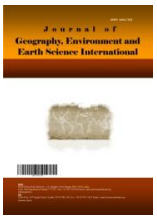

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Nonylphenol and Its Ethoxylates in Water Environment

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Endocrine disrupting compounds (EDCs), including Alkylphenols and their ethoxylates, precisely Nonylphenol and its ethoxylates, are organic molecules that are of greatest current concern because of their ability to have a toxic or an inhibitory effect on living organisms by their presence or accumulation in environment such as water, sediments, soils and atmosphere. They are used in the production of surfactants, industrial formulations, pharmaceuticals, personal care products etc... The primary objective of this article is to review the literature concerning classification of Nonylphenol and its ethoxylates based on physical and chemical characteristics and technical feasibility of their usages. It also involved different ways of their introduction into environment, analytical methods (HPLC, GC-MS, GC-MS-TOF) for their environmental detection and quantification, and finally methods for their removal. Technologies proposed for nonylphenol and its ethoxylates degradation includes biodegradation, physical processes, conventional and non-conventional adsorption-oriented processes and photodegradation processes including photocatalytic oxidation which have a potential to reach complete mineralization.

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Keywords: Nonylphenol ethoxylates; wastewater; chromatographic analyses; degradation.

1. INTRODUCTION

A new concern has emerged recently in our water environment, called endocrine disruptors (EDs) that may affect the reproductive functions. Water contamination with EDs poses potential environmental problems which lead the Japan Environmental Agency (JEA) to publish strategic programs on environmental endocrine disruptors [1]. Among those suspected substances, are included alkylphenol ethoxylates (APEOs), especially nonylphenol ethoxylates (NPEOs). Alkylphenols (APs) constitute a large family of chemicals and are organic compounds synthesized through alkylation of phenols. The base of the molecule is a phenol ring which is substituted, usually in the para position, a radical (Fig. 1). The most representative among APs are nonylphenols and octylphenols which comprise both hydrophobic branched group nonyl or Octyl and hydrophilic moiety. Nonylphenol (NP) constitute about 80% of alkylphenols in use and octylphenol constitute the remaining 20%. Nonylphenols come in the form of a pale yellow viscous liquid and give off a slight phenolic odor. They are generally available in solution with impurities and are also commercial formulations of mixture. The greater part of nonylphenol is used to produce nonylphenol ethoxylates which are not stable in the environment. A wide range of oligomers is available, varying in the length of the hydrophilic ethoxylates chain (typically between 4 and 50 EO units) which confers different properties to the molecule (cleaning products, degreasers, detergents, scouring fibers in dyeing, cosmetics etc…). Nonylphenol ethoxylates production is a source of both releases of nonylphenol and nonylphenol ethoxylates; mainly via aqueous discharges. Several studies conducted on the degradation of alkylphenols in sewage and wastewater treatments reviewed by Maguire [2] and Danish EPA [3] nevertheless concludes that the treatment of domestic sewage is less efficient for Alkylphenol compounds. Several transformations occur when APEOs are introduced into sewage treatment systems. There is first a loss of ethoxylate (EO) groups from the original molecule generally and gradually form more toxic and estrogenic short chain metabolites, such as alkylphenols, alkylphenol monoethoxylate AP1EO and alkylphenol diethoxylate AP2EO, and finally the ultimate degradation products in seldom cases are CO_2 and water. Laboratory tests showed the acute toxicity of nonylphenol to invertebrates, fish, mammals and algae [4,5]. Therefore, future researches should focus on the investigation of appropriate treatment methods that can prevent the release of EDs into the natural waters. Advanced oxidation processes (AOPs) have been described as potential methods of EDs destruction in the water environment [6]. Many studies have specifically focused on many aspects taken alone of those chemicals such as their environmental occurrence, natural decomposition process, development new technologies biodegradation or photocalytic degradation etc… It was important to put the great part of these information together from their manufacturing through their use, environmental entrance, methods for environmental detection and quantification to their degradation ways. The primary objective of this article to review the literature concerning classification of Nonylphenol and its ethoxylates based on physical and chemical characteristics, and technical feasibility of their usages. It also involved different ways of their introduction into environment, analytical methods (HPLC, GC-MS, GC-MS-TOF) for environmental detection and quantification, and finally methods for their removal.

