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Evaluation of a TiO_2 photocatalysis treatment on nitrophenols and nitramines contaminated plant wastewaters by solid-phase extraction coupled with ESI HPLC–MS

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Dinoseb
Dinoterb
Hexahydro-1,3,5-trinitro-1,3,5-triazine
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
UV/TiO_2

A B S T R A C T

Nitration reactions of aromatic compounds are commonly involved in different industrial processes for pharmaceutical, pesticide or military uses. For many years, most of the manufacturing sites used lagooning systems to treat their process effluents. In view of a photocatalytic degradation assay, the wastewater of a lagoon was investigated by using HPLC coupled with mass spectrometry. The wastewater was highly concentrated in RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and two herbicides Dinoterb (2-*tert*-butyl-4,6-dinitrophenol) and Dinoseb (2-*sec*-butyl-4,6-dinitrophenol). First of all, an analytical method using solid-phase extraction (SPE) combined with HPLC ESI MS/MS was put in work for identification and titration of RDX, HMX and the two dinitrophenols in a complex natural matrix. Then, the UV/TiO_2 treatment was investigated for pollutants removal. Dinitrophenolic compounds were significantly degraded after a 8-h-exposition of the wastewater/TiO_2 suspension, whereas RDX and HMX were poorly affected.

1. Introduction

For several decades, a wide range of nitro-aromatic and nitramine molecules were processed on the same manufacturing site for pyrotechnic synthesis (e.g. RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), TNT (trinitrotoluene), picric acid or for pesticide synthesis (e.g. nitrophenols such as Dinoseb (2-*sec*-butyl-4,6-dinitrophenol), Dinoterb (2-*tert*-butyl-4,6-dinitrophenol)). Wastewater from these plants is often contaminated with complex mixtures of these different xenobiotics. Considering the persistence of nitro-aromatic compounds, this wastewater is today a source of contamination for soils, groundwater and surface water [1]. In addition, most of the derivatives are known to be toxic. RDX and its metabolites are currently reported to damage soil and water organisms [2–4]. Robidoux et al. have described significant effects of HMX on the growth and reproduction of the earthworm (*Eisenia andrei*). The Dinoseb 96 h LC_{50} value for Chinook salmon (*Salmo salar*) alevins has been established at 70.6 ppb and 87% mortality for Chinook salmon alevins was observed after a 96-h-exposure to 100 ppb [5]. Dinoterb is reported to have hepatotoxic effects between 10 and 100 $\mu mol\,L^{-1}$ after 2 h of incubation on rat hepatocytes and becomes much more toxic for a 24-h exposure. Dinoterb was withdrawn from sale in April 1998 by the European Authorities (decision 98/269/CE) and nitrophenols are registered as priority pollutants (HR-3 grade) by the US EPA (US EPA, 1976).

To overcome these environmental problems, several biochemical techniques (ultrafiltration, coagulation, evaporation, etc.) have been tried [6,7] but owing to their high cost, few have ever been applied on an industrial scale. Biodegradation processes are reported to be successful on wastewater sludges [8,9]. Previous study showed that consumption of Dinoterb was obtained after 5 days in presence of *Pseudomonas citronellolis* and glucose [10]. But, the time necessary to degrade all nitrophenolic compounds contained in the sludge was of 10 weeks.

In recent years, several works have been focused on the destruction of these synthetic wastes using different oxidation technologies such as chemical oxidation [11], advanced oxidation processes (AOP) [12] catalytic wet air oxidation (CWAO) (Oliviero et al., 2003) or electrochemical oxidation [13]. Photocatalytic processes [14] may be an alternative method to allow improving of degradation duration. Heterogeneous photocatalysis, involving

Abbreviations: HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; TNT, tri-nitro-toluene; ESI, electospray ionization; LOD, limit of detection; LOQ, limit of quantification; NL, noise level; SPE, solid-phase extraction; TIC, total ionic current.

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photoinduced redox reactions at the surface of semiconductor minerals, is a promising technique for the treatment of water contaminated by organic molecules [15–17]. Among the semiconductors available, titanium dioxide, or titania, is the most widely used in due to its outstanding stability [18]. Previous studies showed that dinitrobenzene (DNB) could be degraded with photocatalysis by UV/TiO_2 treatment [19]. In these conditions, pH 7 was shown to lead to the most efficient degradation of DNB. At concentration of 50 mg/L, 4 h were necessary to degrade the totality of DNB. Most of studies were realized on pure compounds, and few on mixed compounds coming from industrial wastewater.

