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Nonylphenol deca-ethoxylate removal from wastewater by UV/H_2O_2: Degradation kinetics and toxicity effects

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ABSTRACT

Nonylphenol ethoxylated (NPEOs) nonionic surfactants have been increasingly used in different industrial, commercial and domestic applications. Unfortunately, they are classified as endocrine disrupting chemicals (and also considered as contaminants of emerging concern) having adverse effects on animal and human reproduction. The treatment of nonylphenol-decaethoxylated (NP-10) via H_2O_2/UV-C process at different reaction times (5, 10, 20, 40, 80 min) and H_2O_2 concentrations was investigated. After 80 min treatment the removal rates of NP-10 solution (initial concentration 100 mg/L) in deionized water were 88%, 97% and 98% for 10, 20 and 100 mg/L of H_2O_2 respectively. The same experimental conditions were applied to real wastewater spiked with 100 mg/L of NP-10 showing the following removal rates: 84%, 98% and 99%, respectively. The possible contribution of different radicals to NP-10 degradation by H_2O_2/UV-C treatment was investigated by evaluating the effect of different radical scavengers (namely NO_3^-, NaCl, Na_2SO_4, Na_2CO_3, KH_2PO_4 and phatalate). Toxicity data (*Aliivibrio fischeri*, *Raphidocelis subcapitata* and *Daphnia magna*) on treated solutions and wastewater highlighted the presence of residual toxicity in all samples evidencing that no complete mineralization occurred.

1. Introduction

Nonylphenol ethoxylates (NPEOs) are surface active agents (surfactants) that are part of the broader category of surfactants known as alkylphenol ethoxylates (APEs). Depending on the degree of ethoxylation, NPEOs present octanol-water partitioning coefficients (log K_{ow}) ranging from 4.20 to 4.50 changing its suitability for the specific use, generally, at relatively low cost (Mcleese et al., 1981; Ciabatti et al., 2009). These characteristics make them suitable for different industrial, commercial and domestic applications in surface cleaner, lubricant, shampoo, and detergents (CEPA, 1999). NPEOs can reach from tens to hundreds of mg/L in industrial effluents (Zhou and Zhang, 2017;Chokwe et al., 2017).

Although the toxicity of NPEOs varies, ranging from moderately toxic to toxic to fish and aquatic organisms on an acute basis and increasing as the length of the ethoxylate chain (molecular weight) decreases, a growing concern is posed by their by-products, mainly nonylphenol (NP), because of their potential estrogenic effect to the aquatic biota (Chen et al., 2007). According to NP-10 safety data sheet and PAN-Pestice database (2019), only acute toxicity effects are available suggesting low-medium toxicity levels, nevertheless its potential activity as endocrine disruptor (i.e. various bacteria median effect concentration (EC50) > 1000 mg/L; EC50 = 17 mg/L for *Scenedesmus quadricauda* and 15 mg/L for *Lemna minor*; lethal median concentration (LC50) = 9.3–21.4 mg/L and 20.9 mg/L for *Daphnia magna* and *Gammarus pulex* (48 h), respectively; fish LC50 = 3.8 - 7.7 mg/L for *Pimephales promelas* (96 h) and 16.4 mg/L for *Poecilia reticulata* (48 h)).

NP is a priority hazardous substance (PHS) under the EU's Water Framework Directive (WFD) and is considered an emerging organic pollutant that mimics the natural hormone 17β-estradiol interfering with organisms' reproduction (Lee and Lee, 1996; Solé et al., 2000; Reis et al., 2014). In view of NPEO's toxicity, the European Union under Directive No., 2003/53/EC prohibited the use of NP and

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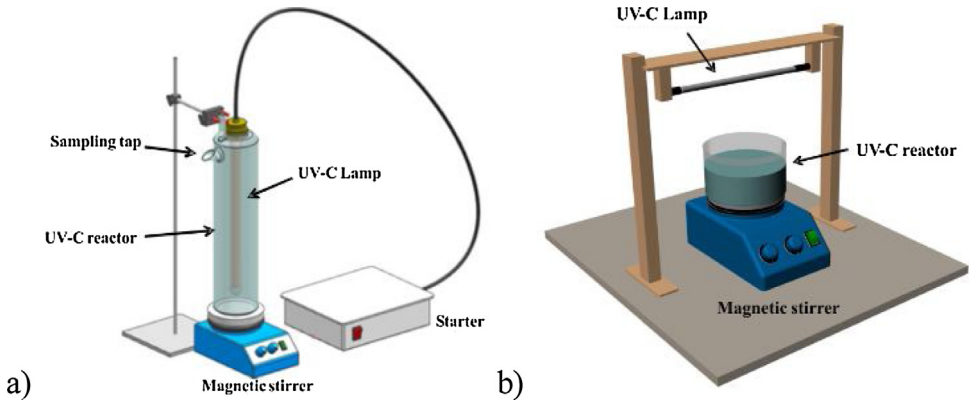

Fig. 1. a) Vertical reactor configuraton; b) Horizontal reactor configuration.