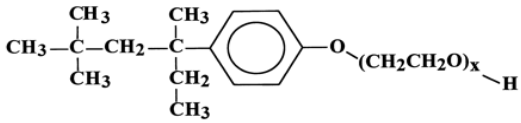

Fig. 1. Typical structure of a highly branched isomer of NPEO$_x$ in which *x* may range from 2 to about 50

2. PHYSICAL AND CHEMICAL PROPERTIES

NP4EO and NP9EO are considered to be representative of NPEOs because of the complete available data [7]. It should be noted that specific gravity, viscosity and aqueous solubility increase with EO chain length, NPEOs more than six EO are soluble in water. In the other hand, pKa of NP is 10.7 and partitioning to air is limited because of low Henry's law constant, and vapor pressure of NP and especially NPEOs [8]. The number of ethoxylates determines the physicochemical properties of the product and is set according to the uses to what it is intended. For example, 4 or 5 nonylphenol ethoxylates are used as detergent-soluble oils, those at 8 or 9 ethoxylates are the basis for high

performance detergents used in the textile industry and those between 13 and 15 ethoxylates are used to prepare emulsifiers for the preparation of solvents and pesticides [2].

3. SOURCES AND RELEASES

The presence of NP and NPEOs in the environment is a result of anthropogenic activity. Technical synthesis of APEOs start with phenol which is alkylated by trimethylpentene, producing octylphenol or with nonene isomers which forms nonylphenol in an acid catalyzed process [7]. Ethoxylation is performed by using KOH/ethanol as a catalyst with a known ratio of ethylene oxide to the alkylphenol. The production of nonylphenol ethoxylates in the EU was 118 000 tons in 1997 [9], 77 800 tonnes are used in the EU [10]. Formulators and distributors of surfactants are the largest industrial releasers. Paints, protective coatings, resins and adhesives producers release less NP and NPEOs than the former two [11] and following industries release more less amounts of NP and NPEOs: formulators of industrial and domestic cleaning products, degreasers and detergents etc...

4. EXPOSURE CHARACTERIZATION

Many factors influence the physical, chemical properties and ecosystem-specific properties. For example: the nature and concentration of microbial populations; the nature and concentration of dissolved and suspended material; temperature; degree of insolation, etc… In general, volatilization and adsorption to suspended solids and sediment; chemical and photochemical degradation or transformation; uptake and transformation by microorganisms are the most mechanisms of chemicals removal in aquatic ecosystems. NP and NPEOs are not expected to readily volatilize into air and are expected to degrade rapidly in the atmosphere [12]. In general, several transformations occur when APEOs are introduced into sewage treatment systems. APEOs with more than eight EO units are readily degraded in effluent treatment systems with>92% efficiency [13]. An initial loss of ethoxy groups is the first step of biodegradation mechanism under aerobic and anaerobic treatment conditions, leading to the production of NP1EO and NP2EO and their carboxylate derivatives NP1EC and NP2EC and the final product NP [14] which are more persistent, toxic and estrogenic [2]. The simplified degradation pathway is shown in Fig. 2. NP (in particular), NP1EO and NP2EO are more lipophilic than the parent NPEOs and tend to accumulate in sludges and sediments, while NPECs are generally found in the final effluents [13]. The final effluent composition is dependent on the treatment process used in the facility [15].