The goal of the present study is to degrade nitrated compounds contained in wastewater by using a photocatalytic treatment. Firstly, an assessment of compounds present in the wastewater was realized at the start of the treatment. Thus, a simple and selective method let to analyze two nitramine compounds (RDX and HMX) and two dinitrophenolic herbicides (Dinoterb and Dinoseb) in wastewater contained in an old industrial lagoon. After SPE of the wastewater, the compounds were investigated by a multi-residue approach using ESI–LC/MS in the negative mode and taking into account the same molecular weight and the proximal physicochemical characteristics of Dinoseb and Dinoterb by the MS/MS mode. This approach comes in response to the need for sensitive and reliable analytical methods for the simultaneous assay of organic compounds from several families and the need of new treatments able to degrade hazardous nitrated compounds. Finally, this paper reports the photocatalytic degradation of nitrophenols in a multi-residue wastewater containing several herbicides and explosives.

2. Methods

2.1. Samples

Our contaminated material, wastewater from an old decantation lagoon which received effluent from a military manufacturing plant for about 100 years, contained at least four nitrified cyclic compounds (RDX, HMX, Dinoseb (2-*sec*-butyl-4,6-dinitrophenol) and Dinoterb (2-*tert*-butyl-4,6-dinitrophenol). The samples were stored at 4 °C until extraction.

2.2. Chemicals

Standard Dinoseb and Dinoterb herbicides (Fig. 1A) were purchased from Cluzeau Info Labo (Paris, France). Standard explosives RDX and HMX (Fig. 1B) were obtained from Restek (Paris, France). Methanol, acetonitrile and HPLC grade water were obtained from Fisher Analytics (Illkirch, France). Helium was provided by air liquid (Labège, France). Nitrogen (purity > 99.9%) was provided by a nitrogen generator NM18LA (F-DBS, Courtaboeuf, France).

2.3. Extraction of explosives and herbicides

As the solubility of these organic compounds changes with pH, the wastewater pH was adjusted to 7.5. Solid-phase extraction (SPE) Porapak RDX cartridges (Waters, Massachusetts) were used to extract both explosive and herbicide compounds. SPE cartridges were conditioned prior to sample extraction with 5 mL acetonitrile. Acetonitrile was then flushed from the cartridges using 30 mL of reagent grade water. Care was taken to ensure that the cartridges were never allowed to dry after the initial cleaning. A 5-mL aliquot of sample was vacuum-siphoned at a flow rate of 10 mL/mn through the SPE cartridge. Studied compounds were then eluted from the SPE cartridge with 5 mL of acetonitrile since their solubility in this solvent is higher than in water. The eluate was diluted to 1/50 and transferred to an HPLC auto-sampler vial (Thermo Fisher) for analysis.

2.4. Analysis of explosives and herbicides

The concentrations of HMX, RDX, Dinoseb and Dinoterb were identified using a high-performance liquid chromatography-mass spectrometry (LC–MS) system (Surveyor Pump, Thermo; Surveyor Autosampler, Thermo). Ten microliters of the extract were injected into the HPLC system equipped with a reverse-phase column

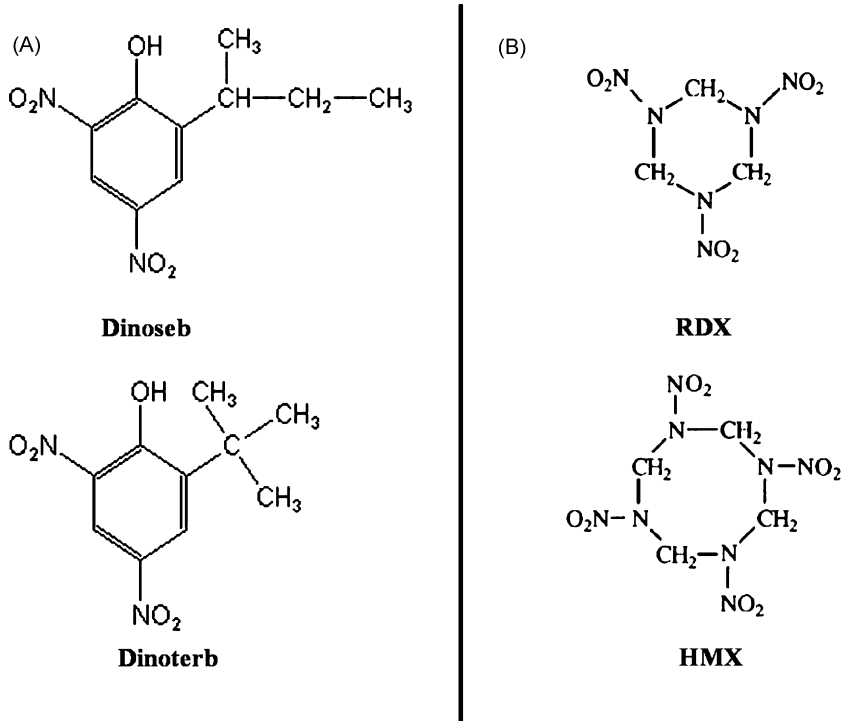

Fig. 1. Molecular structure of the herbicides (Dinoseb and Dinoterb) and explosives (RDX and HMX) studied.