NPEO's and recommended their replacement with costly alcohol ethoxylates. Currently, manufacturers within the EU cannot produce textiles or clothing containing NP or NPEO, but this does not mean that they can be found in wastewater generated from the wash-off of extra-UE manufactured clothes (Lofrano et al., 2016a,b). The EU 2004 ban on manufacture of textiles and clothing containing NP(EOs) led to a fall in NP in UK water bodies, but up to 20% of the NP levels found in UK water bodies comes from wash-off from imported textiles and clothing (UK Environment Agency, 2013).

Moreover, NP still occurs in the aquatic environment with concentrations varying widely in surface water from tens of ng/L (Brix et al., 2010) to dozens of mg/L (Peng et al., 2008). Due to low cost and hig efficiency, NPEO are still in use in developing countries where significantly high concentrations (up to some tens of mg/ L) are detected in the effluent of industrial wastewater treatment plants (WTPs) (Mao et al., 2012). They are being discharged continuously in to the environment and thus a proper management of such kind of wastewater is urgently required. Unfortunately, conventional biological (such as activated sludge) processes are not effective in the treatment of so high (tens of mg/L) NPEO concentrations, therefore a suitable additional treatment is necessary to improve their reduction/removal. Accordingly, various processes have been investigated such as ozonation (Lenz et al., 2004; Ledakowicz et al., 2005), adsorption (Fan et al., 2011) and advanced oxidation processes (AOPs). Among AOPs, dfferent methods have been studied in NPEO degradation, namely gamma radiation/H_2O_2 (Abbas et al., 2015), UVC/H_2O_2, photo-Fenton (Karci et al., 2013), ($S_2O_2^{8-}$)/UV-C (Olmez-Hanci et al., 2013), heterogeneous Fenton-like process (Shahbazi et al., 2014), heterogeneous photocatalysis, eletrochemical oxidation and photo-assisted electrochemical oxidation (Da Silva et al., 2015). However, although AOPs are known to affect water/wastewater toxicity (Rizzo, 2011; Lofrano et al., 2017), only in few cases the final effluent was checked for residual ecotoxicity (Lenz et al., 2004; Ledakowicz et al., 2005; Karci et al., 2013; da Silva et al., 2015), and, frequently, only one biological model was used limiting data interpretation for ecological risk assessment of NPEOs (Karci et al., 2013).

Amongst AOPs, H_2O_2/UV-C is a well-established process, not sensibly affected by pH (Parsons, 2004).

In the present study, the degradation of the nonionic surfactant Tergitol™ type NP-10 (CAS number: 127087-87-0), used in cleaners and detergents, paper and textile processing, paints and coatings, agrochemicals and metalworking fluid was investigated by using H_2O_2/UV-C process. Experiments were carried out in two reactor configurations to evaluate the effect of i) deionized water and spiked real wastewater, ii) scavengers (CO_3^- and phtalates) and intereferring substances (NO_3^- and SO_4^-). The ecotoxicity of untreated and treated samples was investigated considering a battery of toxicity tests (*Aliivibrio fischeri*, *Raphidocelis subcapitata*, and *Daphnia magna*).

2. Materials and methods

2.1. Chemicals and analytical techniques

Tergitol™ type NP-10 ($C_{35}H_{64}O_{11}$) was purchased from Sigma-Aldrich (USA). The formulation was a colourless and highly water soluble. Ultrapure water (UW) (Milli-Q® system Elix 10, Merck Millipore, Billarica, MA, USA) was used for preparation of test solutions. A stock solution of H_2O_2 (30% w/w; Sigma Aldrich, St. Louis, MO, USA,) was used.

A high-performance liquid chromatography (HPLC) system equipped with a module pump (Thermo SpectraSystem P2000) and an UV–vis detector (Thermo SpectraSystem) was used for Tergitol™ determination. Tergitol™ separation was achieved by Hypersil ODS C18 (150 mm × 4.6 mm, 5 μm particle size Thermo Fisher Scientific, Waltham, MA, USA) reversed phase column using a mobile phase of methanol:water (90:10, v/v) at a flow rate of 1.0 mL/min. Injection volume, absorbance wavelength, excitation and emission wavelengths were set at 30 μL, 275 nm, 230 nm and 310 nm, respectively. Tergitol™ concentration was determined according to the calculation of peak areas by external calibration. The limit of detection was identified as signal-to-noise ratio (S/N) equal to 0.050 mg/L.

Wastewater, originate from a municipal wastewater treatment plant (WWTP), located in Campania region (Italy) receiving wastewater collected from urban households, agro-industries, zootechnical activities, hospices and other facilities. The WWTP had an average capacity of 300,000 p.e., and an average flow rate ranging of 45,000 $m^3\ d^{-1}$. The treatment process includes: i) Mechanical pre-treatment (screening and pumping stations, grit and oil removal); ii) Rainwater section (primary sedimentation and aerated storage); iii) Secondary treatment (nitrification-denitrification and final settling); and iv) Tertiary treatment (gravity filtration on sand), and disinfection with peracetic acid. Wastewater samples were characterised for biological oxygen demand (BOD_5), chemical oxygen demand (COD), total suspended solids (TSS), nitrogen as ammonia (N-NH_3), nitrate (NO_3^-), and nitrite (NO_2^-), and total phosphorus (Total P) according to APHA (2012).