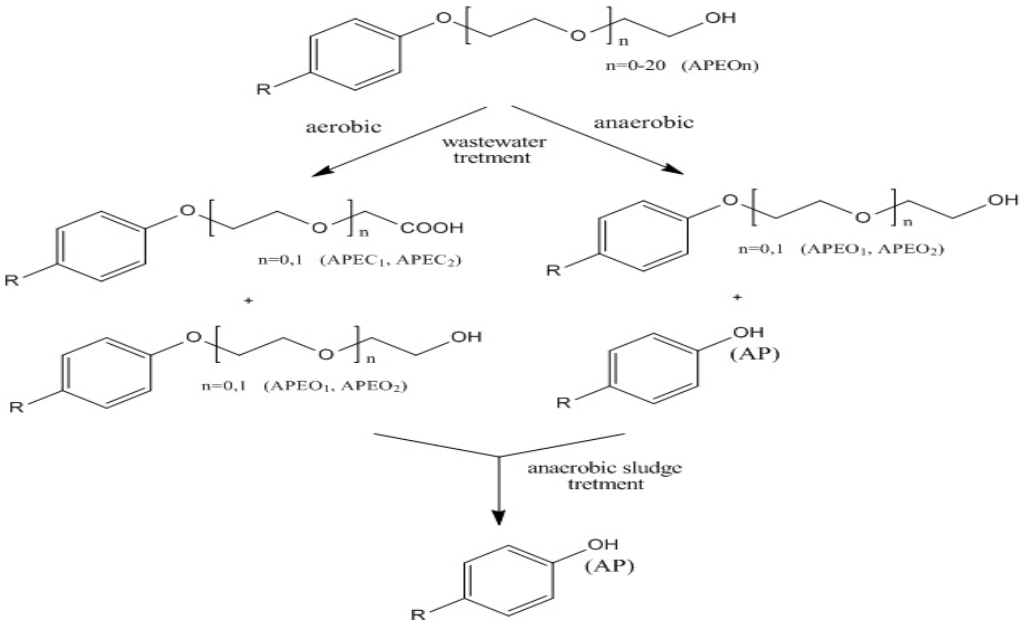

Fig. 2. Degradation of alkylphenols and their polyethoxylates from Milinovic [16]

5. ENVIRONMENTAL CONCENTRATIONS

Actual APEOs concentrations measured in chemical monitoring programs can be used to describe their fate and to evaluate their potential effects on the aquatic environment. A study [17], provided a statistically valid set of sites of likely APEOs environmental exposure in the U.S. Both water and sediment were sampled from three points along the rivers and analyzed for NP, NP1EO, NP2E0 and the aggregate total of higher NPEO oligomers. In separate works cited in [18], significant levels (up to 18 ppb) of NP1EO, and NP2EO were reported in a highly polluted Swiss river, along with up to 2 ppb of nonylphenol and up to 120 ppb of NPEO carboxylates. Swiss data for nonylphenol, collected in 1983-1985, contrast with U.S. data by being several-fold higher than the highest concentration found in U.S rivers. A follow-up study of the same Swiss river in 1997 reported a large reduction of concentrations, attributed to both restrictions and bans of NPEOs from cleaning products and improved wastewater treatment [19]. Monitoring data on NP, NP1EO, NP2EO and OP in Canada, including effluents, sludge and receiving waters are generally consistent with U.S. data [2], except for a small number of highly polluted sites. Similarly, limited monitoring in UK rivers and estuaries for NP showed very low levels except at points of untreated industrial wastewater discharge [20]. In Canada, high concentrations of NPEOs (maximum concentration 8811 µg/L) have been found in industrial wastewater and municipal effluents [2]. These results are higher than kouakou's works [21] done at the northen china with up to around 1113.4 µg/L for NP and 743 µg/L for NPEOs (also high) in non-treated industrial wastewater. Well-treated effluents typically have very low levels of NPEOs. Treatment properties strongly influence concentrations and relative proportions of NPEOs released in final effluents. Sediment samples from the 30 rivers contained higher levels of NP and NPEO, than did the water samples [22], a consequence of the strong adsorption of these water-insoluble components into the organic fraction of the sediments. Overall, 95% of the sediment samples contained less than 580 pgkg NP and 89 pgtkg NPEO, Maximum levels found were 2,960 ppb of NP (Grand Calumet River) and 175 ppb of NP1EO. Bennie et al. [23] reported a concentration of NP of 2.72 mg/kg. After 320 days, residual NP, NP1EO and NP2EO concentrations were respectively 0.5, 0.1 and 0.01 mg/kg [24].

6. TOXICITY

Classified as very toxic to aquatic organisms by the European Union, NP may have long-term negative effects in the aquatic environment [25]. The toxicity of NP in sediment has been determined for a single freshwater invertebrate species, larvae of the midge *Chironomus tentans*, over a 14-days exposure period [26]. Two spiked-sediment studies have examined the toxicity of NP to marine invertebrates. One study evaluated NP lethality to the amphipod *Ampelisca abdita* [27]. One study found that during a three-month exposure to NP, 50% of the Japanese medaka male fish developed both male and female sex organs when exposed to 50 parts per billion of NP, and 85% of the fish developed both sex organs when exposed to 100 parts per billion of NP [28]. No fish within the control group developed the hermaphroditic (both sex organs) condition. Another study found sexual deformities in oyster larvae exposed to levels of NP that are often present in the aquatic environment. Alkylphenols also have effects on the endocrine system. Indeed, many of these substances have shown estrogenic activity when tested on recombining yeast cells [4], hepatocytes of rainbow trout [29] and cancer cells of human mammary glands [5]. In Many countries, large corporations and scientific entities have classified NPEOs metabolites as toxic. Canada classified NPEOs metabolites as toxic as they have long-term harmful effect on the environment or its biological diversity [30]. NPEOs metabolites can cause an organism to become stupefied and lose consciousness, cover organisms with a soap-like coating that inhibits them from moving and disrupt normal hormonal functioning in the body and thus are considered endocrine-disrupting chemicals. Endocrine disrupting chemicals (EDs) interrupt normal bodily functioning by blocking, interfering with, or mimicking natural hormones in the body. Even infinitesimal amounts of certain synthetic chemicals can cause endocrine disruption [31]. Studies show that endocrine disruption: causes organisms to develop both male and female sex organs; increases mortality and damage to the liver and kidney; decreases testicular growth, the formation of sperm and testosterone levels in male fish; disrupts normal male to female sex-ratios, metabolism, development, growth and reproduction [30].

