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Research Article

Chemical Characterization of Specific Micropollutants from Textile Industry Effluents in Fez City, Morocco

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Textile industry is one of the most polluting industries in the world. It has a high importance in terms of its environment impact, since it consumes a considerably large amount of water and produces highly polluted discharge water. In this work, characterization of toxic organic compounds is proposed. Based on gas chromatography coupled to mass spectrometry (GC/MS) screening analysis, organic micropollutant diversity of textile effluents from a local textile processing factory was investigated. In the present work, physicochemical characterization of the studied textile effluents showed considerably high values of principal pollution parameters above the prescribed discharge water limits. Heavy metals like zinc (Zn), copper (Cu), iron (Fe), nickel (Ni), cadmium (Cd), chromium (Cr), and lead (Pb) were found to be present within the permissible limits. The results of GC/MS revealed the presence of various organic compounds belonging to a wide range of chemical classes. Main groups of chemical compounds detected in these effluents were aromatic carboxylic acids, alkanes, aromatic amines, phthalates, aliphatic carboxylic acids, and linear aliphatic alcohols. The results of this study allowed significant contributions to the chemical characterization of textile industry contaminants and identification of indicators that can be considered an important tool for assessment of the potential impact of textile activities to the contamination of aquatic environment and health hazard.

1. Introduction

Because of the increase of various types of industrial effluents, there is a growing concern regarding the potentially adverse effects of textile effluents on aquatic biota and humans due to the contamination of water used in textile industry. Being emitted at a significant concentration level, organic compounds in textile effluents normally present a high structural diversity and reveal notable ecotoxicological effects. Determination of nonhalogenated solvents (toluene, xylenes, ethylbenzene, and diisobutylketone) in textile industrial wastewater was performed with head-space solid phase microextraction h-SPME [1]. However, indicative compounds reflecting specific industrial processes and the corresponding chemicals have been reported rarely. More surprisingly, Castillo and Barcelo [2] have reported the appearance of phenol, nonylphenol isomers, and phthalate esters in the effluents of a textile industry in Portugal. Pinheiro et al. [3] and Bilgi and Demir [4] have found that the degradation products of azo dyes, such as 6-acetylamino-3-aminonaphthalene-2-sulfonic acid, *N*-(3,4-bishydroxymethylphenyl) acetamide, aromatic amines, and anilines, can pose a hazard to the aquatic environment. The effects of the contaminants have been investigated in many large-scale studies over a long period of time, and the results are worrisome [5–10].

Significant amounts of polyethylene glycol, polyethoxylate decylalcohol, and linear alkylbenzene sulfonates were found to be major constituents in textile wastewaters. High concentration levels were found for some benzenes and naphthalene sulfonates which are used in the textile industry as dye bath auxiliaries [11]. The authors argued that

toxicity observed in the effluents from textile industries to *Daphnia magna* can be attributed to nonylphenol isomers, alcohol polyethoxylated, nonylphenol ethoxylates, and several phthalates. However, most of these studies focused on the contamination of aquatic systems and did not analyze the effect of specific compound composition of the industrial effluents.

Moroccan industrial sector is composed of 6070 units in which 31% are textile and leather industries. These industries consume significant quantities of dye and chemicals products in the various manufacturing synopsis [12–14]. For wet processing, 1 kg of cotton needs about 150 l of water, 0.6 kg NaCl, and 50 g of reactive dyes [15]. The chemical reagents used in textile industry are diverse in chemical composition ranging from inorganic to organic. Depending on the manufacturing conditions, a significant fraction of the chemicals used is released into the environment through wastewater. Wastewater generated from textile industry, especially dyeing effluents, contain organic dyes, chemicals, auxiliaries, salts, detergents, heavy metals, mineral oils, and high rates of COD [16–18]. Generally, dyeing effluents contain the major part of pollutants generated from textile industry [19] having high pH, temperature, chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solids (TDSs), and total suspended solids (TSSs) [20, 21] and low biodegradability [22].

The discharge of textile effluents into natural aquatic and terrestrial ecosystems poses serious problems. The hazard linked to these effluents resides mainly in the presence of micropollutants. These chemical compounds are persistent contaminants and bioactive which means that they are not completely biodegradable and cannot be removed with conventional water treatment technologies.

It has to be stated that there is a lack of systematic investigations on organic pollutants in textile effluents as well as of the information on their environmental relevance. Like other city industries in the country, textile industries of Fez city discharge their wastewater into the sewage network without any prior treatment. Moreover, in our previous work, we found high genotoxicity and phytotoxicity potential of textile effluents from the studied site of Fez city [9]. Therefore, due to their complex chemical composition, the present study is focused on (i) physicochemical evaluation of local textile mill effluents in Fez city, Morocco, (ii) characterization of organic pollutants in textile effluents from a local processing factory, and (iii) isolation of specific compounds that might act as source indicators responsible of high toxic load of these effluents. These indicator substances, typical for textile production industries and unique signatures of textile effluents, shall allow efficient source identification in polluted aquatic systems.

2. Materials and Methods

2.1. Study Area and Sample Collection. Samples of textile effluent used in this study were collected from a textile factory of 3200 m^2 surface, located at Sidi Brahim industrial area in Fez, Morocco. This factory produces cotton and polyester clothes, discharging more than 400 m^3/day of wastewater, which originates from different manufacturing processes (singeing, desizing, scouring, bleaching, mercerizing, dyeing, printing, and finishing). The scheme of sampling site is shown in Figure 1. The wastewater samples were filled in cleaned polyethylene bottles with coated screw caps and stored in the dark at a temperature of 4°C.