2.2. Experimental set-up

H_2O_2/UV-C advanced oxidation experiments included two configurations: a) UV-C lamp, encased in a quartz tube, axially centered respect to the reactor and immersed into the solution (vertical configuration, VC); b) UV-C lamp horizontally positioned 10 cm above the water surface of the reactor (horizontal configuration, HC). The

VC included a stirred cylindrical photo-reactor (2 L), equipped at the top with inlets for feeding reagents, and ports for measuring temperature and withdrawing samples (Fig. 1a). The HC included a stirred photoreactor (0.5 L) placed under the UV-C lamp (Fig. 1b). Both reactors were made of glass and covered with an aluminium foil during functioning. The UV-C source was a 16 W low-pressure mercury vapor lamp (UV emission 5.3 W/55.2 mW/cm^2/m, Novus, Italy) with an incident photon flow rate of 1.023×10^{-8} Einstein/s and 0.728×10^{-8} Einstein/s at 253.7 nm, in VC and HC, respectively, as determined via actinometry (Hatchard and Parker, 1956).

2.3. Experimental plan

The first experimental scenario included various H_2O_2 concentrations (10, 20, 100 mg/L) and reaction times (5, 10, 20, 40, 80 min) looking for the best operative conditions of H_2O_2/UV-C process in deionized water (DW), comparing VC and HC configurations for the degradation of Tergitol™ concentration (100 mg/L). The H_2O_2/UV-C process was carried out at room temperature (25 ± 2 °C) and natural solution pH (5.5). Control experiments were also conducted to observe Tergitol™ degradation in the absence of either UV-C or H_2O_2.

The second experimental scenario included the serial addition to testing solution of compounds usually working as scavengers of hydroxyl radicals : (NaCl (1000 mg/L Cl–); Na_2CO_3 (300 mg/L CO_3^{2-}), KH_2PO_4 (10 mg/L PO_4^{3}), $NaNO_3$ (50 and 500 mg/LNO_3), 852 mg/L of phthalate (corresponding to 1000 mg O_2/L of COD) as well as interfering substances Na_2SO_4 (500 mg/L SO_4^{2-}), in order to evaluate their potential effects.

In the third experimental scenario, real wastewater (WW) taken from a wastewater treatment plant (BOD_5 = 18 mg/L; COD = 48.5 mg/L; TSS = 46 mg/L; N-NH_3 = 1.42; N-NO_3^- = 0.25 mg/L; N-NO_2- = 3.34 mg/L; total P = 1.23 mg/L) was spiked with 100 mg/L Tergitol™ evaluating the influence of matrix on the behaviour of the process.

Analysis was carried out at least in duplicate and reported as mean and semi-dispersion.

After withdrawal of the samples, the residual H_2O_2 was immediately quenched with few mL of catalase at 0.1 g/L to allow subsequent toxicity analysis.

2.4. Ecotoxicity

Toxicity tests with *A. fischeri, R. subcapitata,* and *D. magna* were carried out on treated (100 mg/L of Tergitol™ in deionized water and real wastewater spiked with 100 mg/l of Tergitol™ after 80 min of photo-oxidation treatment) and untreated wastewater samples Tergitol™. According to quality assurance and quality control procedures, bioassays included the assessment of negative and positive controls according to the corresponding standard method. In particular, the acute bioluminescence inhibition assay was carried out using *A. fischeri* (NRRL-B-11177) according to ISO (2007). The luminescence was measured with a Microtox® analyser (Model 500, AZUR Environmental) after 5 and 15 min at 15 °C. Tests were carried out in triplicate. Data were analysed with Microtox Omni software and the result expressed as percentage of bioluminescence inhibition.

The chronic growth inhibition test with *R. subcapitata* was carried out according to ISO (2012). Cultures were kept in Erlenmeyer flasks. The initial inoculum contained 10^4 cell/mL. The specific growth inhibition rate was calculated considering 6 replicates exposed at 20 ± 1 °C for 72 h under continuous illumination (6000 lx). Effect data were expressed as percentage of growth inhibition.