7. EXTRACTION METHODS

The determination of polar contaminants in water samples is normally preceded by analytes of

interest extraction. This extraction should be as selective as possible in order to minimize the coextraction of matrix that may interfere with analyte detection. Several extraction techniques for aqueous samples are available, with Solid Phase Extraction (SPE) being the standard procedure. Liquid-Liquid Extraction has remained important for only a few applications, e.g., the determination of haloacetic acids [32]. In fact, the US-EPA has two methods available for their determination: one based on SPE [33] and the other based on LLE [34], however, the volume of extracting solvent has been minimized to 4 mL with alternatives to SPE are microextraction techniques, namely SPME and, more recently, LPME, as they consume less organic solvent or sample volume (or virtually none in the case of SPME) [35]. Other techniques used for the analysis of volatile compounds, like headspace and purge and trap, are applicable to very few of the polar target analytes considered here [36] because of the often ionic character and high water solubility of many polar compounds.

7.1 Liquid-Liquid Extraction

The process of liquid-liquid extraction involves the distribution of a compound between two solvents that are insoluble in each other [34]. By taking advantage of the differing solubilities of a solute in a pair of solvents, compounds can be selectively transported from one liquid phase to the other. Liquid/liquid extraction is the most common technique used to separate a desired organic product from a reaction mixture or to isolate an organic substance from its natural source [37]. The technique works well if your target compound is more soluble in one of two immiscible solvents. Extraction usually involves shaking a solution that contains the target with an immiscible solvent in which the desired substance is more soluble than it is in the starting solution. Upon standing, the solvents form two layers that can be separated. The extraction may have to be repeated several times to effect complete separation.

7.2 Solid Phase Extraction

The last few years have been characterized by a wide interest in this technique. The introduction of a wide spectrum of sorptive materials into analytical procedures gave a new stimulus for the development of SPE methodology [38]. The principle of SPE is similar to that of liquid-liquid extraction (LLE), involving a partitioning of solutes between two phases. However, instead of two immiscible liquid phases, as in LLE, SPE involves partitioning between a liquid (sample matrix or solvent with analytes) and a solid (sorbent) phase. The general procedure is to load a solution onto the solid phase, wash away undesired components, and then extract the desired analytes with another solvent into a collection tube [39] as shown in Fig. 3. SPE is very convenient; it can be automated and adapted to various analytes by a proper selection from the wide range of sorbent materials available. With respect to the applied washing and elution solvents, the most frequently used groups of sorbents can be divided into the following categories: reversed-phased (RP), normal-phase (NP) and ion-exchange (IE) [40]. Thus, C-18 cartridges and disks have been successfully employed for the extraction NPEOs in river, sand filtered and treated water [41]. Of these materials, the Oasis HLB product appears to be the most extensively used sorbent for the extraction of polar compounds and especially acidic compounds, like herbicides, disinfection by-products, and acidic drugs [42]. It has also been employed for the SPE of neutral compounds like phosphoric acid tri-esters [43].

7.3 Microextractions

SPE has already made remarkable progress compared to LLE in terms of solvent consumption and automation. A step further was achieved by solid-phase microextraction (SPME) and liquid-phase microextraction (LPME), where either no organic solvent is employed (SPME) or only a few microliters (LPME). SPME was developed in 1989 [44] and became commercially available in 1993. In this technique, the analytes are first concentrated into a sorbent coated on a fused silica fiber that is exposed directly to the sample (direct sampling) or to its headspace (headspace sampling). After partitioning into this sorbent, the analytes can be desorbed either thermally by immersing the fiber into a GC injector or by an organic solvent if they are to be analyzed by LC [45]. Moreover, SPME can easily be automated and nowadays, there are several sorbents available which cover a wide polarity range, and the main difficulty of the analysis of polar compounds relies on the need for derivatization of many of these compounds prior to their determination by GC. In this way, SPME can be combined with silylation reactions [46]. LPME is more recent than SPME and is based on partition of the analytes between the sample and a small volume (a few µL) of an acceptor solution.