2.2. Physicochemical Analysis of Textile Effluents. Physicochemical analyses of textile effluents were performed to evaluate some major parameters including pH, temperature (T), electric conductivity (EC), total suspended solids (TSSs), total dissolved solids (TDSs), chemical oxygen demand (COD), biological oxygen demand during 5 days at 20°C (BOD_5), P-phosphates (P-PO_4^{3-}), N-nitrates, and N-nitrites. These parameters were determined in accordance with the method reported by Giorgetti et al. [9].

Metal ions (Fe, Cd, Pb, Cr, Cu, Zn, and Ni) and divalent cations (Mg^{2+} and Ca^{2+}) were determined using the plasma-absorption emission spectroscopy method with an atomic absorption spectrophotometer (Activa, Horiba Jobin Yvon) [9]. The results obtained in experiments were expressed in terms of means (average) and standard deviation (SD). The standard deviation was calculated using Microsoft Excel, and results were presented as mean ± SD value.

2.3. Extraction and Gas Chromatography Coupled to Mass Spectrometry Analysis. Before subjecting to GC/MS analysis, the organic compounds contained in textile wastewater samples were extracted. A sequential liquid-liquid extraction procedure was applied to approximately 500 ml of textile wastewater using dichloromethane. Equal volume of dichloromethane was used for extraction. Thereafter, the organic layers were concentrated (approx. 1 ml) by rotary evaporation at 40°C under reduced pressure and dried by filtration over 1 g of anhydrous granulated sodium sulfate. The final concentration volume of wastewater extracts was 50 μl.

Organic compounds contained in textile wastewater samples were determined in accordance with the method reported by Giorgetti et al. [9] using gas chromatography-mass spectrometry under negative chemical ionization mode (Thermo Polaris Q mass spectrometer linked to a TRACE GC Ultra and Thermo Electron Corporation gas chromatograph). The identification of organic compounds was based on comparison of EIþ$^+$-mass spectra with those of the reference compounds or mass spectral databases (NIST/EPA/NIM Mass Spectral Library NIST00, Wiley/NSB Registry of Mass Spectral data) and gas chromatographic retention times. The quantification of organic compounds (relative quantity) was computed from the GC-FID peak areas using the normalization method.

3. Results and Discussion

3.1. Physicochemical Characterization of Textile Effluents. The textile effluent samples collected from the studied site during production process were characterized with common parameters (color, temperature, pH, EC, TSS, and COD).

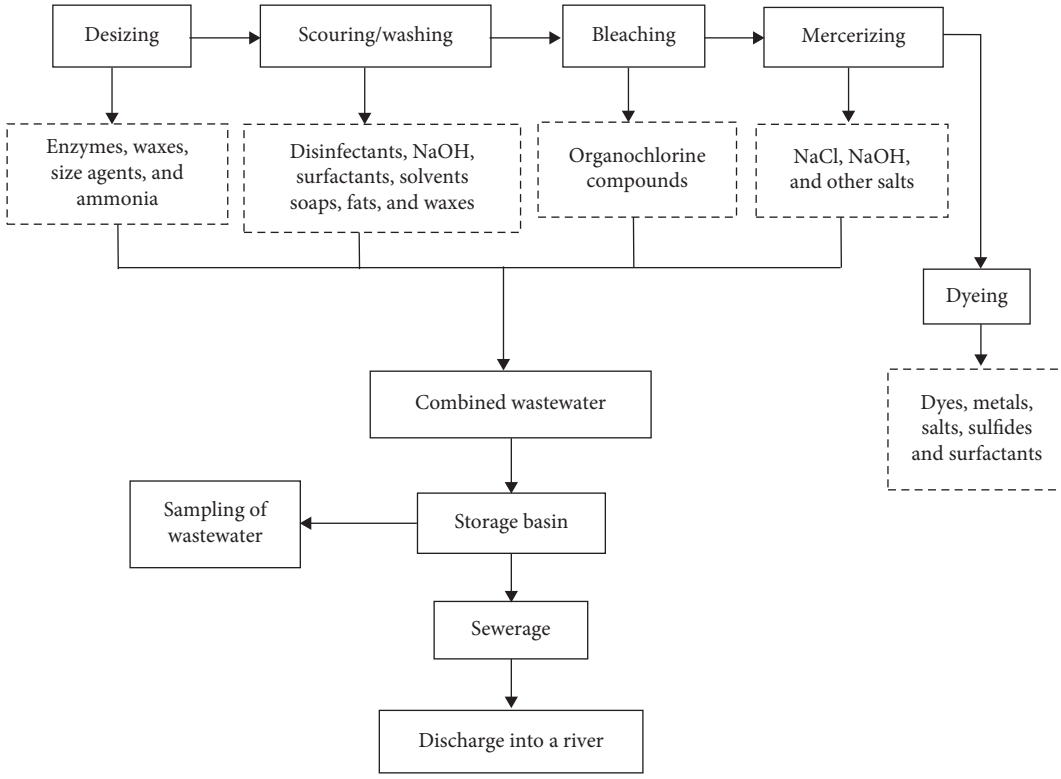

Figure 1: Scheme of production processes in sampling site and the main pollutants from each step.

The mean and standard deviations were calculated using 3 different effluents during the experimental period. Main results are presented in Table 1.

The studied textile effluents are characterized by a variation in color from blue, dark blue, and black. This variation of discharged textile effluents color is due to the variation of the dyes and pigments used during production process. The pH of textile effluent samples varied from 7.2 to 8.1 with a mean value of 7.73 indicating the alkalinity of the effluent samples. The results were similar to the study conducted by Islam and Mostafa [23]. These values of pH were within the limit set by Moroccan Discharge Quality Standards [24] (M.D.Q.S) and World Health Organization (WHO) standards.

