Advance Research in Textile Engineering

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Austin Publishing Group

Review Article

Study, Nonylphenol Analysis of Textile Liquid Discharges of the City of Marrakech

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Received: August 09, 2021; **Accepted:** September 06, 2021; **Published:** September 13, 2021

Abstract

Nonyphenols, especially the ethoxylated derivatives of nonylphenol (NPE) known as ethoxylated alkylphenols (APEs), are synthesized for their surfactant properties, which allow a better dispersion of liquids and the miscibility of certain substances such as oil and water. More than 40 years have been used as detergents, emulsifiers, wetting agents and dispersing agents and even cosmetic products such as shampoos. These organic molecules are very persistent and well known by their predatory toxicities on the skin, the eye, the respiratory tract, the kidneys and the liver, they are endocrine disruptors. The textile industry via some ennobling chemicals, tissue contamination and liquid discharges by these molecules remains a concern for the industry and the quality of these discharges. Our goal is to verify the contamination of liquid discharges from a textile industry using certain chemicals in the dyeing process.

Keywords: Nonylphenol; Textile; Liquid waste; Endocrine disruptor

Introduction

Nonylphenols (NP) are synthetic organic molecules belonging to the family of alkylphenols. Nonylphenols (NP) constitute a family of chemical compounds of formula $C_6H_4(OH)C_9H_{19}$ having a benzene ring and a linear or branched carbon a 9 carbon chain, the degree of branching and their positions are very variable according to the isomers. These molecules are present in the form of a pale yellow viscous liquid that gives off a slight phenolic odor. They are usually available in solution with impurities (including dinonylphenol), with commercial mix formulations (nonylphenol/dinonylphenol). Large amounts of nonylphenols are used to produce nonylphenol ethoxylates, which are then incorporated into formulations, and which are not stable in the environment, they are rapidly degraded to Nonylphenol (NP). They are used extensively as detergent precursors, as fuel additives and lubricants, as polymers, such as phenolic resins, in perfumes, such as thermoplastic elastomers, antioxidants, flame retardant materials.

The main compounds of nonylphenols (NP)

- Linear n-nonylphenols: a mixture of isomers of nonylphenols whose alkyl chain is linear (Figure 1).
- Branched n-nonylphenols: a mixture of nonylphenols with branched chains, all in positions 2, 3 and 4 on the benzene ring, corresponding to the main proportion of industrial nonylphenols (Figure 2).

Physical and chemical properties of nonylphenols

The physical and chemical property affecting the environmental persistence of (NP) whose mean chain length is summarized in Table 1.

Origin and presence in the environment

There is no known natural source of Nonylphenol (NP) and Nonylphenol Ethoxylates (NPE). Their presence in the environment results solely from human activity. Sewage treatment plants are the largest emitters of nonylphenols to the aquatic environment. Nonylphenol diffuse emissions are mainly related to agricultural application of sewage sludge or landfills. The use of nonylphenol ethoxylates in the fertilizer industry could result in diffuse emissions of these substances into the soil. It should be noted that the presence of nonylphenols (NP) in the environment is mainly due to the degradation of nonylphenol ethoxylates (NPEs) (Figure 3) [1].

Nonylphenols (NP) with low solubility in water are preferentially distributed in organic matter; however, their presence is effective in surface water, groundwater and drinking water. The main source of nonylphenols (NPs) in surface water (rivers, lakes, estuaries), oceans and sediments comes from effluents from wastewater treatment plants and from runoff from landfills. In river water, nonylphenols (NP) are found at concentrations between $0.6 ng.L^{-1}$ and $15 \mu g.L^{-1}$. For groundwater, contamination is a problem because the biological and chemical characteristics of these waters are not favorable to the degradation of nonylphenols (low oxygen, few microorganisms) [2]. As a result, significant nonylphenol (NP) concentrations were found in soils highly exposed to sewage sludge (1.4 to 1.6 $mgkg^{-1}$) and runoff (34 to 14 $\mu g.kg^{-1}$) compared to soils exposed to unmodified soils or soils fertilized with manure or a limited amount of sewage sludge (0.01 to 0.98 $\mu g.kg^{-1}$ [1].) Nonylphenols (NP) were also detected in the atmosphere at concentrations ranging from 2.2 to 70 $ng.m^{-3}$.

