclopentane	1,2,3-Trimethylbenzene	3,4,5-Trimethyl-1-hexene
Nonane	2,3-Dimethylhexane	1,2-Dimethylcyclohexane	1,3,5-Trimethylbenzene	1-Octadecene
Decane	2-Methylheptane	<i>cis</i> -1-Ethyl-2-methylcyclopentane	1-Methyl-2-propylbenzene	1-Decene
Undecane	3-Methylheptane	Ethylcyclohexane	1-Methyl-3-propylbenzene	
Dodecane	2,4-Dimethylhexane	1,2,3-Trimethylcyclohexane	1,1-Dimethylpropylbenzene	2-Undecene
Tridecane	2,6-Dimethylheptane	1,1,3-Trimethylcyclohexane	1-Methyl-3-(1-methylethyl)benzene	1-Undecene
Tetradecane	2,4-Dimethylheptane	Propylcyclopentane	1-Methyl-4-(1-methylethyl)benzene	1-Tridecene
Pentadecane	2,3-Dimethylheptane	1-Buthyl-2-pentylcyclopentane	1-Methyl-2-(1-methylethyl)benzene	1-Dodecene
Hexadecane	3-Ethyl-2-methylhexane	1-Methyl-2-propylcyclopentane	Methyl-(1-methylethyl)benzene	7-Methyl-6-tridecene
Heptadecane	3-Ethyl-2-methylheptane	1-Ethyl-3-methylcyclopentane	1-Ethyl-2,3-dimethylbenzene	
Octadecane	2-Methyloctane	1-Ethyl-4-methylcyclohexane	1-Ethyl-2,4-dimethylbenzene	
Nonadecane	3-Methyloctane	1-Methylpropylcyclohexane	1-Ethyl-2,4,5-trimethylbenzene	
Tetacosane	4-Methyloctane	1-Pentyl-2-propyl-cyclopentane	4-Ethyl-1,2-dimethylbenzene	
Heneicosane	3,5-Dimethyloctane	Pentylcyclohexane	1,2,4,5-Tetramethylbenzene	
	2,6-Dimethyloctane	1,1-Dimethyl-2-propylcyclohexane	1,2,3,4-Tetramethylbenzene	
	3-Ethylheptane	1-Ethyl-2,2,6-trimethylcyclohexane	1,3-Diethyl-5-methylbenzene	
	4-Ethylheptane	2-Buthyl-1,1,3-trimethylcyclohexane	1-Methylnaphthalene	
	4-Ethylloctane	1,2-Dimethylcyclooctane	2-Methylnaphthalene	
	2-Methylnonane	Cyclododecane	2,6-Dimethylnaphthalene	
	3-Methylnonane	Cyclopentadecane	1,7-Dimethylnaphthalene	
	4-Methylnonane	1,1,3,3,5-Pentamethyl-2,3-dihydroindene	1,6-Dimethylnaphthalene	
	2,5-Dimethyloctane	9,9-Dimethyl-1,4-dihydro-1,4-methanonaphthalene	2,7-Dimethylnaphthalene	
	4,5-Dimethyloctane	Decahydro-4,4,8,9,10-pentamethylnaphthalene	1,4,6-Triimethylnaphthalene	
	3-Ethylloctane		1,6,7-Triimethylnaphthalene	
	2,6-Dimethylnonane		Dimethylnaphthalene	
	4,5-Dimethylnonane		1,2,3,4-Tetrahydro-1,8-dimethylnaphthalene	
	3,7-Dimethylnonane		7-Ethyl-1,4-dimethylazulene	
	2,7-Dimethylnonane			
	5-Methyldecane			
	4-Methyldecane			
	2-Methyldecane			
	3-Methyldecane			
	2,6-Dimethyldecane			
	5-Methylundecane			
	5-(1-Methylpropyl)nonane			
	5-Ethyl-2-methyloctane			
	4-Methylundecane			
	2-Methylundecane			
	3-Methylundecane			
	2,4-Dimethylundecane			
	2,6-Dimethylundecane			
	2-Methyldodecane			
	3-Methyldodecane			
	4-Methyldodecane			
	6-Methyldodecane			
	4,6-Dimethyldodecane			
	4-Methyltridecane			
	7-Methyltridecane			
	2-Methyltridecane			
	3-Methyltridecane			
	3-Methyltetradecane			
	2-Methyltetradecane			
	4-Methyltetradecane			
	7-Methyltetradecane			
	2,6,10-Trimethyldodecane			
	3,8-Dimethyldecane			
	2,6,10,14-Tetramethylhexadecane			

for photochemical applications. The topological structure of Y-type zeolite consists of an interconnected three-dimensional network of relatively large spherical cavities, termed primary supercages (diameter of about 13 Å); each supercage is connected tetrahedrally to four other secondary supercages through