The temperature recorded in textile effluents was high (40–45°C) and exceeded the standards set by M.D.Q.S and WHO. The high temperature of these effluents can induce corrosion of the sewerage network by catalyzing redox reactions [25]. On the other hand, the elevation of the temperature of these waters facilitates the release of hydrogen sulfide (H_2S) which is a gas with greenhouse effect and dangerous for human health.

The EC indicates dissolved substances in an aqueous system. It depends on the dissociation of ions, their concentration, temperature, and migration in the electric field, but it does not give any idea about the type of ions present [26]. The EC average of textile effluents was 5476.66 μs cm^{-1}, which is higher than the permissible limits set by M.D.Q.S and WHO indicating the high levels of pollution. The results are similar to those published by Ali et al. [27]. The total dissolved solids (TDSs) are the organic contaminants and inorganic insoluble, suspended particles, sulfates, phosphates, sodium chloride, etc., which ruffled the water quality [28].

The amount of TDS which was found to be 1510, 3025, and 2400 mg·l^{-1}, respectively, in the textile effluents A, B, and C was similar to the observation made by Ali et al. [27]. These effluents show TDS concentrations higher than the permissible limits set by M.D.Q.S and WHO (TDS average = 2311.11 mg·l^{-1}) indicating that the discharged effluents have the potential to deteriorate the surface water quality and aquatic life as well. The total suspended solids (TSSs) of textile effluent samples were found to be in the range of 900–2200 mg·l^{-1}, which is slightly similar to the results shown by Ali et al. [27] and varied from 400 to 1500 mg l^{-1}. All these TSS values are notably higher than the permissible limit of TSS as per M.D.Q.S and WHO standard (30 and 100 mg·l^{-1}, respectively).

Chemical oxygen demand (COD) shows the presence of both the biodegradable and non-biodegradable matter content in the textile effluents. In this study, total COD in various textile effluents varied from 1026 to 2433 mg·l^{-1}, exceeding the limits set by M.D.Q.S and WHO. Shammi et al. [29] reported that the COD of textile effluents was found between 832 and 1023 mg·l^{-1}, which were lower than the present findings. The highest COD value was recorded in effluent B and the lowest was found in effluent A. Biological oxygen demand (BOD_5) measures the amount of oxygen used by microorganisms in the biological process in water. BOD_5 is found to be higher in all the samples indicating the

Table 1: Physicochemical characterization of textile effluents compared with M.D.Q.S and WHO standards.

Parameters	Units	M.D.Q.S limits	WHO standards	Effluent A	Effluent B	Effluent C	Average	S.D (±)
Color	—	—	—	Blue	Dark blue	Black	—	—
T	°C	30	40	45	40	41	42	2.64
pH		5.5–8.5	6.5–8.5	7.2	7.9	8.1	7.73	0.47
EC	$\mu s \cdot cm^{-1}$	2700	1200	1240	13670	1520	5476.66	7097.01
TDS	$mg \cdot l^{-1}$	—	2000	1510	3025	2400	2311.66	761.35
TSS	$mg \cdot l^{-1}$	30	100	900	2200	1200	1433.33	680.68
COD	$mg \cdot l^{-1}$	120	250	1026	2433	1766	1741.66	706.81
BOD	$mg \cdot l^{-1}$	40	30	200	880	360	480	355.52
$P\text{-}PO_4^{3-}$	$mg \cdot l^{-1}$	—	—	0.461	0.788	1.147	0.798	0.343
$N\text{-}NH_4^+$	$mg \cdot l^{-1}$	—	—	0.670	1	7.3	2.99	3.73
$N\text{-}NO_3^-$	$mg \cdot l^{-1}$	—	—	10.8	0.29	1.45	4.18	5.76
Ca	$mg \cdot l^{-1}$	—	—	88.54	210.44	13.8	104.26	99.25
Mg	$mg \cdot l^{-1}$	—	—	25.29	51.97	4.85	27.37	23.62
Zn	$mg \cdot l^{-1}$	5	1	0.04	0.28	0.05	0.123	0.13
Cu	$mg \cdot l^{-1}$	3	0.1	0.004	0.032	0.002	0.0126	0.016
Fe	$mg \cdot l^{-1}$	5	10	0.649	0.584	0.401	0.544	0.128
Ni	$mg \cdot l^{-1}$	5	3	0.02	0.01	0.001	0.010	0.009
Pb	$mg \cdot l^{-1}$	1	0.1	0.05	0.002	0.03	0.031	0.024
Cd	$mg \cdot l^{-1}$	0.2	2	0.001	0.032	0.041	0.024	0.020
Cr	$mg \cdot l^{-1}$	0.5	2	0.021	0.011	0.045	0.025	0.017

more percentage of bacterial content utilizing the oxygen, probably due to the presence of higher organic content in the samples [28].

The amount of N-Nitrate ($N\text{-}NO_3^-$) in studied effluents averaged 4.18 $mg \cdot l^{-1}$, which was higher than the results of Somensi et al. [30]. N-Nitrite ($N\text{-}NH_4^+$) averaged 2.99 $mg \cdot l^{-1}$ which was lower than the findings of Fang et al. [31]. Concerning P-Phosphate ($P\text{-}PO_4^{3-}$), low concentrations were recorded in textile effluent samples (average = 0.798 $mg \cdot l^{-1}$), which were lower than the results of Somensi et al. [30].