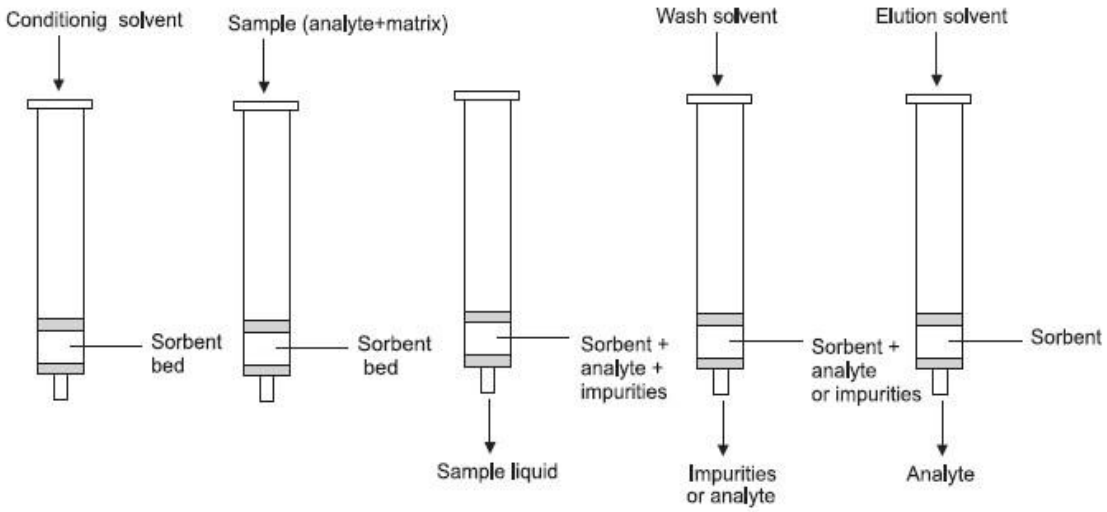

Fig. 3. Solid phase extraction steps

8. ANALYTICAL METHODS

The development of synthetic surface-active materials emphazed a need for analytical methods for their determination in various types of samples. Several reviews were published [47,48] showing that various techniques were applied for determination of nonionic surfactants. The analysis of a mixture of homologues (reversed-phase system) [49] and oligomers (normal-phase system) [50] can be obtained in a relatively short time by high-performance liquid chromatography. Aromatic nonionic surfactants can be directly detected with high sensitivity using UV-spectrometry and spectrofluorometric, while nonaromatic nonionic surfactants must be first transformed into respective derivatives. Gas chromatography could represent an ideal technique for analyzing complex oligomer mixtures, due to its high resolution power and high sensitivity but it is not suitable for the analysis of nonionic surfactants because of the low volatility and high polarity of high oligomers. To avoid this limitation, some authors [51] have applied derivatization of primary alcohol group into trimethysilylether to increase volatility.

8.1 High Performance Liquid Chromatography (HPLC)

Because of the obvious drawbacks of GC analysis (see below), HPLC has become the favored method of analysis for APEO. The major advantage of HPLC is its ability to separate and quantitate the various homologues and oligomers by length of the alkyl and ethoxylate chains. Reversed-phase HPLC provides information about the alkyl chain length, whereas normal-phase HPLC resolves the ethoxylate oligomers [52]. APEO possess a ring chromophore which enables direct UV (at 277-280 nm) [53] or fluorescence detection using excitation and emission wavelengths of 230 and 302-310 nm [54], respectively. Normal-phase HPLC is applied to obtain information about the etboxylate chain distribution of APEOs. They are often quantitatively analyzed by normal-phase HPLC because their biodegradation involves stepwise shortening of the ethoxylate chain. Normal-phase HPLC enables the separation of the persistent alkylphenols and lower ethoxylated APEO, whereas these may coelute in RP-HPLC. A wide range of possible columns, eluents and detection techniques can be used for the analysis of APEO [55].