Newborn daphnids (< 24 h old) were exposed to sample according to the ISO 6341 method. Daphnids were grown at 20 ± 1 °C under a light source of 4000 lx using cool lamps. Control tests were carried out at the same temperature without light emission. They were fed with *R. subcapitata* (300,000 cells/mL) and baker yeast (*Schizosaccharomyces cerevisiae*, 200,000 cells/mL). Toxicity tests included 5 daphnids per replicate (i.e. four replicates) in 10 mL and at least five serial dilutions of samples. After 24 h, dead larvae were recorded. Whenever possible, toxicity was expressed as median effective concentration (EC50, %) or as percentage of effect (PE, %) at the highest tested concentration (%, w/v) according to ISO 6341 method. When EC50 were available, the toxici unit (TU50) value was provided (TU50 = 100/EC50). The significance of differences between average values of different experimental treatments and controls was assessed by the analysis of variance (ANOVA) considering a significance threshold level always set at 5%. When ANOVA revealed significant differences among treatments, *post-hoc* tests were carried out with Tukey's test. Statistical analyses were performed using Microsoft® Excel 2013/XLSTAT©-Pro (Version 7.2, 2003, Addinsoft, Inc., Brooklyn, NY, USA).

Finally, toxicity data were integrated according to Persoone et al. (2003) and Lofrano et al. (2016a,b). The hazard classification system is both based on PE or TU50 includes a Class I for PE b 20% (score 0) (or TU50 < 0.4), Class II for 20% ≤ PE b 50% (score 1) (or 0.4 < TU50 < 1), Class III for 50% ≤ PE b 100% (score 2) (or 1 < TU50 < 10), Class IV when PE = 100% in at least one test (score 3) (10 < TU50 < 100) and a Class V when PE = 100% in all bioassays (score 4) (TU50 > 100). Finally, the integrated class weight score was determined by averaging the values corresponding to each microbiotest class normalised to the most sensitive organism (highest score).

3. Results and discussion

3.1. Kinetic studies

Experiments on Tergitol™ at 100 mg/L carried out under dark (100 mg/L of H_2O_2) proved that the use of H_2O_2 applied alone did not allow any reduction in NP-10 concentration (Fig. 2a,b). Preliminary measurements of UV absorbance spectra (200–400 nm) of untreated Tergitol™ indicated two distinct absorbance bands < 300 nm: i) a peak at 224 nm and ii) another peak at 275 nm characteristic of many phenolic compounds (Kim et al., 2005), evidencing that Tergitol™ absorbs light in the UV—C region. The photolysis of 100 mg/L of Tergitol™ resulted in 20% and 30% removal efficiency after 80 min in HC and VC, respectively (Fig. 2 a,b). In Karci et al. (2013), the UV—C photolysis of 100 mg/L NP-10 was evaluated in a 3250 mL-capacity, horizontally positioned and batch-operated cylindrical photoreactor with the UV—C light source (40 W lamp, 1.4×10^{-5} Einstein L^{-1} s^{-1} at 253.7 nm) located in the center of the photoreactor in a quartz sleeve. According to their results a removal rate of 92% was obtained after 120 min, evidencing that the efficiency was strongly affected by lamp power, geometry and reaction time.

Chen et al. (2007) evaluated the photolysis of 200 mg/L NP-10 using a 125 W high-pressure mercury lamp with the primary wavelength of 365 nm; an absorbance peak at 270 nm corresponding to the broken benzene ring was observed after 6 h irradiation.

H_2O_2/UV-C process resulted in a Tergitol™ removal of 87, 90 and 99% in VC configuration after 80 min treatment, whereas a removal of 79, 87 and 95% was achieved in HC configuration after the same treatment time, with 10, 20 and 100 mg/L of H_2O_2, respectively.

The rather poor NP-10 removal kinetics (k NP-10 = 0.046 ± 0.0007 min^{-1}) and efficiencies obtained via photolyisis process were improved by increasing the initial H_2O_2 concentra-

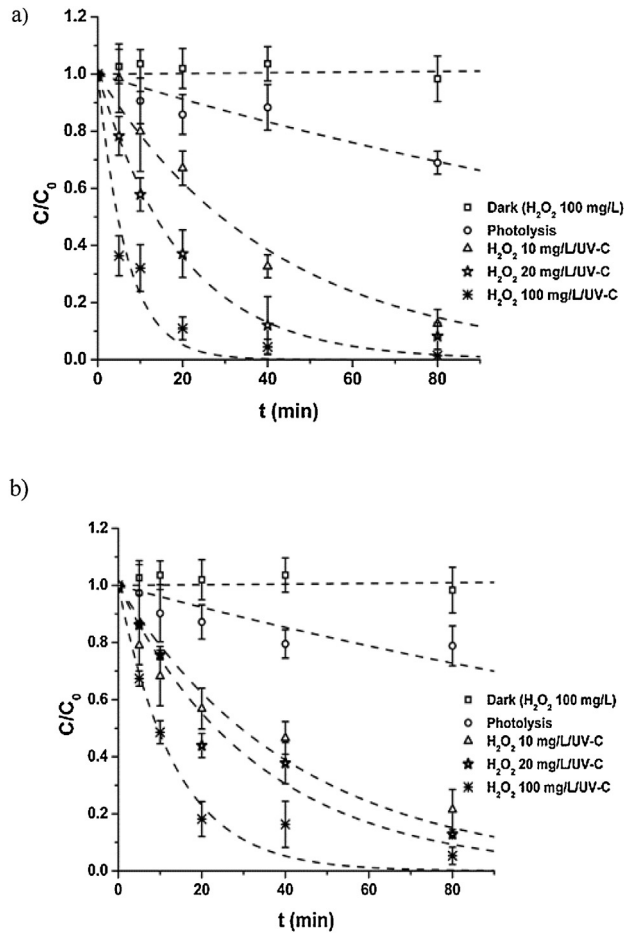

Fig. 2. Kinetic curves of Tergitol^{TM} (initial concentration 100 mg/L) under different processes: a) vertical configuration; b) horizontal configuration.