Table 1
Source parameters for LCQ ion trap mass spectrometer for electrospray ionization configuration.

ESI source	Ion optics
Mode: negative	Capillary temp (°C): 280
Ion spray voltage (kV): 4	Multiple 1 offset (V): 2.25
Sheath gas flow rate (UA): 40	Tube lens offset (V): 0
Aux/sweep gas flow rate (UA): 10	Multiple 2 offset (V): 5
Capillary voltage (V): −6	Multiple RF Amp (V_{p-p}, sp): 400

(Hypersil ODS C18, 3 μ, 4.6 mm I.D. × 150 mm, Thermo). The solvent systems used were a mixture of solvent A (methanol) and solvent B (HPLC grade water). Compounds were eluted at a flow rate of 0.8 mL min^{-1} under a gradient starting with 26% of solvent A, ending at 74% of solvent A in 18 mn.

Mass spectrometry was performed with an ion trap spectrometer (LCQ Advantage Max, Thermo). The tune function was used to optimize essential parameters of the ESI–MS system. Other conditions, such as capillary temperature or nitrogen gas flow, were manually optimized. The final ESI–MS conditions are reported in Table 1. For all ESI–MS and ESI–MS/MS measurements, solutions of explosives were continuously infused by means of a syringe pump. Scan parameters were set from m/z 100 to 600 amu in full-scan investigations. A negative-ion ESI mass spectrum of Dinoseb and Dinoterb was acquired by flow injection into an eluent consisting of methanol:water (50:50), leading to a common molecular ion with an m/z value of 239 amu. The MS/MS mode was used to separate Dinoseb and Dinoterb. The collision energy for each ion transition was optimized to produce the highest intensity of the selected ion peak and common optimized relative collision energy of 42% was used for all MS/MS works.

The concentrations of potential explosives and herbicides were investigated using a high-performance liquid chromatography separation device coupled with detector-mass spectrometry (LC–MS) by comparing the areas under the curve obtained to those of the corresponding calibration sample. Concentrations of herbicides (Dinoseb and Dinoterb) and explosives (RDX and HMX) were quantified using the Excalibur data system from Thermo Fisher.

2.5. TiO_2/UV treatment

The following protocol results from a previous study realized on olive mill wastewater photocatalytic successful treatment [20]. For this experiment, sludge was diluted to 1/100 and filtered through a 0.45-μm glass fiber filter to avoid the presence of a particular phase and crystalline forms of the studied products. The photocatalyst was TiO_2 Degussa P25. It was added at a level of 1 g/L. The reactor had a working volume of 100 cm^3. The reactor was composed of a water-cooled double-walled Pyrex glass tube. The reaction mixture was continuously homogenized by magnetic stirring. It was illuminated by a vertical UV tube TLAD Philips 415W/05 (300–450 nm with an emission maximum at 365 nm). During the reaction, the suspension was maintained under constant oxygen bubbling. The medium was mixed in the dark (TiO_2 only condition) during half an hour prior to irradiation. This time was sufficient to reveal chemical compounds as explosives or pesticides adsorption on the catalyst [21–23]. Samples were collected at $t = 0$ h before irradiation and at 0.5, 1, 2, 4, and 8 h during illumination. They were filtered using 0.45 μm Millipore filters to eliminate the excess of TiO_2 prior to analysis.

3. Results and discussion

3.1. Assessment before the beginning of photochemical treatment

Solid-phase extraction carried out with a specially cleaned divinyl benzene-vinylpyrrolidone copolymer resin (Porapak RDX) was commonly used to detect nitramines and nitro-aromatic explosive compounds in water [24]. In this study, SPE was used to clean complex wastewater samples from the impurity and mineral salt load in contrast to the common use as a pre-concentration step for explosives [25]. The recovery percentages on extraction cartridges of a mix of Dinoseb, Dinoterb, RDX and HMX (0.5 μg mL^{-1} per compound) were evaluated at 87 (±2%), 87 (±3%), 86 (±1%) and 90% (±3%), respectively.