8.2 Liquid Chromatography/mass Spectrometry (LC-MS)

Due to the complexity of the mixtures, quantitative determination of APs and APEOs remains a challenge. Published methods involve either high performance liquid chromatography coupled with various forms of detection. Normal-phase liquid chromatography has been applied to separate APEOs based on EO units, and reversed-phase HPLC to separate APEOs based on hydrophobic characteristics [52]. Simultaneous chromatographic separations for APEOs based on EO units and hydrophobic alkyl chain was then a challenge. When mass spectrometry has been used for detection, exact

mass extraction was applied to resolve different APEOs from a single chromatographic peak. Thus, liquid chromatography–mass spectrometry (LC–MS) is increasingly being used for the determination of the full range of APEOs. Liquid chromatography with mass spectrometry (LC–MS) enables the determination of steroids and alkylphenols without derivatization. Methods based on mass spectrometry tandem mass spectrometry (MS–MS) detection are reported to be approximately ten times more sensitive than MS detection for treated effluent [56,57,58]. Doubly carboxylated compounds have been identified [59] and Loos et al. [60] have studied the occurrence of octyl- and nonylphenol, their ethoxylates and their carboxylates in Belgian and Italian wastewater by LC–MS–MS.

8.3 Gas Chromatography-mass Spectroscopy (GC-MS)

In general, chromatography is used to separate mixtures of chemicals into individual components. In liquid chromatography (LC), the mobile phase is a solvent. In gas chromatography (GC), the mobile phase is an inert gas such as helium. The mobile phase carries the sample mixture through a stationary phase. The stationary phase (in a tube called column) is a usually chemical that can selectively attract components in a sample mixture. Columns can be glass or stainless steel of various dimensions. The mixture of compounds in the mobile phase interacts with the stationary phase. Each compound in the mixture interacts at a different rate. And elute according to their interaction rate. As the individual compounds elute from the GC column, they enter the electron ionization (mass spectrum) detector. The mass spectrum is essentially a fingerprint for the molecule. This fingerprint can be used to identify the compound. Many studies have used this equipment for NP and its ethoxylates analyses [61,62,63,64].

8.4 GCxGCxMS/TOF

The comprehensive GC x GC technique was introduced by Phillips and co-workers [65] and has been reviewed [66]. A GC x GC system consists of two columns with different retention mechanisms, which are connected in series. In the truly multidimensional system, the separation mechanisms in the first and the second columns are different and independent of each other. However, in practice, the sampling rate in the first dimension is limited by the duration of a single separation cycle in the second dimension. Thus, it would be advantageous to use as short a time for second-dimension to be efficient. Consequently, a compromise usually has to be struck between the first dimension sampling frequency and the second dimension separation time [67]. Theoretical studies indicated that the optimum primary dimension sampling frequency is achieved when each primary dimension peak is sampled three to four times [68]. It has been reported that it may actually be better to use columns with the same diameter in both dimensions in preliminary GC x GC experiments [67].

9. DEGRADATION METHODS

Because of their hazardous behaviors, the production and the use of nonylphenol and its ethoxylates were banned and/or further regulations were applied to protect the environment in many countries. However, significant concentrations are still found in effluents from water resource recovery facilities and in rivers and wastewater treatment plants seem to be inefficient for their removal. Other treatments methods should therefore be considered before releasing effluents into environment. Many studies have been done on degradation of these chemicals, especially on biodegradation and photodegradation.

9.1 Biodegradation

Some studies have used biological species for their degradation experiments such as [63] who studied degradation of the xenoestrogen nonylphenol by aquatic fungi and their laccases isolated from nonylphenol-contaminated river water. Maki [69] used Pseudomonas sp. Strain TR01 for alkylphenol ethoxylates degradation. Results showed that the isolated pseudomonad bacterium has unique substrate assimilability: it metabolizes the EO chain only when the chain linked to bulky hydrophobic groups. Liu [70] also worked on biodegradation using bacteria by focusing on Metabolic pathway of xenoestrogenic short ethoxy chain-nonylphenol to nonylphenol by aerobic bacteria. Otherwise, hayashi [61] have studied nonylphenol polyethoxylates aerobic biodegradation in the presence of organic matter such as methanol, glucose, and yeast extract, showed the formation of the corresponding nonylphenol polyethoxy carboxylates by the oxidation of the terminal alcoholic group. However, aerobic biodegradation tests without organic matter revealed that NP2EO and NP3EO were