The removal of nonylphenol (NP) from water by drinking water treatment plants is highly variable. Only the chlorination step has shown an interesting efficiency (up to 90% elimination) [3].

Nonylphenol (NP) Toxicity

Nonylphenols (NPs) (family of alkylphenols) are known to be endocrine disruptors and may cause reproductive, developmental and immunological disorders [4]. NPs are known to have estrogenic activity, that is to say having the ability to mimic natural sex

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Citation: Ouhammou M, Jaouad A and Mahrouz M. Study, Nonylphenol Analysis of Textile Liquid Discharges of the City of Marrakech. Adv Res Text Eng. 2021; 6(2): 1066.

Figure 1: Linear n-nonylphenols.

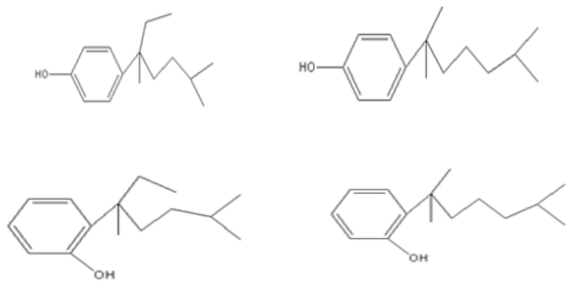

Figure 2: Branched n-nonylphenols.

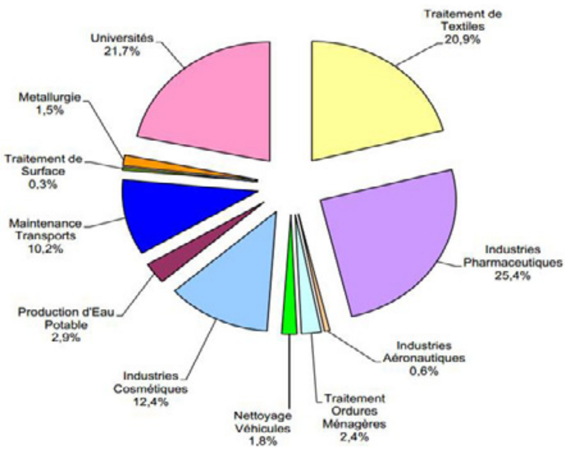

Figure 3: Contribution of different sectors of activity in nonylphenols (NP).

hormones, which can lead to the feminization of fish, for example with induction of vitellogenin in male trout [5]. In animals, they can cause a decrease in fertility, a slowing of growth and a decrease in size. In humans, the effects of nonylphenols are still poorly known due to lack of studies. Effects have recently been demonstrated on sperm functions in mammals [6], and deterioration of DNA in human sperm and human lymphocytes [7]. Endocrine disruptors have three different modes of action. They can play a mimetic role (estrogen effect), a role of blocking (antiestrogenic effect) or a role of disturbance (anti-androgenic effect).

Toxicity in Humans

Exposure routes

4-Nonylphenols (4-NP) is an endocrine disruptor. Indeed, this molecule can be attached to the receptors for 17β-estradiol, located in the liver and can mimic, block or enhance its action [8]. The human population is largely exposed to alkylphenols through inputs via contaminated food and drinking water; nonylphenols have been detected in different foods [9], and in plastic bags can migrate to food and drinking water [10]. Other routes of human contamination of these compounds include contact with personal beauty products and detergents [11].