Retention times, molecular weights, detected ions, limits of detection (LODs) and limits of quantification (LOQs) of standards using ESI–LC–MS are presented in Table 2. The use of a gradient elution method allowed us to distinguish both explosives from Dinoseb and Dinoterb. The criteria for estimating the LODs were the smallest amount injected that yielded a signal-to-noise ratio greater than 3 for the mass chromatogram based on the characteristic ions. LODs were measured for these compounds by a triplicate injection from a series of solutions in methanol. The concentrations used for LODs determination were 1, 2, 5, 10 and 50 μg/L and those used for HPLC calibration were 1, 5, 10 and 25 μg/L. The correlation coefficient varied in the range of 0.950–0.999 for all the investigated analytes.

As shown by Fig. 2, the total ion current (TIC) chromatogram obtained in the ESI negative mode (A) authorized the extraction of the mass spectra of each component of the explosive mix (B, C and D) showing the characteristic ions of each one. HMX is well identified by LC–MS in the negative mode since the $[M+NO_2-H]^-$ cluster ion constitutes the most abundant ion (mass spectrum B). Another cluster ion is observed at m/z 355, and concerns the $[M+NNO_2-H]^-$ structure. Like HMX, RDX forms the same couple of cluster ions $[M+NO_2-H]^-$ and $[M+NNO_2-H]^-$ (mass spectrum C). This case has been reported previously [26]. Fragmentation processes characterized by losses of CH_2NNO_2, NNO_2, NO_2 and NNO are represented by the ions $m/z = 226$ and $m/z = 197$ under our experimental conditions for these molecules. This route predominates with TNT, characterized by a signal at 226 corresponding to the deprotonated parent ion $[TNT-H]^-$, whereas $m/z = 197$ concerns the ion $[TNT-NO]^-$ resting form in accordance with other studies [26,27].

As shown in Fig. 3, a good separation between the herbicides was observed for Dinoseb and Dinoterb as seen by their common molecular ion m/z 239. In addition to their different retention times, MS/MS gives another proof of their respective identities (Fig. 4). The ESI–MS/MS spectrum showed two specific ions at $m/z = 194$ and $m/z = 221$ for Dinoseb, while Dinoterb had a single specific ion at $m/z = 207$. Studies of the MS/MS spectra of Dinoseb showed that the ion $m/z = 194$ in the MS/MS spectrum is formed through the cleavage in the neutral molecule CH_3NO released from the side chain and the remaining nitrophenolate [28].

Table 2
Retention time, molecular weight (MW), detected ions, limits of detection (LODs) (μg L^{-1}) and method detection limits (LOQs) in mass spectrometry (μg L^{-1}) for the studied compounds.

Retention time	Analyte	MW (g mol^{-1})	Ions detected in negative ESI (relative abundance)	LOD in mass (μg L^{-1})	LOQS (μg L^{-1})
8.39	Dinoseb	240	239	5	100
10.20	Dinoterb	240	239	5	100
4.47	HMX	296	295	1	200
8.25	RDX	222	267	20	300