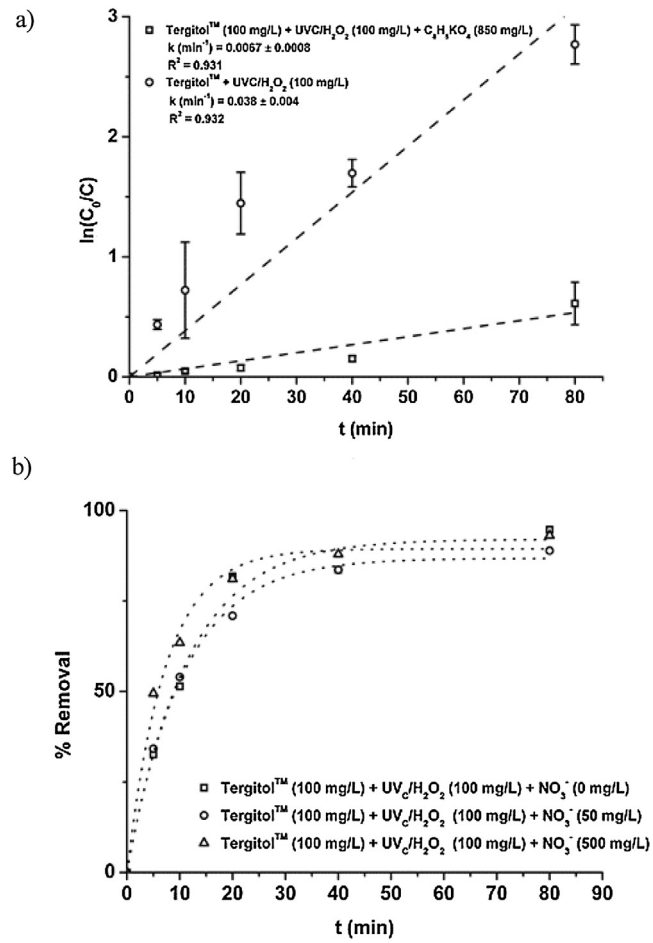

Fig. 3. Effects of: a) phatlates and b) nitrate on photoxidation rate of Tergitol^{TM} in VC reactor, over the time.

Table 1
Kinetic constants ± standard deviations for Tergitol^{TM} degradation by H_2O_2/UV-C in VC and HC configurations, respectively.

H_2O_2 dose (mg/L)	k_{VC} (min^{-1})	k_{HC} (min^{-1})
10	0.024 ± 0.002	0.024 ± 0.003
20	0.051 ± 0.003	0.030 ± 0.003
100	0.150 ± 0.007	0.074 ± 0.008

tion in accordance with the findings of Karci et al. (2013) which reported that the highest NP-10 removal rate coefficient (k NP-10 = 0.59 ± 0.030 min^{-1}) was achieved with H_2O_2/UV-C process at a H_2O_2 concentration of 340 mg L^{-1}

As shown in Table 1, Tergitol^{TM} abatement rates increased upon increasing the initial H_2O_2 concentrations from 10 to 100 mg/L, showing kinetic constants higher in VC compared to HC, except at an initial oxidant concentration of 20 mg/L. The positive effect of increasing H_2O_2 concentrations has already been evidenced in former related studies (Arslan-Alaton, 2010) and was attributed to the enhanced HO• production.

In the present study after 20 min of photoxidation with 100 mg/L of H_2O_2 the removal of 100 mg/L NP-10 in VC and HC set up reactor was 89% and 82%, respectively.

3.2. Interefering compounds

Under the operating conditions described above (100 mg/L Tergitol^{TM} and 100 mg/L H_2O_2), none of the interefering substances (NaCl, Na_2CO_3, KH_2PO_4, Na_2SO_4) showed a significant effect at the investigated concentrations, but phthalates and only partially nitrate. As matter of fact, 17% of removal of Tergitol^{TM} was achieved after 80 min of photoxidation in presence of 852 mg/L of phthalate (Fig. 3a).

The irradiation of nitrate-rich water leads to nitrite formation with a reaction quantum yield dependent on the excitation wavelength, temperature, pH and nitrate concentration (Mack and Bolton, 1999). Photolysis of nitrate and nitrite results in the formation of reactive species such as the·OH radical but also NO·, NO_2·, ONOO·. As shown in Fig. 3b, the removal kinetics slightly improved by increasing the nitrate concentration.