Exposure *via* food contamination

Food seems to be the main source of human contamination with alkylphenols. In a food monitoring study in Germany, nonylphenol concentrations were measured in all food samples analyzed, with concentrations ranging from 0.1 to 19.4 μg/kg [9]. In another study, nonylphenol concentrations ranging from 5.8 to 235.5 μg/kg were found in food samples in Taiwan [12]. Indeed, high levels of NP have been found in aquatic organisms and in many foods (0.1 to 235 μg/kg) [2,13].

Exposure by skin contact

Another route of contamination of alkylphenols is the use of personal care products. Indeed, it has been reported that intake of alkylphenols, especially nonylphenols, exists in perfumes (1.57mg/kg/day), moisturizers (22.6mg/kg/day), facial makeup (0.0037mg/kg/day) and deodorants (0.28mg/kg/day). A second route of dermal exposure of alkylphenols is their use in detergents and other cleaning products [13]. It has been reported that the direct exposure to laundry detergents, that is, for hand washes of delicate tissues, is 0.0091mg/kg/day of nonylphenols. Finally, the last route of dermal exposure to

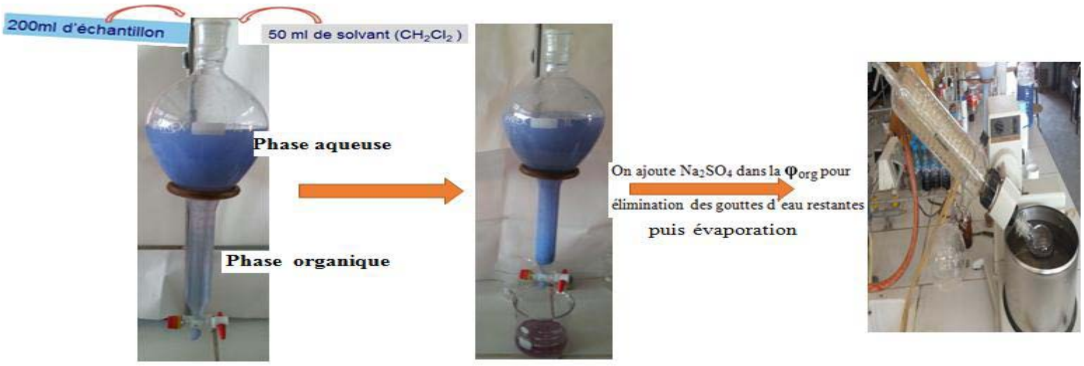

Figure 4: Liquid-liquid extraction by dichloromethane of nonylphenols in textile liquid discharges (dyeing).

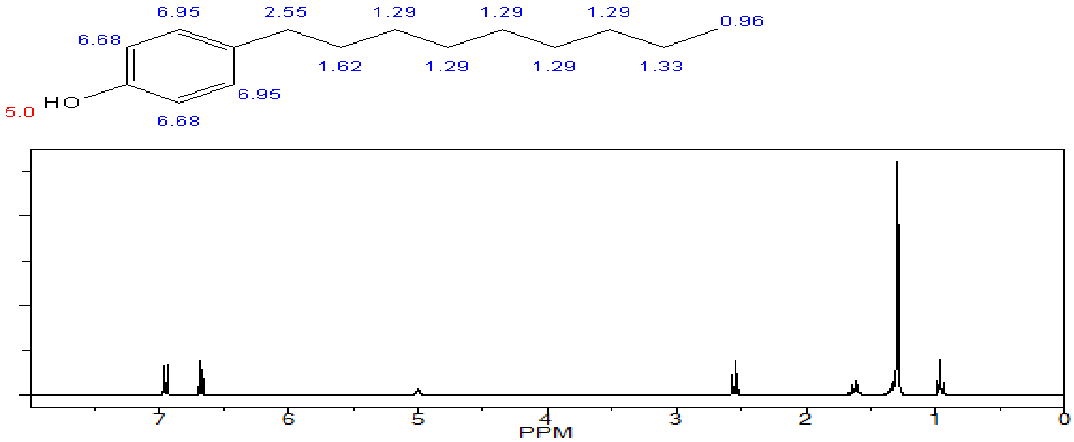

Figure 5: The 1H NMR spectrum of the 4-nonylphenol isomer.

alkylphenol is the use of latex paints, or oil, where the daily intake for a seven-day exposure per year for a construction worker is 0.022mg/day.kg/day [13].