7.4–7.6 Å windows. Extra framework cations are necessary for the neutralization of charges due to the presence of tetrahedral aluminium. These cations can easily interact with guest molecules. To charge-compensating cations are known to occupy three different positions in the internal structure of Y-zeolites: the first type (site

Table 2
Energy of suitable molecules (DFT results)

Molecule	Energy (hartree)	ΔE (kcal/mol)
	-275.22131558	
	-274.55871494	415.79
	-276.42027944	
	-275.76569472	410.92

I), with 16 cations per unit cell, is located on the hexagonal prism faces between the sodalite units; The second type (site II), with 32 cations per unit cell, is located in the open hexagonal faces. The third type (site III), with eight cations per unit cell, is located in the walls of the largest cavity. Only cations at sites II and III are expected to be readily accessible to the organic molecule adsorbed within a supercage.

Figs. 5 and 6 collect the results we obtained. Fig. 5 reports the chromatograms of crude oil before and after photocatalysis. We observed an extensive degradation of the crude oil, but in lower entity than in case we used only titanium dioxide (Fig. 6). The presence of the zeolite protects crude oil from photodegradation. This effect can be due only to light scattering considering that the zeolite is transparent to UV–vis light. After 100 h irradiation the sample was degraded: linear alkanes were degraded for 79.85%, branched alkanes were reduced for 45.38%, cyclic alkanes for 58.10%, while aromatic compounds were reduced for 91.85%.

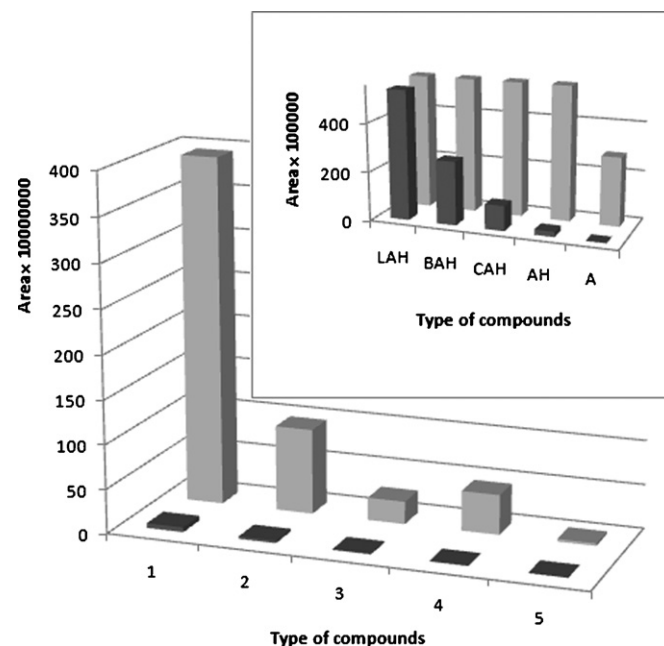
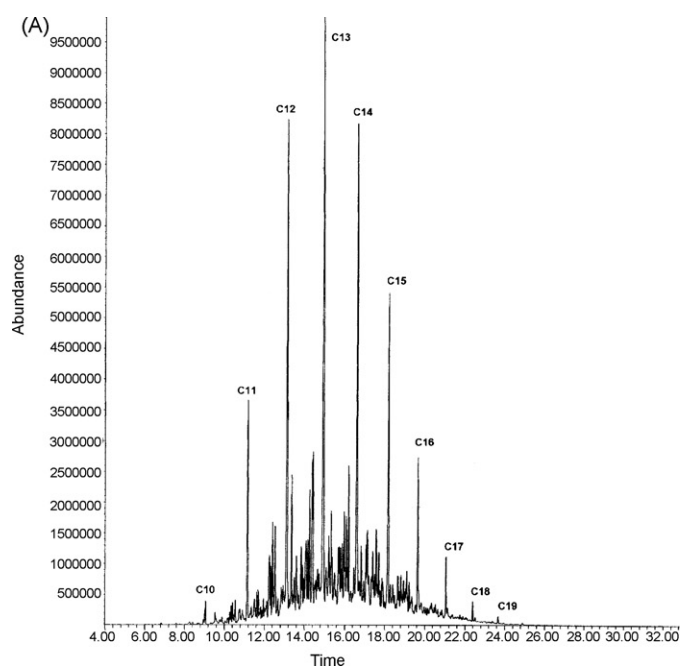