It is possibly due to the OH radical production from the NO_3^- absorption of UV according to the following reaction:

$$NO_3^- + h\nu + H^+ \rightarrow {}^{\cdot}NO_2 + {}^{\cdot}OH$$

Assuming that the molar ratio between nitrate and hydroxyl radicals was 1: 6.6 and 1:0.65 for 50 mg/L and 500 mg/L of nitrate respectively, it can be stated that in the first case there is a slight scanvenger effect of nitrate, whereas in the second one there is a contribution of radical nitrite to the oxidation reaction at short time.

Unlike of our results, the presence of nitrate (5 mg/L) affected removal of bisphenol A (BPA) in previous experiments with UV/H_2O_2 (Park et al., 2014). However, it worth to notice that the molar ratio between nitrate and hydroxyl radicals in their case was

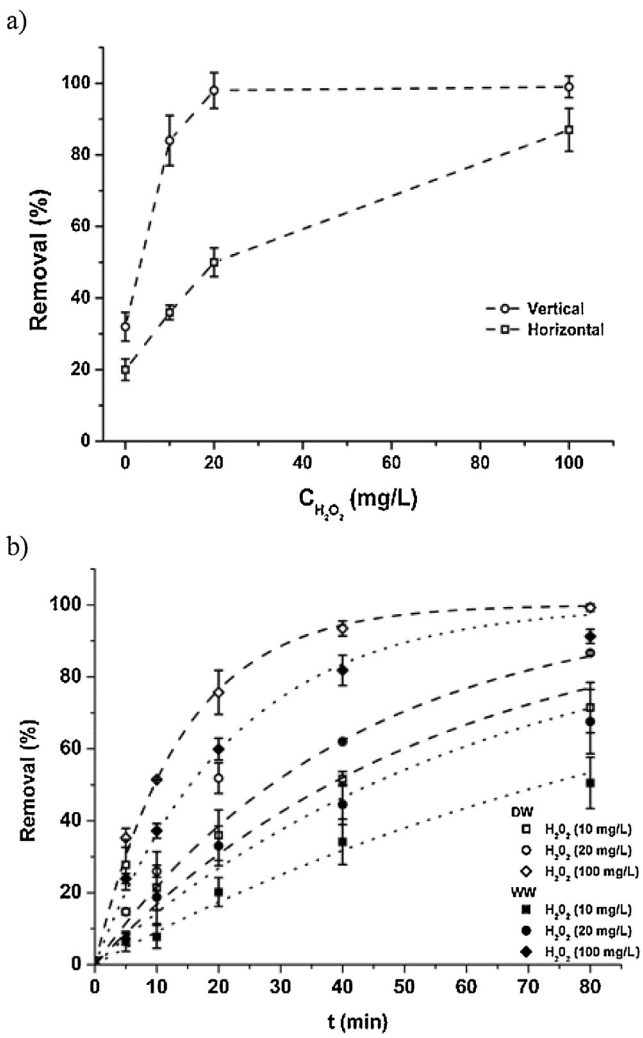

Fig. 4. a) Comparison between photoxidation removal of 100 mg/L Tergitol^{TM} from DW and WW in VC and HC reactor at the different values of H_2O_2 concentrations; b) comparison between photoxidation kinetic curves of 100 mg/L of Tergitol^{TM} from DW and WW, in VC reactor. Dashed lines are the curve fit for DW samples whereas dot lines are the curve fit of WW samples.