predominant metabolites of the long-chain oligomer precursor system which undergo fast and complete shortening. Degradation rates were higher for the longchain oligomers than for shorter ones. The degradation pathway of NPnEos was greatly influenced by the presence or absence of organic matter. Organic materials such as those given above apparently play a significant role in the formation of the carboxylated metabolites of NPnEOs. Teurneau [71] have studied Biodegradation of Nonylphenol Ethoxylates. The scope of this study was to investigate the biodegradability of nonylphenol ethoxylates under aerobic and anaerobic conditions and to understand the mechanism of degradation and influencing factors. Degradation of nonylphenol ethoxylates was studied under aerobic and anaerobic conditions at 27 and 10°C, using acclimated and non-acclimated consortia of organisms in batch experiments using compounds with 2, 4, 10 and 40 ethoxylate units as model substances. An upflow anaerobic sludge blanket reactor was also run being fed with nonylphenol 10 ethoxylate. The degradation rates were higher at 27°C than at 10°C. It was also observed that the longer ethoxylates were degraded to a higher extent. However, using the acclimated bacterial consortium at 10°C, the highest removal rates were obtained for the nonylphenol 10 ethoxylate both under aerobic and anaerobic conditions. For the acclimated bacteria, the initial rate of degradation was higher under aerobic conditions than under anaerobic conditions and then for the nonacclimated inoculum. Surprisingly, there were indications of substantial degradation of nonylphenol 4 ethoxylate (NP4EO) by the non-acclimated organisms under aerobic conditions. Preliminary analysis of the granula and effluent of the methanogenic reactor showed degradation of nonylphenol 10 EO and accumulation of smaller EO chains. The addition of surfactant seemed to enhance the performance of the methanogenic community under these conditions. NPEOs and NPare introduced into soil when wastewater is used as irrigating water in agriculture like shown in Taiyuan city in Kouakou's works [21] or sewage sludge is used as soil fertilizer [72], potentially leading to their accumulation into soil and crops. Once applied to soils, they may come into contact with crops, which can accumulate them via the root system [73]. The greater the persitence of these chemicals in soils, the greater the potential for crops uptake. Sjostrom [74] have studied their degradation and plant uptake in four contrasting agricutural soils. Results showed that NP12EO degraded rapidly (initial half time 0.3-5 days). Concentrations became undetectable within 70-90 days, with a small increase in NP concentrations after 30 days. NP initially degraded quickly 'mean half time 11.5 days), but in three soils a recalcitrant fraction of 26-35% remained. Removal of NP from the soil by plant uptake was negligible (0.01-0.02% of initial NP). Root concentrations were substantially higher than shoot and seed concentrations.

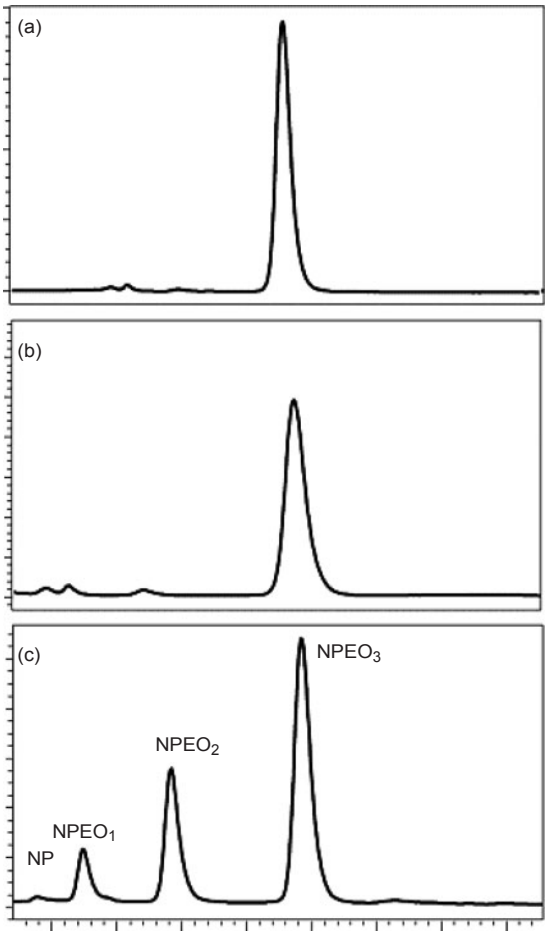

Fig. 4. HPLC chromatogram of nonylphenol triethoxylate (NPEO3) after 96h UVA irradiation: in Milli-Q water solution (a); in solution containing 1000µmolL−1 H2O2 (b); and in solution containing 100 µmolL−1 FeIII (c). [94]