Divalent cations Ca^{2+} and Mg^{2+} showed high concentration ($mg \cdot l^{-1}$) variability in the effluent samples, reflected by high standard deviation values (104.26 ± 99.25 and 27.37 ± 23.62, respectively). Finally, heavy metal analysis of textile effluents showed low concentrations compared to the M.D.Q.S and WHO standard. The average concentration ($mg\ l^{-1}$) of heavy metals like Cu(0.0126), Ni (0.01), Pb (0.031), Cd (0.024), and Cr (III) (0.025) was considerably low ($<0.04\ mg \cdot l^{-1}$) while it kept $> 0.1\ mg\ l^{-1}$ in case of Zn (0.13) and Fe (0.544). The relative dominance (average) of heavy metals in textile effluents was observed in the following sequence: Fe > Zn > Pb > Cr > Cd > Cu > Ni.

Table 1 shows great variability in the quality of textile effluents and revealed a reasonably high load of pollution indicators compared to the prescribed M.D.Q.S and WHO limits. Color of textile effluents is due to dyes and pigments dissolved in water that absorb light and emit light at specific wavelengths. Coloration of textile effluents is a great environmental concern since it reduces the oxygen concentration in water due to the presence of hydrosulfide group compounds. Also, it blocks the passage of light through the water body and is detrimental to the water ecosystem [32].The temperature of textile effluent was considerably high (average = 42°C) which reduces solubility of gases in water that is ultimately expressed as low BOD_5/COD. The BOD_5/COD ratio was 0.27 (average), which was very low in comparison to domestic wastewater (0.5). Therefore, the biodegradability of the effluent was found to be low according to the criteria of Ahn et al. [33].Generally, alkaline pH of textile effluents is associated with the process of bleaching [34–38], and it is extremely undesirable in water ecosystems. Conductivity is a pollution parameter which is sensitive to variation in dissolved ions and mineral salts [39]. Electric conductivity recorded in textile effluent was considerably high and reflected a high concentration of mineral salt.

There was observed high values of TSS and TDS in effluent samples which correspond to filterable and nonfilterable residues, respectively. TSS and TDS are important repositories for toxic heavy metals and dyes [40, 41] causing rapid depletion of dissolved oxygen leading to oxygen sag in the receiving water [42]. Even if the levels of metal ion concentrations in effluents were low and reached the permissible limits of M.D.Q.S and WHO, they are considered toxic and tend to persist indefinitely, circulating and eventually accumulating throughout the food chain [27, 43–45]. The inorganic heavy metals, such as Cd, Cu, Cr, Fe, Mn, Ni, and Zn, originating from ionic salts are directly absorbed by the marine and fresh water biota or are incorporated in ground water in both cases, i.e., the consumption of polluted ground water and marine foods may lead to diseases like cancer, brain diseases, and psychiatric diseases. Concerning heavy metals present in textile dyes as a chromophoric group, they are not biodegradable; hence, they accumulate in primary organs in the body and lead to various symptoms of diseases [46].

Similar to the toxic dyes and pigments of organic nature, such as C.I. Pigment Yellow-12 (3,3-dichloro benzedine), C.I. Disperse Yellow-7 (P-amino azobenzene), and C.I. Direct Yellow-1 (benzedine), salts, acids, alkalis, and bleaching and finishing agents are also highly harmful and affect the health of biota to a great extent. The effects of the

pollutants may not be quite evident immediately but with the passage of time their imperceptible effects are of fatal nature [47]. Hence, the presence of dyes and metals cause severe damage to the aquatic biology. Consequently, the self-purification ability of the stream and conventional biological treatment systems are hindered [42].

It can then be concluded that the textile wastewater used in this experiment was highly variable and suffered from low biodegradability and high inorganic solid content (both soluble and suspended). This wide variation in the characteristics of textile wastewater is due to the complexity of materials used in the textile industry during the processing of textiles.

3.2. Organic Compounds of Textile Effluents. Textile effluents from the studied site were subject to organic analyses. Based on the GC/MS analysis of different textile effluents from the studied site, identification of a large number of various organic contaminants has been performed. The obtained results demonstrated high structural diversity of organic chemical pollutants in the textile wastewaters. It is important to notice that only a restricted number of samples have been investigated as a preliminary evaluation of a potential impact of textile contaminants from diverse production processes at industrial site on the aquatic environment. Selected environmentally relevant specific organic compounds identified in three different textile effluents are presented in Tables 2–4 and are arranged according to their retention time. The chromatograms of extracts containing various organic constituents in terms of structural diversity and quantitative composition of textile effluents A, B, and C are illustrated in Figures 2–4 (peak numbers correspond to the organic compounds shown in Tables 2–4).

Fast characterization of the identified compounds revealed the presence of organic pollutants belonging to a wide range of chemical classes such as aromatic carboxylic acids, alkanes, benzoic compounds, phthalates, aliphatic carboxylic acids, aromatic amines, and linear aliphatic alcohols (Tables 2–4). Generally, aromatic carboxylic acids were predominant in effluent A. 1,2-Benzendicarboxylic acid, 4-methyl-dimethyl ester; benzoic acid, 2,3-dimethyl-6-(3-methyl-1-oxobutyl); propane dioic acid (3chlorophenyl) methylene, diethyl ester; and benzoic acid, 4-(tetrazol-1-yl) methyl were detected with a relative abundance (RA) of 37.3, 14.5, 1.08, and 0.16%, respectively (peaks 5, 4, 12, and 10, respectively, in Figure 2).