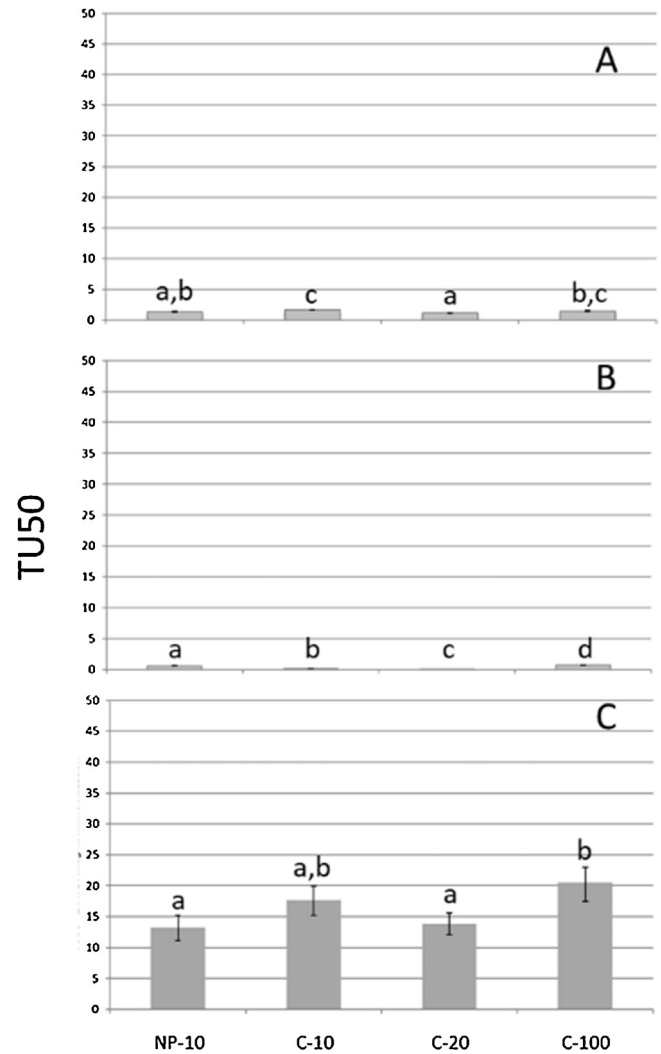

Fig. 5. Toxicity (as TU50) of Tergitol^{TM} solutions (100 mg/L) treated with UV-C (VC) at three increasing concentrations of H_2O_2 (NP-10 = 0 mg/L; C-10 = 10 mg/L; C-20 = 20 mg/L; and C-100 = 100 mg/L) assessed considering A = *A. fischeri*, B = *R. subcapitata*, and C = *D. magna*; data with different letters (a–b) are significantly different (Tukey's, $p < 0.05$).

1:23 and 1:46 corresponding to 150 mg/l and 300 mg/l of hydrogen peroxide respectively.

3.3. Real wastewater

According to the results achieved with deionized water, the removal of Tergitol^{TM} in VC reactor was higher compared to HC reactor in real wastewater for all the H_2O_2 concentrations (Fig. 4a). Therefore, the kinetic study for the evaluation of the influence of the water matrix was carried only in VC. As expected the kinetics contant in DW ($0.0184 \pm 0.0013\,min^{-1}$, $0.024 \pm 0.004\,min^{-1}$, $0.072 \pm 0.004\,min^{-1}$ for 10, 20 and 100 mgL^{-1} of H_2O_2 respectively) were higher than in WW ($0.0096 \pm 0.0003\,min^{-1}$, $0.0156 \pm 0.0011\,min^{-1}$, $0.045 \pm 0.002\,min^{-1}$ for 10, 20 and 100 mgL^{-1} of H_2O_2 respectively). By increasing the H_2O_2 concentration from 10 to 100 mg/L, after 80 min of photoxidation the Tergitol^{TM} removal was about 76.97%, 85.76%, 99.69% and 53.43%, 71.31%, 97.28% in DW and WW, respectively. After 50 min, the treatment with 100 mg/l of H_2O_2 carried out in DW achieved about 97% of Tergitol^{TM} removal, 30 min more of photoxidation were required to achieve the same value of Tergitol^{TM} removal in WW.

3.4. Ecotoxicology tests

3.4.1. Deionized water-based solutions

Toxicity data on DW-based solutions spiked with 100 mg/L of NP-10 and after 80 min of photoxidation treatment with UV-C (VC) at increasing H_2O_2 concentrations (NP-10 = 0 mg/L; C-10 = 10 mg/L; C-20 = 20 mg/L; and C-100 = 100 mg/L) were summarized in Fig. 5 (A–C). Results showed species-specific effects with increasing level of toxicity displayed by *R. subcapitata* < *A. fischeri* < *D. magna*. Bacteria (Fig. 5A) did not show any significant toxicity removal after C-20 and C-100, and a slight toxicity increase after C-10. Microalgae (Fig. 5B) presented relatively low toxicity effects with a significant reduction of toxicity from 31% (Tergitol^{TM}) to 1% (C-10), while toxicity increased in C-20 (8%) and C-100 (39%). In the case of *D. magna* (Fig. 5C), the toxicity was significantly higher compared to Fig. 5A and B, especially after C-100 treatment. No significant reduction of toxicity was detected after Tergitol^{TM} treatment, nevertheless it was significantly removed (> 90%). According to Lofrano et al. (2016a, b) and Persoone et al. (2003), toxicity data were integrated. Samples were deemed as presenting between "slight acute toxicity" and "acute toxicity" with a hazard classification score of 1.3 (1 (*A. fischeri*) + 1 (*R. subcapitata*) + 3 (*D. magna*)]/3 (*D. magna*)).