Inhalation exposure

Exposure to alkylphenols (nonylphenols) by inhalation appears to be the least important route in human pathways. However, it has been reported that nonylphenol intakes in aerosol paints and household cleaning products reach values of 0.0043 and 0.065 mg/kg/day, respectively [13]. Another study, carried out in the United States, the analysis of indoor dusts of a house, likely to be inhaled by organisms, revealed a concentration of alkylphenols (mainly NP) of 26.7µg/g [14].

Analysis of Nonylphenols

Nonylphenol is a synthetic compound that is a precursor in the manufacture of polyethoxylated nonylphenols used as surfactants in several industrial and domestic products. It is also used for the manufacture of phenolic resins. These products are classified as estrogenomimetic and could be considered potential endocrine disruptors in several species.

Several studies have shown the presence of these contaminants in sludge, liquid wastewater discharges, sediments, aquatic organisms and surface water.

Extraction of nonylphenols

Liquid-liquid extraction is a common application to extract nonylphenol (NP), octylphenol (OP) compounds from the water matrix [15]. The matrix is studied by double or triple extraction (volumes ranging from 50 to 100 ml), and by grouping the extracts in a single phase [16].

Overall, the sample volume required for extraction is large (from 500 to 1,000 ml). In our case, the sample is a liquid rejection of a dyeing textile industry located at the industrial zone sidi Ghanem of the city of Marrakech.

The extraction is carried out in an amber glass bottle, stirred for 15 to 20 minutes on a "back-and-forth" system before decantation in a separating funnel [17], with a ratio of 4 (Volume/Volume: 200ml/50ml). Some studies have shown that the best extraction solvent is dichloromethane (DCM) with yields ranging from 87 to 98% [18].

Indeed, the (DCM) is poorly miscible in water, it extracts in a wide range of polarity, it has a low boiling temperature, which has the effect of increasing the speed of its evaporation, and finally it is denser than water and is therefore in the lower phase during extraction into separating funnels [15]. The use of anhydrous sodium sulphate in the organic phase, after the extraction step, allows the elimination of the remaining drops of water [17], [19].

Table 1: Physico-chemical properties of nonylphenol NP.

4-nonylphénol	
Brute formula	$C_{15}H_{24}O$
Aspect	Liquid
Odour	Slightly phenolic
Color	Moderately volatile viscous yellow-pale
pH	5-7
Density at 20°C	0.95
Melting temperature	-10 à +5°C
Boiling temperature	290-320°C
Auto-ignition temperature	370°C
Flash point	141 à 155°C
Density of vapor	76 air=1 Vapor pressure 0.3 Pa à 25°C
Molecular weight	220, 3505 ± 0,014 g/mol C 81.76%, H 10.98%, O 7.26%,
Volumic mass	0 952g·cm^{-3} à 20°C1
Solubility in water (20°C)	Insoluble in water 6mg/l
Identification of risks	4-Nonylphenol is low in flammability (flash point between 141°C et 155°C).

Table 2: Average characteristics of textile industrial wastewater (dyeing).