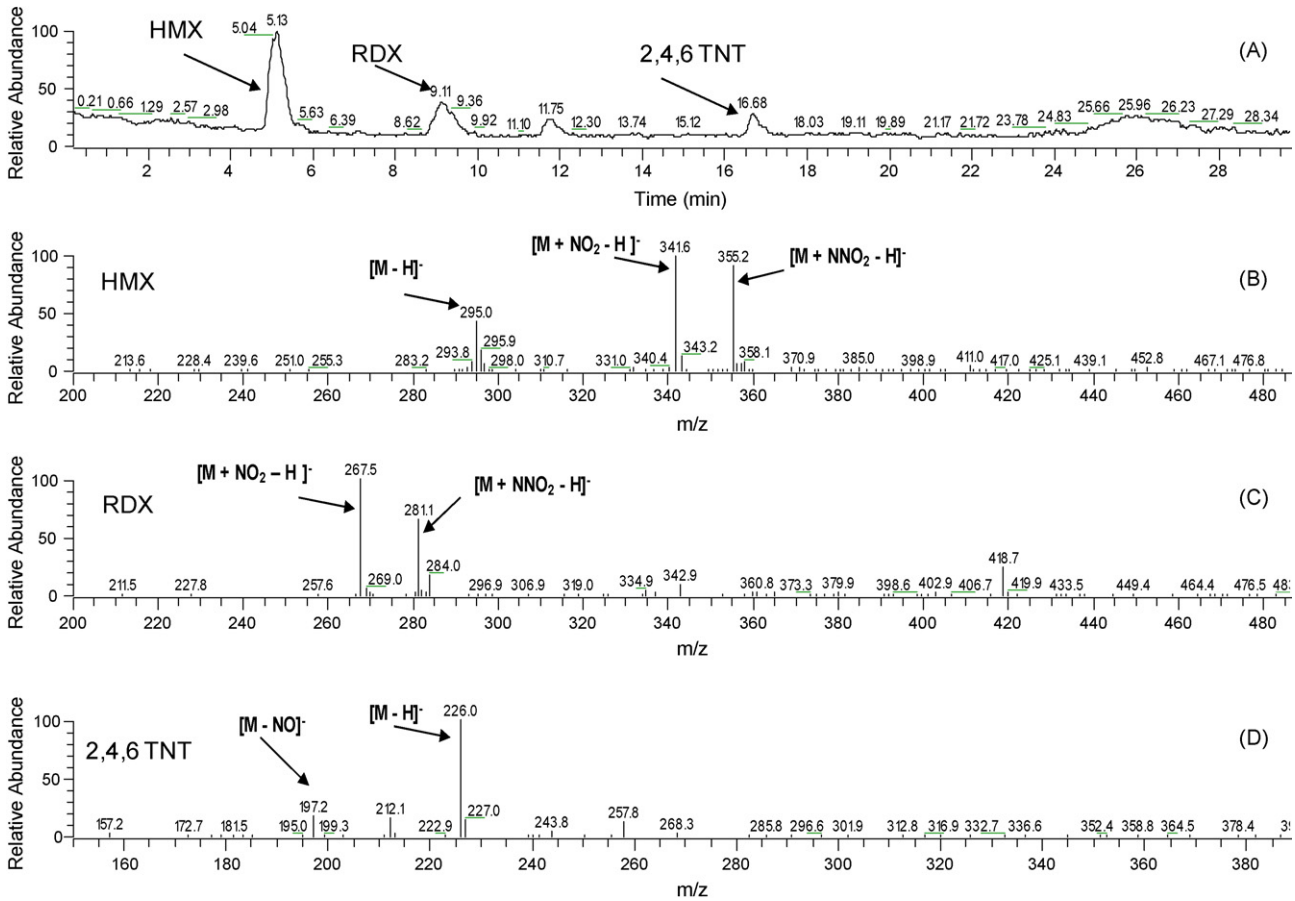

Fig. 2. Mass analysis of standard explosives. (A) Total ionic current for the explosive mix obtained in the ESI mode. (B) Mass spectrum for HMX. (C) Mass spectrum for RDX. (D) Mass spectrum for TNT.

This study demonstrates that the use of an SPE method combined with HPLC ESI MS/MS is suited to the analysis of compounds presenting two different ring cycles (nitramine and nitrophenolic compounds) in a complex matrix leading to good separation. As shown in Fig. 5, Dinoseb and RDX have the same retention time. Quantification could be carried out by the specific ions of RDX ($m/z = 267$ and $m/z = 281$) and Dinoseb ($m/z = 239$), respectively in the total mass chromatogram.

Under the chromatographic conditions described in our study the concentrations of HMX, RDX, Dinoseb and Dinoterb were 4.03, 25, 15.6 and 4.65 mg L^{-1}, respectively, in the wastewater sample at $t = 0$ (before the UV irradiation).

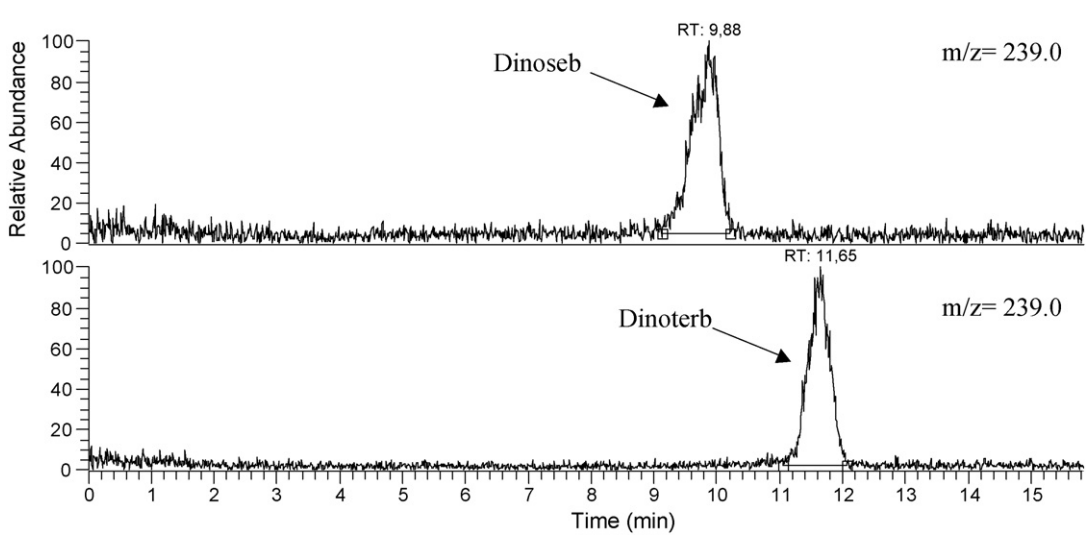

Fig. 3. Negative-ion ESI mass chromatograms obtained for the two dinitrophenols Dinoseb and Dinoterb.