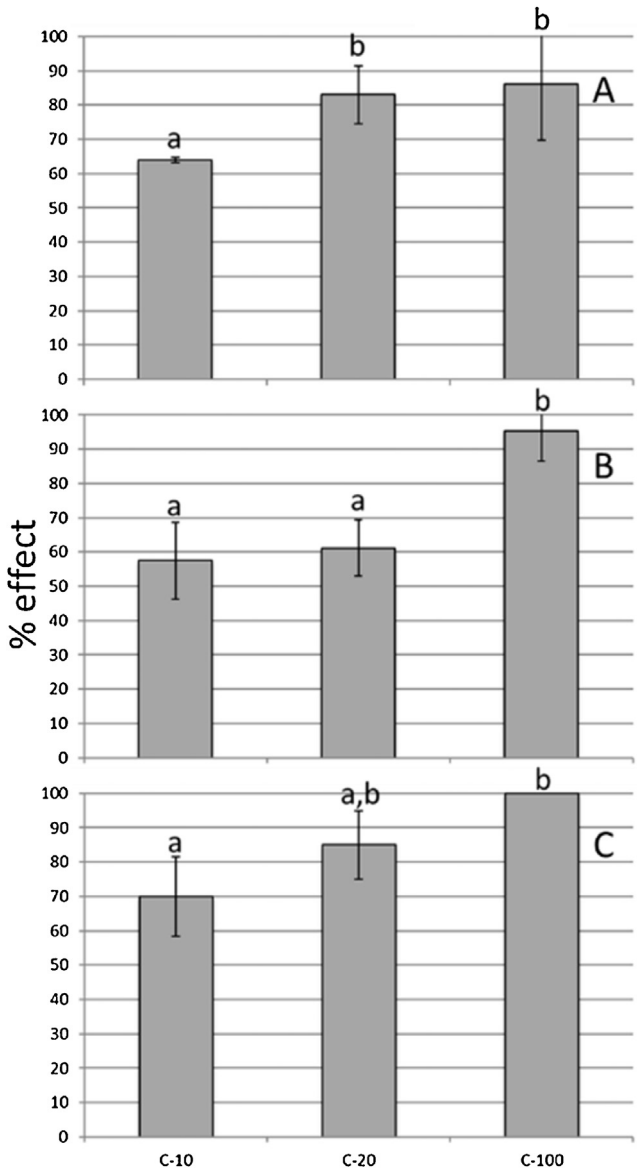

Fig. 6. Toxicity effects (as % of effect) of wastewater samples spiked with 100 mg/L of NP-10 and treated with UV-C at three increasing concentrations of H_2O_2 (C-10 = 10 mg/L; C-20 = 20 mg/L; and C-100 = 100 mg/L) assessed considering A = *A. fischeri*, B = *R. subcapitata*, and C = *D. magna*; data with different letters (a–b) are significantly different (Tukey's, $p < 0.05$).

Results stated that Tergitol™ mineralization was not complete, and by-products can still exert an adverse effect on target biological models. Similarly, it was observed in Karci et al. (2013) were acute the H_2O_2/UV-C process ultimately resulted in a higher acute inhibitory effect (27% inhibition) than the original NP-10 solution.

3.4.2. Wastewater based experiments

Toxicity data on real WW spiked with 100 mg/L of Tergitol™ and after 80 min of photoxidation treatment UV-C (at increasing H_2O_2 concentrations (NP-10 = 0 mg/L; C-10 = 10 mg/L; C-20 = 20 mg/L; and C-100 = 100 mg/L) in VC reactor, after 80 min, were summarized in Fig. 6(A–C) expressed as percentage of effect. The toxicity of wastewater *per se*, before spiking, induced a 12%, 10% and 15% effect in *A. fischeri*, *R. subcapitata* and *D. magna,* respectively. These background data were used to normalize the values reported in Fig. 6(A–C). After the photoxidation treatment in presence of H_2O_2 increasing concentrations, toxicity values were only slightly higher than in DW (Fig. 5) for *A. fischeri* (Fig. 6A) and *R. subcapitata* (Fig. 6B), while toxicity in *D. magna* (Fig. 6C) was reduced especially for C-10 and C20, while residual toxicity can be detected for C-100 (i.e. the toxicity in Fig. 6 was expressed as % of effect and not as TU50 like in Fig. 5). In all cases, the best performance was obtained with 10 mg/L of H_2O_2. According to Lofrano et al. (2016a,Lofrano et al., 2016b and Persoone et al. (2003), toxicity data were integrated. Samples were deemed as presenting between "acute toxicity" and "high acute toxicity" with a hazard classification score of 2.7 (2 (*A. fischeri*) + 3 (*R. subcapitata*) + 3 (*D. magna*)]/3 (*D. magna*)).

4. Conclusions

Promising removal efficiency (up to 99%) was observed after UV-C/H_2O_2 process considering the vertical configuration of the reactor after 80 min of reaction time of Tergitol™ spiked deionized water. Similarly, in Tergitol™ spiked wastewaters, the removal efficiency was up to 96% after UV-C/H_2O_2 process considering the vertical configuration of the reactor after 80 min. In both Tergitol™ spiked deionized water and real wastewater, the efficiency of post-treatment toxicity reduction/removal remained poor, mainly due to reaction by-products evidencing medium-high levels of residual toxicity. Thus, further research is needed to optimize the treatment process scheme to improve the final ecotoxicological quality of the effluent.

The characterization of the degradation products could help to the estimation of their contribution to the overall toxicity. If the degradation products of Tergitol would be biodegradables, a subsequent biological treatment step could be integrated for the removal of organic matter and residual toxicity after 80 min-H_2O_2/UV-C treatment.

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