Aromatic carboxylic acids present in textile effluents are reported to be constituents of natural tanning agents and dyes [11]. Referring to the group of alkanes, 2-pentoxy-tetrahydropyran, 2-propyltetrahydropyran, and 2,2-dimethylbutane were the predominant ones with RA of 17.45 (peak 2), 3.72 (peak 3) and 1.58% (peak 1), respectively (Figure 2). 2-Ethylthiolane, S,S-dioxide was identified as a sulfur containing compound with RA of 12.83% (peak 7 in Figure 2). Aliphatic carboxylic acids were detected from C2 to C6 (e.g., methane carboxylic acid and acetic acid, 1-methyl ester (peak 9 and 6 in Figure 2)). It has been reported that the short chain of carboxylic acids detected in textile effluents has a metabolic origin and the long chain of carboxylic acids is originating from fatty acids, fatting agents, and microbial biomass [11]. Concerning the group of phenols, phenol,4-[2-[2-(chloromethyl)-1,3-dioxolan-2-yl]ethyl]-, acetate was detected (RA = 0.10%, Table 2). It is reported that phenols detected in samples from textile industry are used in the manufacture of dyes [3]. Phenolic compounds are toxic and their toxicity can be explained by the substitution of this surface-active agent with new products, as polyethoxylated alcohols. It was reported a correlation with toxicity accumulation and oestrogenic effects that phenolic compounds are induced in some animals and organisms [48]. Regular monitoring of phenolic compounds is essential due to their toxicity and bioaccumulation effects in animals and plants [48].

Other compounds were also present in the studied wastewater such as linear aliphatic alcohols (e.g., ethyl alcohol and acetol; Table 2) and chlorinated compounds (e.g., Benzene, 1-chloro-2-diethoxymethyl- (peak 11, Figure 2) and propanedioic acid, (3chlorophenyl) methylene, and diethyl ester (peak 12, Figure 2)). Linear aliphatic alcohols are used in textile industry as solvents and antifoaming agents; chlorinated compounds are known as a by-product of bleaching step during textile processing [49]. Some epidemiological studies have shown the association between exposure to chlorination by-products and the increased risk of low birth weight, congenital abnormalities (neural tube defects and heart abnormalities) [50–52], spontaneous abortion [53–55], and death at birth [56, 57].

Concerning textile effluent B, we note the predominance of two toxic compounds: phtalimide dioxime acetamide (RA = 30.45%, peak 13 in Figure 3) and N-benzyl-2-(2,3-dihydro-2-methyl-5-phenyl-1,3,4-thiadiazol-2-yl)
(RA = 47.35%, peak 14 in Figure 3) belonging to chemical group of phthalates and nitrobenzyl, respectively. The chromatogram obtained for textile effluent B (the more toxic one) and the spectrum corresponding to both predominant toxic compounds are shown in Figure 3.

This complex effluent also contains aromatic carboxylic acids (acid, 2,4-bis[(trimethylsilyl)oxy]-, trimethylsilyl ester (peak 17, Figure 3)), aliphatic carboxylic acids (methane carbothiolic acid (peak 9, Figure 3)), and alkanes (ethane, 1,1-diethoxy (peak 15, Figure 3)). Like effluent A, this effluent also contains aliphatic alcohols (ethanol, 2-(1-methylethoxy)-(RA = 0.47%; Table 3) and aliphatic carboxylic acids (pentanoic acid, 3-methyl-4-oxo, (RA = 0.17%; Table 3), butanoic acid, 2-methyl-, ethyl ester (RA = 0.13%; Table 3) and butanedioic acid, diethyl ester, (RA = 0.25%; Table 3)) but at less abundance. Benzoic compounds such as benzene, 1-methyl-2-propyl; benzene, (1,2-dimethoxyethyl)-; and benzene, 1-chloro-2-diethoxymethyl- (peaks 16, 18, and 20, respectively, Figure 3) were detected with RA < 0.9%.

As described in Table 4, textile effluent C is characterized by the presence of important amounts of toxic aromatic amines and phtalates (naphtho[2,3-d]-1,3-dioxol-5-ol, 3a,4,9,9a-tetrahydro-2,2-dimethyl-, cis; RA = 14.10%; peak 29, Figure 4). The derivatives of phthalate (DBP, DEP, and BEP) are commonly used as wetting agent, dispersant, and softener in the application of disperse dyes and also as a plasticizer for polyvinylchloride (PVC). For example, the 3-nitrophthalic acid is used in the preparation of quinophthalene series of dyes which are useful in dyeing of hydrophobic fibers like nylon and polyester [58] as is the case in the factory of Fez city.

Table 2: Organic compounds identified in real textile effluent A.