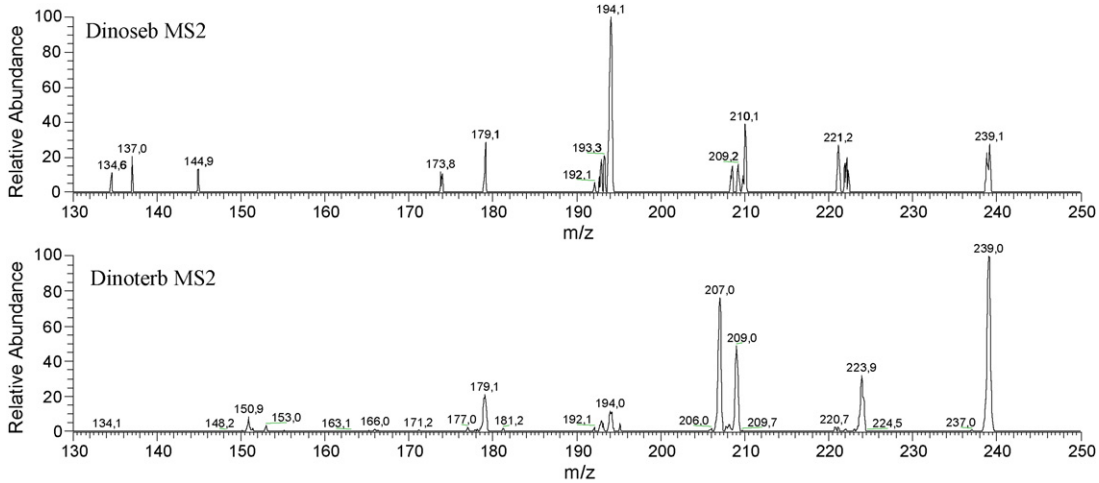

Fig. 4. Negative ion ESI–MS/MS mass spectrum of dinitrophenols Dinoseb and Dinoterb.

3.2. Photocatalytic treatment

Several methods of treating TNT, or other nitrophenolic or nitramine compounds in contaminated water have been developed. It was shown that TNT photocatalytic degradation was more effective at neutral pH [21]. Another study showed that photocatalysis is an effective process for the degradation of TNT, RDX and HMX. These compounds could be completely degraded in 150 min with 1.0 g/L TiO_2 at pH 7 [29]. Thus, in our experimental conditions, pH was adjusted to 7 by hydrochloric acid addition before beginning the photocatalytic treatment. The initial pH was stable at 7.4 at start and during the dark period (30 min before illumination). It slightly decreased to 7.2 during the 8 h of UV illumination.

The development of the analytical method previously described in this study allowed us to monitor RDX, HMX, Dinoterb and Dinoseb concentrations during the photocatalytic treatment. Chromatograms of Dinoseb and Dinoterb during UV treatment are presented in Fig. 6. Dinoseb and Dinoterb are no longer detected after 8 h exposition. As shown by Fig. 7, after 8 h exposition, 98.1% of Dinoterb and 94.6% of Dinoseb were degraded. In these conditions, only 13.7% of RDX was degraded, whereas HMX was not degraded. In 8 h, nitramines were weakly affected by the photocatalytic treatment, showing that this treatment is less destructive for these compounds as for the phenolic ones. This could be associated with the absence of a marked pH variation corresponding to nitramines decomposition [22,30].