9.2 Photodegradation

Among APEOs, nonylphenol ethoxylates are widely used, with NP9EO being one of the most common nonionic surfactants [75]. This compound (75%) is under the limit of

biodegradability [76] according to the Argentine regulation, which defines that a substance is biodegradable if it can be 80% degraded after 28 days of biological treatment [77]. In addition, the presence of APEOs in biological treatment plants causes serious problems, thus rendering biodegradation inefficient and incomplete. For this reason, biological treatment of APEOs has to be improved. Photochemical advanced oxidation technologies (PAOTs) represent innovative technologies for water decontamination that can allow total or partial elimination of compounds resistant to conventional treatments. Among them, direct UV-C photolysis, UV-C/H2O2-photolysis, photo-Fenton, and TiO2 heterogeneous photocatalysis are the most investigated [78,79]. In the literature, there are various examples of the treatment of APEOs by PAOTs, a number of them using TiO2 photocatalysis [75,76,80]. Ahel [13] have demonstrated that 4-nonylphenol is photolysed in acqueous solution by using a medium pressure Hg lamp. Under irradiating from solar simulator in the presence of TiO2 catalyst, a total mineralization of 4-n-nonylphenol in 30 min was achieved. Degradation of NP9EO by sonolysis has been reported by Destaillats [81] but this method seems to be less operative above the critical micellar concentration [82]. Electrochemical oxidation at modified SnO_2 electrodes has also been tested by Ihos et al. [83]. Ozonation was proposed, but it yielded low total organic carbon (TOC) removal and the main generated products were hazardous alkylphenols [84]. Fe (III)-photoinduced processes and Fenton's reagent (1:1 Fe (II)/H_2O_2 molar ratio) gave good results, and the latter was proposed as a pretreatment for a biological treatment by Kitis et al. [85]. Degradation of NPnEO by both UV-B and UV-A irradiation has been described in those following studies [86,87]. Neamtu et investigated the photolysis of NP using a solar simulator in the absence/presence of dissolved organic matter, HCO^{3-}, NO^{3-} and Fe(III) ions. Results indicate that the oxidation rate increases in the presence of Fe(III) ions and DOM with dissolved organic carbon concentrations not higher than 3mg/L. Under certain experimental conditions, different results can be achived. Wang et al have proved that under their experimental conditions in the presence of Fe(III) ions, NP3EO is degraded successively into NP2EO, NP1EO and NP as shown in Fig. 4, while in the presence of H_2O_2 almost no degradation occured. Under others experimental conditions described by Kouakou [88] have demonstrated that NP degradation rate is better when H_2O_2 is present in solution than when other catalyst are used and achieved after 8 hours about 65% of degradation of NP initial concentration. It should be also noted that main degradation products were Benzaldehyde, 4-methox and Phthalic acid, Diisobutyl ester which are respectively supposed to be more less ecotoxic and subject to biodegradation in the environment. Processes such as combinations of H_2O_2, O_3 and UV, Fenton's reagent, super-critical water oxidation and ionizing radiation have all been used at full scale [89]. It should be noted that research on the application of AOPs in dual or triple combinations of individual processes offer significant kinetic and performance advantages. Methods of AOP employed in studying the degradability of endocrine disruptors in water are: direct (with UV) and indirect photolysis (with UV/O_3 [84], UV/H_2O_2 [90], UV/ Fenton, UV/Fenton/oxalate [91]); photocatalysis with TiO_2 or other semiconductors; and dark advanced oxidation reactions with ozone, electrochemical processes and ultrasonic cavitations [92,93].

10. CONCLUSION

Alkylphenols are used to synthesize polyethoxylated derivatives, mainly nonylphenol polyethoxylates for numerous applications. For instance, domestic detergents, dispersing agents, and industrial and institutional cleaners. These compounds are found in various environmental compartiments and can find their way directly into environment, through industrial effluent, or they can transit via sewage treatment plants. Many studies have also focused on methods for their detection and quantification using various equipments such as HPLC, LC-MS, GC-MS etc… Once their entrance into environment long chain ethoxylated derivatives of nonylphenol are degraded naturally or in wastewater treatment plants into shorten chain and nonylphenols which have been reported to be more toxic than their parents compounds. As sewage treatment plants do eliminate a part of these substances, several studies have focused on lab-scale degradation using different methods involving biological, physical or chemical processes such as PAOTs that can allow total or partial elimination of these compounds. Various efficiencies have achieved and few among them produced non or less toxic byproducts, or reached complete mineralization (production of CO_2 and H_2O) which remain the most important goal at this moment for further researches.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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