Compound	RT (min)	RA (%)
Ethyl alcohol	4.35	0.11
Tert-butyl hydroperoxide	4.89	0.32
Methane, trimethoxy-	5.38	0.20
Butane, 2,2-dimethyl-[1]	**6.11**	**1.58**
2-Pentoxy-tetrahydropyran[2]	**6.95**	**17.45**
2-Propyltetrahydropyran[3]	**7.30**	**3.72**
Benzoic acid, 2,3-dimethyl-6-(3-methyl-1-oxobutyl)[4]	**7.70**	**14.5**
1,2-Benzendicarboxylic acid, 4-methyl-, dimethyl ester[5]	**8.09**	**37.3**
Acetic acid, 1-methyl ester[6]	**8.41**	**1.66**
2-Ethylthiolane, S,S-dioxide[7]	**8.76**	**12.89**
Pentane, 2,2-dimethyl-	9.08	0.17
Acetic acid, 1-methylethyl ester	9.41	0.13
Cyclohexane	9.93	0.34
Hexane, 2,4-dimethyl-	10.09	0.13
Hydroxylamine,O-(2 methylpropyl)	10.20	0.10
Diacetyl sulfide	10.90	0.29
Propanoic acid, ethyl ester	11.04	0.13
Toluene[8]	**13.49**	**0.24**
Acetaldehyde, tetramer	14.70	0.30
2-(Acetomethyl)-1- butene	15.00	0.21
Isocrotonic acid (2-Butanoic acid)	15.28	0.32
Acetol	15.69	0.23
Methanecarbothilic acid[9]	**17.96**	**1.53**
Acetic acid, ethoxy-, ethyl ester	18.14	0.11
Ketone, methyl 2-methyl-1,3-oxothiolan-2-yl	19.14	0.31
Oxirane, (1-methylbutyl)-	20.44	0.35
2-Isopropyl-3-vinyloxirane	20.97	0.10
Glyceraldehyde diethylacetal	24.39	0.22
Benzene, 1-methyl-2-(1-methylethyl)-	25.10	0.18
Undecane, 2,6-dimethyl-	25.93	0.19
Octadecane, 3-ethyl-5-(2-ethylbutyl)-	26.57	0.09
Pentadecanoic acid,2,6,10,14-tetramethyl-, methyl ester	26.74	0.10
1-Butanol, 3-methyl-, acetate	29.80	0.21
Benzoic acid, 4-(tetrazol-1-yl)methyl-[10]	**43.13**	**0.16**
4-Nitrobenzyl idenene malonic acid, diethyl ester	43.53	0.45
Benzene, 1-chloro-2-diethoxymethyl-[11]	**46.69**	**0.47**
Propanedioic acid, (3chlorophenyl) methylene, diethyl ester[12]	**47.09**	**1.08**
Ethanol,2-[4-(1,1dimethylethyl)phenoxy]	48.01	0.12
Phenol,4-[2-[2-(chloromethyl)-1,3-dioxolan-2-yl]ethyl]-, acetate	48.33	0.10
Propane dioic acid, [(4methoxyphenyl) methylene]-, diethyl ester	49.37	0.25
Cyclohexane-1,3-dicarboxylic acid, 2-(4-methoxyphenyl)-4,6-dioxo-, diethyl ester	53.26	0.12
Hexadecane, 2-methyl-	53.36	0.12
Tetratriacontane	54.35	0.09
2-Secoandrosta-1,6-diene-17,19-diol,2-cyano-4-methylene-, diacetate	55.76	0.59
10a,12a-Dimethyl-hexadecahydro-2-oxa-chrysen-3-one	56.91	0.13
Phthalic acid, 6-ethyloct-3-yl 2-ethylhexyl ester	59.03	0.39
Dodecanoic acid	60.79	0.10
Docosanoic acid, 2-hydroxy-, methyl ester	61.95	0.12

RT: retention time; RA: relative abundance. [1–12]Organic compounds corresponding to peak numbers on the chromatogram referring to effluent A in Figure 2.

Aromatic amines 2-amino-4-hydroxy-6-p-cyanophenylpropylpteridine and 3-amino-3-(2,4-dichloro-phenyl)-propionic acid are the dominant ones with RA of 32.81 and 11.59%, respectively (peaks 26 and 27, Figure 4). 2,6-Diamino-4-cyclohexyl-4H-thiopyran-3,5-dicarbonitrile is a nitro substituted aromatic compound detected in this effluent at considerable RA of 15.78% (peak 28, Figure 4).

Azo dyes are recalcitrant, non-biodegradable, and persistent among all chemical classes of dyes. Aromatic amines detected in the studied effluents are the result of the reduction of the azo bond of azo dyes. The first concerns with human exposure to carcinogenic aromatic amines arose in the dye manufacturing industry as early as the late nineteenth century [5]. Therefore, most of the attention concerning the possible hazards arising from the use of azo dyes has been transferred to their reduction products [59–61]. The formation of a carcinogenic amine from the dye Direct Blue 14 by human skin bacteria [62] and the antifungal activity of 13 diazobenzene dyes have been established [63, 64].

Table 3: Organic compounds identified in real textile effluent B.

Compound	RT (min)	RA (%)
Acetone	4.83	0.32
Formic acid, ethyl ester	5.40	0.25
Methylglyoxal	7.24	0.28
Phthalimide dioxime[13]	**7.74**	**30.45**
Acetamide, N-benzyl-2-(2,3-dihydro-2-methyl-5-phenyl-1,3,4-thiadiazol-2-yl)[14]	**8.24**	**47.35**
Methane carbothiolic acid[9]	**8.63**	**3.36**
Acetic acid, 1-methylethyl ester	9.47	0.48
Ethaneperoxoic acid, 1-cyano-1-(2-methylphenyl)ethyl ester	10.94	0.37
Propanoic acid, ethyl ester	11.07	0.42
Ethane, 1,1-diethoxy-[15]	**12.00**	**1.31**
Cyclobutene, 2-propenylidene-	13.51	0.57
Ethanol, 2-(1-methylethoxy)-	14.70	0.47
Acetic acid, 1-methylethyl ester	15.02	0.28
Isocrotonic acid	15.37	0.66
Diacetyl sulfide	15.69	0.34
Methanecarbothiolic acid[9]	**17.97**	**2.56**
Acetic acid, ethoxy-, ethyl ester	18.15	0.18
Pentanoic acid, 3-methyl-4-oxo-	18.50	0.17
Ketone, methyl 2-methyl-1,3-oxothiolan-2-yl	19.15	0.48
Butanoic acid, 2-methyl-, ethyl ester	20.43	0.13
Undecane, 2,6-dimethyl-	22.52	0.18
2,3-Butane diol-diacetate	23.43	0.15
1,1-Ethanediol, diacetate	24.19	0.15
Glyceraldehyde diethylacetal	24.39	0.38
Benzene, 1-methyl-2-propyl-[16]	**24.76**	**0.16**
2,3-Dimethyldecane	25.00	0.13
Ethyl -3-acetoxybutyrate	25.17	0.42
Octane, 5-ethyl-2-methyl-	25.93	0.40
Methanol, oxo-, benzoate	26.94	0.15
Butanedioic acid, diethyl ester	27.33	0.25
4,4-Ethylenedioxy-1-pentylamine	27.75	0.15
Methoxyacetaldehyde diethyl acetal	27.89	0.21
1-Butanol, 3-methyl-, acetate	29.81	0.34
Benzoic acid, 2,4-bis[(trimethylsilyl)oxy]-, trimethylsilyl ester[17]	**41.81**	**0.27**
Benzene, (1-ethoxy-3-butenyl)-[18]	**43.12**	**0.29**
Propanedioic acid, (phenylmethylene)-, diethyl ester[19]	**43.53**	**0.72**
Benzene, 1-chloro-2-diethoxymethyl-[20]	**46.70**	**0.85**
Propanedioic acid, [(3-chlorophenyl)methylene]-, diethyl ester[21]	**47.09**	**1.58**
(5-Chloro-3-cyano-4,6-dimethyl-pyridin-2-ylsulfanyl)-acetic acid ethyl ester	47.74	0.14
Propanedioic acid, [(4-methoxyphenyl)methylene]-, diethyl ester	49.37	0.37
Benzofurane-3-carboxylic acid, 5-methoxy-2-(1-piperidylmethyl)-, ethyl ester	53.25	0.14
2-Isopropyl-10-methylphenanthrene	53.56	0.15
1-Methyl-2,6-diphenyl-4,4-tetramethylene-1,4-dihydropyridine-3,5-dicarbonitrile	55.76	0.83