Fig. 4. SPME analysis of crude oil before (light grey) and after UV irradiation (dark grey) in photocatalytic conditions. LAH: linear aliphatic hydrocarbons; BAH: branched aliphatic hydrocarbons; CAH: cyclic aliphatic hydrocarbons; AH: aromatic hydrocarbons; A: alkenes. The insert in upper right corner represents the same graphic in a different scale.

In this case, we observed an increase of the relative amount of alkenes (42.05%). Probably, they are degradation products of the aromatic compounds. Using titanium dioxide adsorbed on a zeolite we observed that cyclic alkanes are degraded with higher efficiency than branched alkanes. This is not in agreement with the above reported results on the relative stability of the radicals in branched and cyclic alkanes. This result could be due to the different ability of cyclic and branched alkanes to assume a correct conformation to allow the entrance in the supercage of the zeolite.

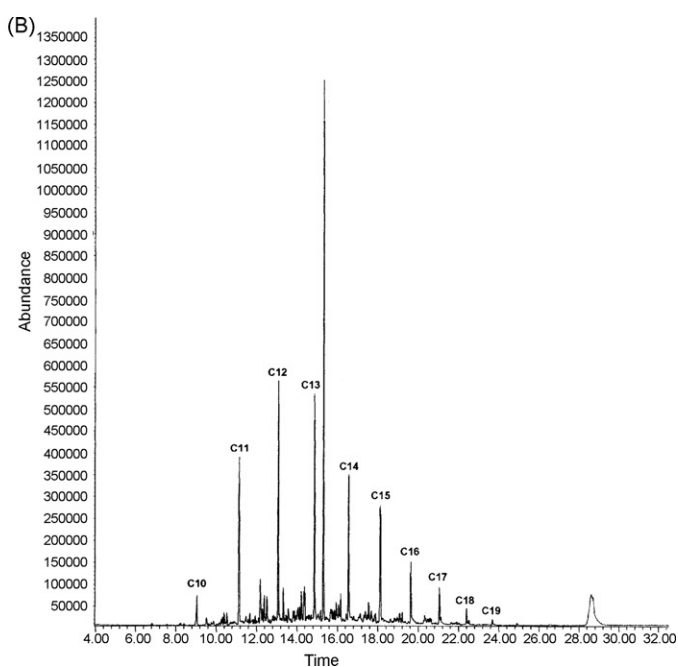


Fig. 3. Chromatogram of crude oil before (A) and after (B) photocatalysis.