The irradiation of TiO_2 yields hydroxyl radicals which are very oxidant species able to react with a great variety of organic chemicals, alone or in mixture. Under this treatment, olive mill wastewater with UV/TiO_2 for 24 h led to the almost complete dis-

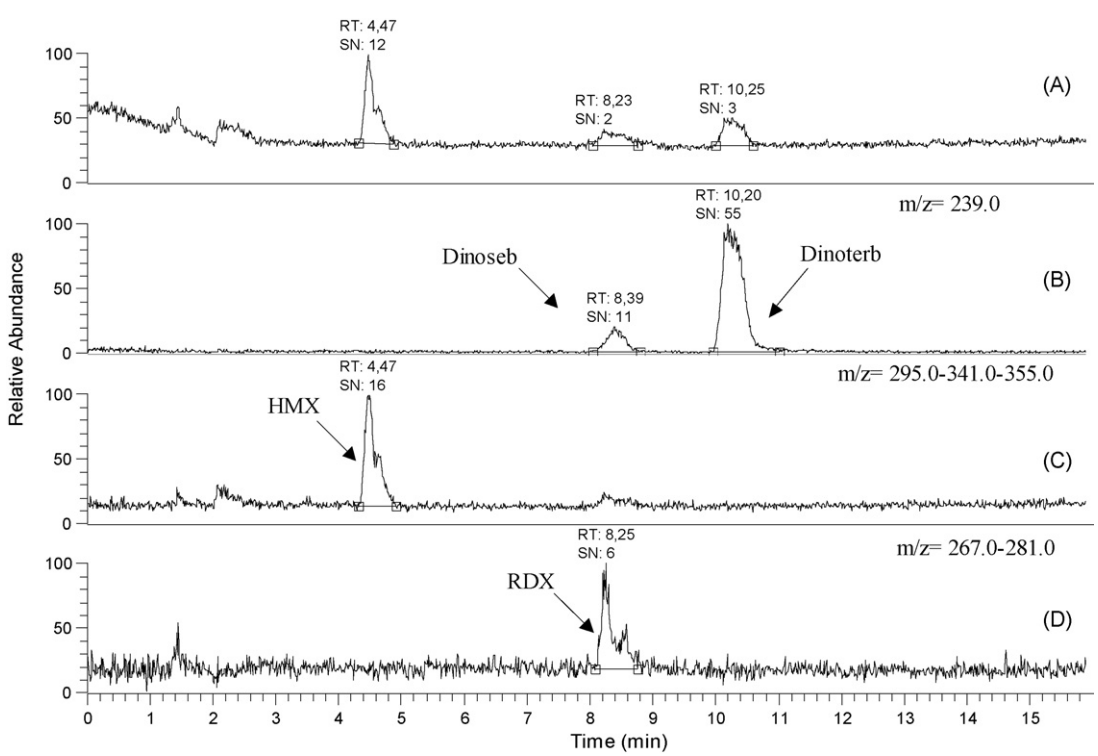

Fig. 5. Negative ion ESI–MS total ionic current chromatogram (A) for the studied wastewater sample and specific ion chromatograms for Dinoseb and Dinoterb (B), for HMX (C) or RDX (D).