RT: retention time; RA: relative abundance. [13–21]Organic compounds corresponding to peak numbers on the chromatogram referring to effluent B in Figure 3.

Since the 1890s, the increase in bladder cancer has been observed among employees working in the dyeing department of textile industry, which is related to their exposition to aromatic amines [65]. These compounds are biorefractory and highly toxic since they can react easily in the blood to convert hemoglobin into methemoglobin, thus preventing the absorption of oxygen [66]. In human beings, these toxic compounds are often metabolized in their acyloxyamine derivatives which bind to guanine, thus altering the DNA [67].

As described in this paper, benzoic derivatives are indicative compounds of textile effluents. Effluent C contains considerable amounts of these compounds; benzene, 1-(2,2-dimethoxyethyl)-4-methoxy (RA = 12.48%) and benzene, (1,2-dimethoxyethyl)-(RA = 6.03%) are major benzoic compounds in this effluent (peaks 24 and 25, Figure 4). Aromatic carboxylic acids present in the studied effluents are a constituent of natural tanning agents and dyes [11]. Linear aliphatic alcohols are used as solvent and antifoaming agents; concerning chlorinated compounds, they are a by-product of bleaching step during textile processing [49]. Phenols detected in samples from the textile industry are used in the manufacture of dyes [3]. Phenol free radicals are responsible for cardiovascular diseases and occupational and environmental lung diseases [68]. Phenols substituted with electron-releasing molecules can frame conceivably poisonous phenoxyl free radicals. Those substituted phenols with electron pulling back impact have high lethality for organisms, which is linked to their lipophilicity [69].

Table 4: Organic compounds identified in real textile effluent C.

Compound	RT (min)	RA (%)
Hydroxylamine, *O*-methyl-	4.08	0.94
Ethane, 2-chloro-1,1-dimethoxy-[22]	**4.28**	**1.85**
Tricyclo[6.3.0.0(2,6)]undecan-10-one, 3-[(2-methoxyethoxy)methoxy]-2-methyl-[23]	**4.73**	**3.78**
Benzene, (1,2,2-trimethoxyethyl)-	5.13	0.03
8a-Methyl-5-methylene-3-([(pyridin-2-ylmethyl)-amino]-methyl)-decahydro-naphtho[2,3-b]furan-2-one	5.18	0.03
Benzene, 1-(2,2-dimethoxyethyl)-4-methoxy-[24]	**5.86**	**12.48**
Tyramine, N-aminoacetyl-		
Benzene, (1,2-dimethoxyethyl)-[25]	**6.30**	**6.03**
Butanoic acid, 3-hydroxy-3-methyl-	6.74	0.04
Acetic acid, hydrazide	6.95	0.01
Propanoic acid, 2,2-dimethyl-, hydrazide	7.11	0.01
2-Amino-4-hydroxy-6-p-cyanophenylpropylpteridine[26]	**7.49**	**5.65**
2-Amino-4-hydroxy-6-p-cyanophenylpropylpteridine[26]	**7.69**	**27.16**
3-Amino-3-(2,4-dichloro-phenyl)-propionic acid[27]	**7.85**	**11.59**
2,6-Diamino-4-cyclohexyl-4H-thiopyran-3,5-dicarbonitrile[28]	**8.33**	**15.78**
Naphtho[2,3-d]-1,3-dioxol-5-ol, 3a,4,9,9a-tetrahydro-2,2-dimethyl-, cis-[29]	**9.56**	**14.10**
Disulfide, propyl 1-(propylthio)ethyl	9.61	0.06
Oxalic acid, ethyl propyl ester	11.13	0.02
Toluene[8]	**13.40**	**0.12**
4-Penten-2-one	14.83	0.01
Nitroxide, bis(1,1-dimethylethyl)	15.38	0.01
Pent-2-ynal, 4,4-dimethyl-	25.30	0.01
1,3,7-Octatriene, 3,7-dimethyl-	25.41	0.01
2-Butanol, (ñ)-	27.32	0.03
2,5-Diethylphenol	31.06	0.03
Benzenemethanol, 4-(1-methylethyl)-	31.42	0.01
1,5-Decadiyne	32.54	0.01
1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester	44.10	0.08
Octadecane, 6-methyl-	45.59	0.01
n-Hexadecanoic acid	47.39	0.01
3,7,11,15-Tetramethylhexadeca-1,3,6,10,14-pentaene	47.70	0.01
7,11,15-Trimethyl-3-methylene-hexadeca-1,6,10,14-tetraene	47.86	0.01
1H-2,8a-Methanocyclopenta[a]cyclopropa[e]cyclodecen-11-one, 1a,2,5,5a,6,9,10,10a-octahydro-5,5a,6-trihydroxy-1,4-bis(hydroxymethyl)-1,7,9-trimethyl-, [1S-(1à,1aà,2à,5á,5aá,6á,8aà,9à,10aà)]-	50.89	0.01
5-Benzofuranacetic acid, 6-ethenyl-2,4,5,6,7,7a-hexahydro-3,6-dimethyl-à-methylene-2-oxo-, methyl ester	51.73	0.01
Heptadecane, 2,3-dimethyl-	55.67	0.04