The settings	The Parameter value
Temperature during sampling (°C)	38
pH	7.68
Conductivity (µS/cm)	3900
MES (mg/l)	200
Turbidity (FTU	97
Dry matter (g/l)	4.97
Ashes (g/l)	1.93
DCO (mg/l)	991.67
DBO_5 (mg/l)	348
DCO/DBO_5	2.84
N-NTK (mg/l)	32.67

Analysis of Nonylphenol (NP) of a Textile Industry (dyeing) in the City of Marrakech

Liquid/liquid extraction of nonylphenols

The experimental study was conducted using industrial wastewater from a dyeing unit. Due to the variation in the composition of the industrial wastewater produced by the dyeing plant, the samples were taken in the middle of the week, an overall release consisting of a mixture of several dyes and additives is analyzed, the Table 2 presents the characteristics of this liquid discharge, there is not a stability of the parameters since the quantity of the chemicals used in the dyeing changes from one day to another and according to the order.

The use of liquid/liquid extraction is generally limited to low polar compounds. In the literature, studies have shown that the best extraction solvent for nonylphenols is dichloromethane with yields ranging from 87 to 98%.

Nonylphenols (NPs) are considered ubiquitous in the environment, that is, they are found in all environmental compartments (from the atmosphere to the natural environment). In addition, they are considered as endocrine disruptors and can therefore cause damage to fauna and flora present in the natural environment.

The protocol used in the extraction of nonylphenols (NP) from the sample or the sample is the liquid-liquid extraction with dichloromethane (Volume/Volume: 200ml/50ml), the addition of anhydrous sodium sulphate in the organic phase, after the extraction step, aims at the elimination of the remaining drops of water, the evaporation of the solvent is done by rota-vapor. Finally, the product obtained by NMR and IR (infrared) is analyzed and then compared with NMR and IR of the nonylphenol most abundant in nature, linear 4-nonylphenol, and Figure 4 shows the Liq-Liq extraction protocol of samples. Textile liquid discharges (dyeing).

NMR and FTIR analysis of nonylphenols

The mass in ppm/l of nonylphenols from liquid dyeing was 3.52 ppm. Analysis of nonylphenols by NMR showed the appearance of (Figure 5 and 6):

- Peak at 0.96 ppm corresponding to the CH_3 proton bound to a saturated aliphatic group.
- Peak at 1.29-1.33 ppm corresponding to CH_2 proton bound

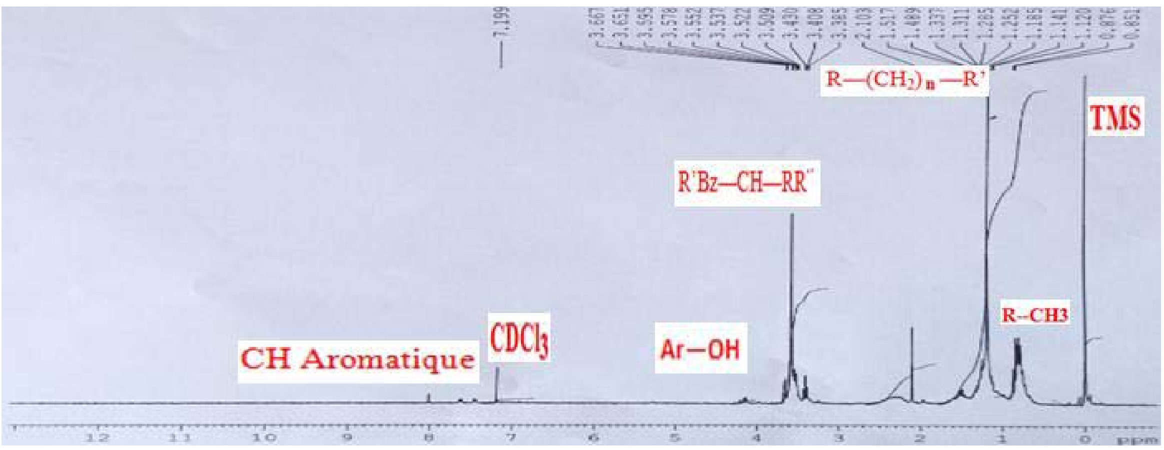

Figure 6: The NMR spectrum of nonylphenol liquid rejection dyeing.