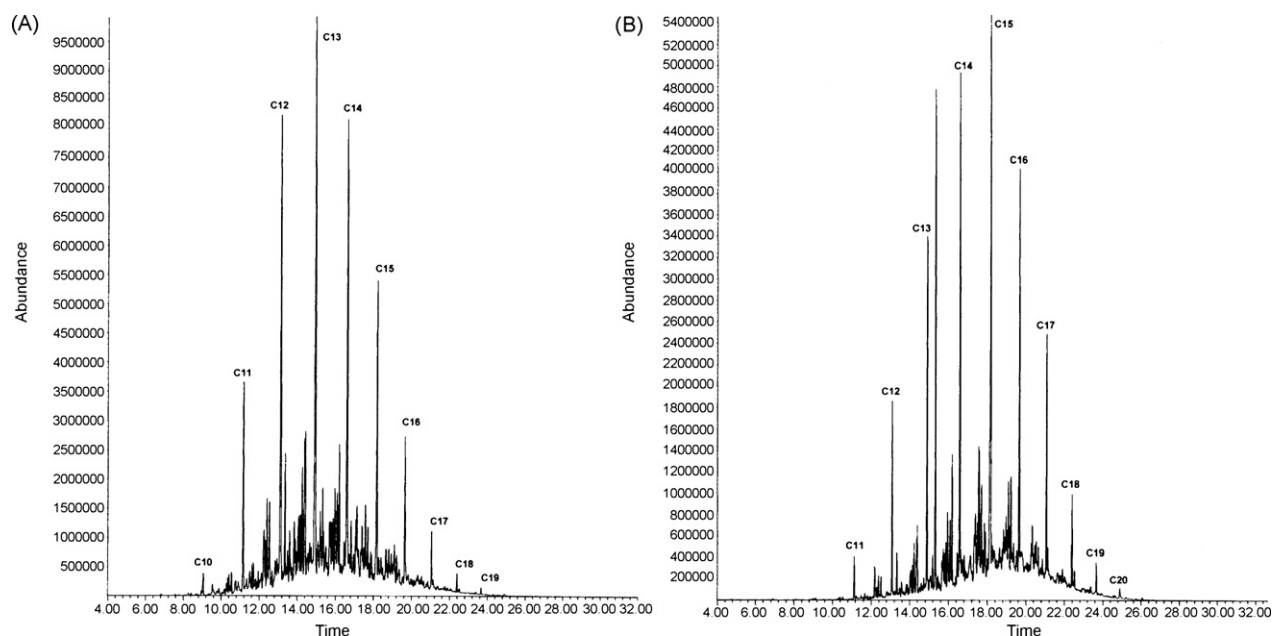


Fig. 5. Chromatogram of crude oil before (A) and after (B) photocatalysis in the presence of zeolite.

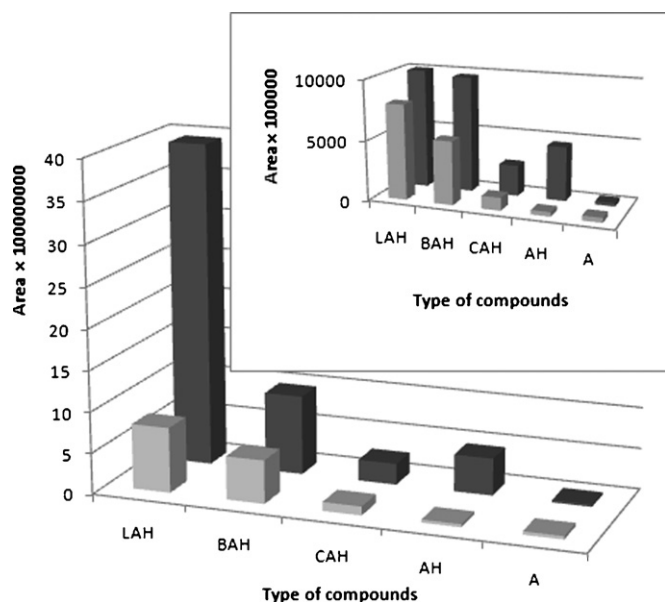


Fig. 6. SPME analysis of crude oil before (dark grey) and after UV irradiation (light grey) in photocatalytic conditions in the presence of a zeolite (NaY). LAH: linear aliphatic hydrocarbons; BAH: branched aliphatic hydrocarbons; CAH: cyclic aliphatic hydrocarbons; AH: aromatic hydrocarbons; A: alkenes. The insert in upper right corner represents the same graphic in a different scale.

It is noteworthy that in this case we observed the formation of some oxidation products: we identified the presence of 3-methylbutanal, hexanal, heptanal, 6-methyl-2-heptanone, octanal, nonanal, 1-tridecanol, 1-tetradecanol, and 1-tetracosanol. We did not observe the formation of oxidation products in the previous experiments.

4. Conclusions

In conclusion, we showed that photocatalysis is the best method for crude oil degradation. It works better than simple photochemi-

cal degradation. Furthermore, the efficiency on the various classes of organic compounds involved is different, probably in order to the different prevalent reaction mechanism present. Photocatalysis slows down when the reaction is performed in zeolite. This effect is due to light scattering.

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