RT: retention time; RA: relative abundance. [22–29]Organic compounds corresponding to peak numbers on the chromatogram referring to effluent C in Figure 4.

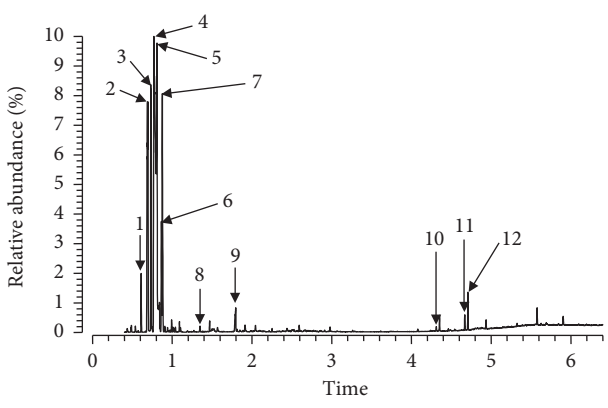

Figure 2: Total ion chromatograms of extracts of textile effluents A from the studied site. Peak numbers correspond to the chemical compounds indicated in Table 2.

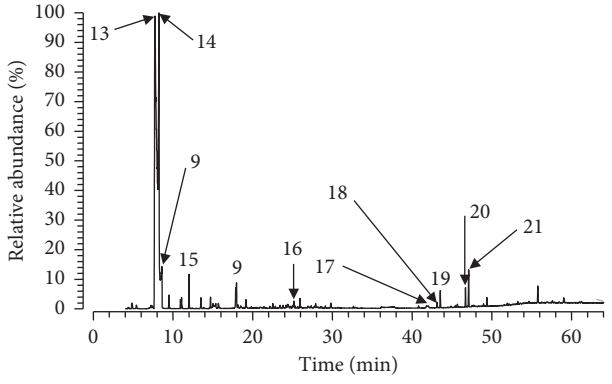

Figure 3: Total ion chromatograms of extracts of textile effluent B from the studied site. Peak numbers correspond to the chemical compounds indicated in Table 3.

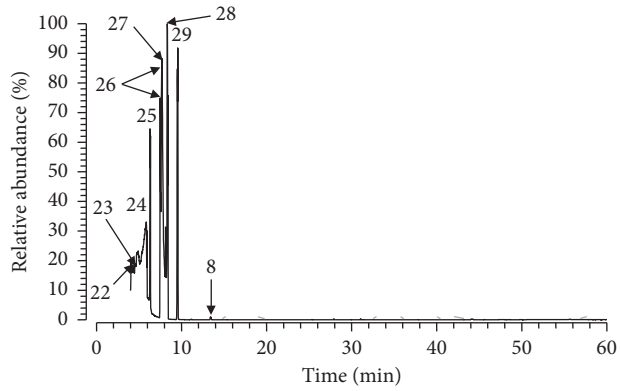

Figure 4: Total ion chromatograms of extracts of textile effluents C from the studied site. Peak numbers correspond to the chemical compounds indicated in Table 4.

Aromatic amines detected in the studied effluents are originating from dyes and pigments and are known to be potential hazards to human health and the environment [32, 70]. Thus, untreated or incompletely treated textile effluent can be harmful to both aquatic and terrestrial life by adversely affecting the natural ecosystem and causing long-term health effects [71].

4. Conclusion

Different effluents from a textile industry of Fez city, Morocco, were collected and analyzed to determine the impact of textile industry on water pollution and human health. The water quality parameters like BOD_5, COD, TSS, and TDS of textile effluents were found to be significantly higher than the maximum permissible limit prescribed by M.D.Q.S and WHO. The results of this study clearly show that textile industry in Fez city, Morocco, is polluting the local aquatic environment. However, the numerous by-products of textile industry characterized in this study like benzoic acid, 2,3-dimethyl-6-(3-methyl-1-oxobutyl); 2-amino-4-hydroxy-6-p-cyanophenylpropylpteridine; phenol, 4-[2-[2-(chloromethyl)-1,3 dioxolan-2-yl]ethyl]; benzene, 1-chloro-2-diethoxymethyl; and naphtho [2,3-d]-1,3-dioxol-5-ol, 3a,4,9,9a-tetrahydro-2,2-dimethyl-, cis, which are potentially toxic, can be used as typical indicators of textile contaminants in polluted aquatic systems. These compounds have a significant health hazard as it has been shown in a multitude of ecotoxicological studies on industrial effluents. The present research highlighted the diversity of organic compounds present in textile effluents. We discussed the toxicity of some organic compounds from the GC/MS analysis results (listed in Tables 2–4). Analysis of this type of effluents is very beneficial to the society and ecosystem. Therefore, there is a need to develop simple, cost-effective and ecofriendly treatment systems for the remediation of textile effluents to minimize water pollution for sustainable environmental and economic development.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

Acknowledgments

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