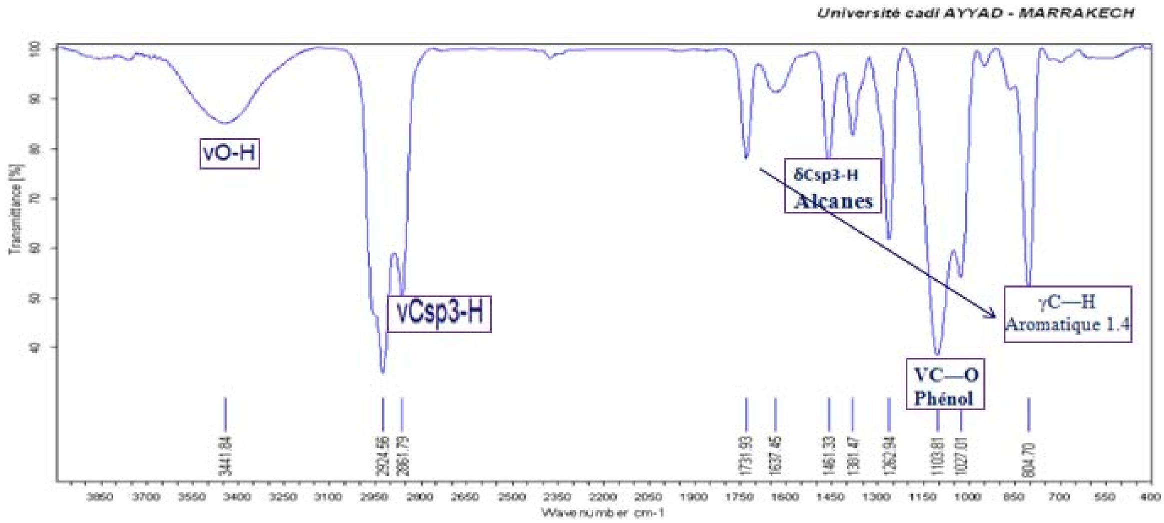

Figure 7: The Infrared spectrum, FTIR of nonylphenold from the textile industry.

to two aliphatic groups as trace on spectrum.

- Peak at 3.4 ppm corresponding to the CH_2 or CH proton bound to two groups, one aromatic and the other aliphatic as a trace on spectrum.
- Signals at 7.3-7.4 ppm corresponds to aromatic hydrogen.

FTIR Fourier infrared analysis of nonylphenols from liquid dyeing textile rejection showed the appearance of the following bands (Figure 7).

- The absorption band at 3452cm^{-1} corresponds to O-H of an alcohol group of a phenol.
- Absorption bands between 2925-2862 cm^{-1} result of Csp3-H elongation vibrations of aliphatic molecules.
- Absorption bands between 1459-1377 cm^{-1} result of the deformation of Csp3-H of aliphatic chain.
- Absorption bands between 1262-1100 cm^{-1} due to Phenol C-O binding stretching vibrations.
- The spectrum also show the bands at 804cm^{-1} attributed off-plane C-H deformation of benzene compound at position 1.4.

Conclusion

This work made it possible to determine the level of contamination of industrial wastewater from a textile-dyeing unit in the city of Marrakech, in nonylphenols or alkylphenols. A high concentration was observed up to 3 ppm for the overall liquid rejection of dyeing. While the norm prohibits the presence of these molecules. At the treatment level of nonylphenols, the use of activated carbon remains the most efficient process by other processes, advanced oxidation process, biological treatment, membrane filtration, lamellar physicochemical settling, from the point of view that nonylphenols or alkylphenols are persistent, so their degradation leads to the formation of generally more stable metabolites.

Acknowledgment

The authors acknowledge the Ministry of Higher Education, Scientific Research and Professional Training of Morocco, Priority Research program (PPR-B-Mahrouz-FS-UCA- Marrakesh).

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