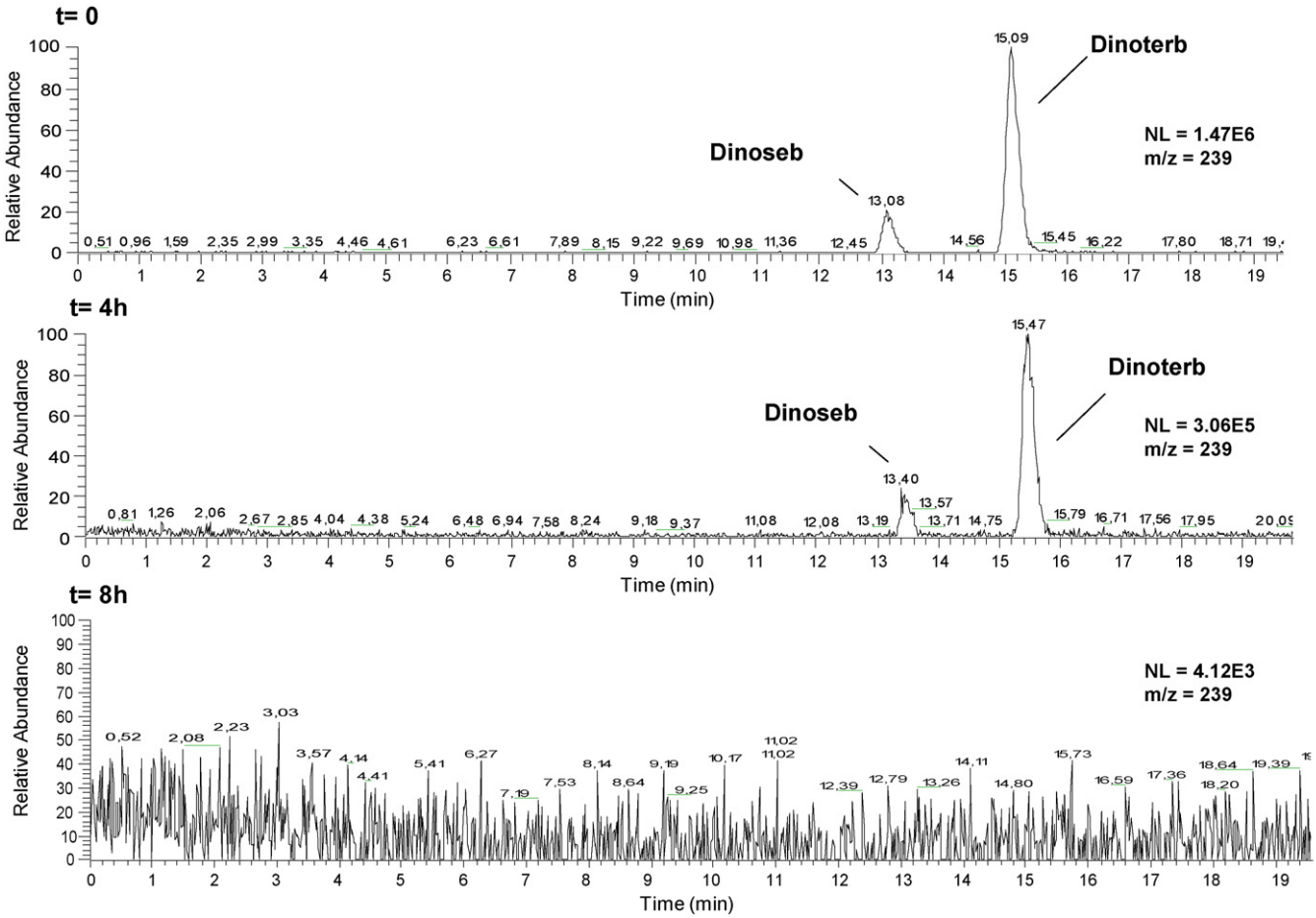

Fig. 6. Negative ion ESI–MS specific ion chromatograms for Dinoseb and Dinoterb during UV/TiO_2 treatment.

appearance of the mixture of phenol compounds [20]. Since these hydroxyl radicals are produced at the surface of the photocatalyst, only chemicals approaching very close the photocatalyst surface can be degraded. The weak reactivity of RDX and the non-reactivity of HMX are due either to their chemical stability or to their incapacity to approach the catalyst surface under this experimental pH condition. The *s*-triazine derivative cyanuric acid which possesses one OH substituent on each of the C of the ring is reported to be resistant to photocatalytic treatment or other types of oxidation treatment involving hydroxyl radicals [31]. The structure of RDX and HMX is quite different from that of cyanuric acid because NO_2 substituents are beared by the cyclic N, and the ring is saturated, but they have in common a very symmetric structure. To improve their degradation, studies would be necessary to determine the adsorption capacities of RDX and HMX, alone or in the reactional mixture, in function of pH and presence of solvent as acetonitrile [30].

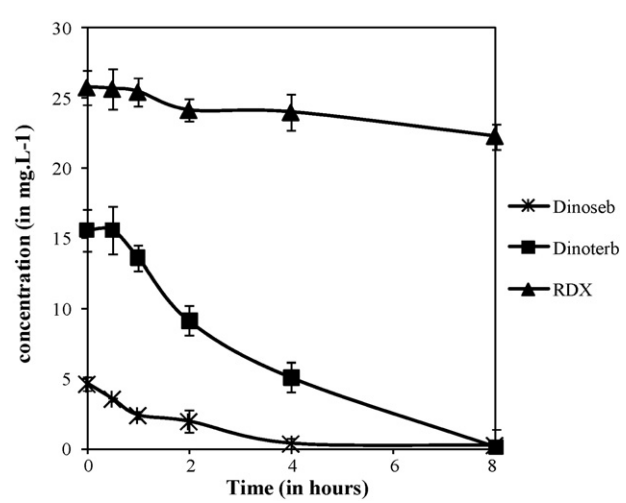

Fig. 7. Time course HPLC analyses of sample filtrate wastewater samples after photochemical UV/TiO_2 treatment.

4. Conclusion

LC/MS/MS appears to be a powerful technique for the analysis of nitramine and nitro-aromatic compounds. This method enables the sensitive and selective assay of two nitramines (RDX and HMX) and two nitroaromatic compounds (Dinoseb and Dinoterb). Other nitro-aromatic compounds like TNT can also be detected even if they were not present in the wastewater studied. This method highlighted a successful photocatalysis TiO_2 treatment leading to 8 h degradation of nitrophenols, comparing to 78 days necessary in liquid anaerobic bioremediation assays. However, RDX and particularly HMX appeared more resistant to TiO_2 photocatalytic treatment.

Acknowledgements

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