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Removal of endocrine-disrupting chemicals from textile industry effluents by nanofiltration

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ABSTRACT

Textile finishing industry wastewaters contain micropollutants such as endocrine-disrupting chemicals in addition to the conventional pollutants since advanced manufacturing activities provide additional features to the textiles to make them shrink-proof, water-proof, wrinkle-proof, rot-proof, distasteful to moths, and mildew, flame-resistant, etc. Endocrine-disrupting chemicals can interfere with the endocrine system, exert endocrine-modulating behavior, and cause adverse health effects, even when exposed to low doses. Therefore, treatment of endocrine-disrupting chemicals is a major concern for textile finishing wastewaters since they cannot be completely removed by widely applied conventional treatment technologies; but rather by using membrane filtration, advanced oxidation, and adsorption technologies. This study aims to investigate the performance of nanofiltration membranes in the post-treatment of endocrine-disrupting chemicals in textile finishing wastewaters. A total of 299 chemicals that were identified as endocrine-disrupting chemicals present and/or likely to be present in surface waters of Turkey were monitored in a textile finishing wastewater, and their removal by nanofiltration was investigated. The experimental results showed that 10 of the 17 compounds determined in textile industry treatment plant effluent, including benzo(g,h,i) perylene, fluorene, phenanthrene, mono-2-ethylhexylphthalate, dicyclohexylphthalate, diethylphthalate, di-*n*-butylphthalate, octamethylcyclotetrasiloxane, mirex (perchloropentacyclodecane) and saccharin were treated below their limit of detection values with nanofiltration. On the other hand, it was determined that nanofiltration was not efficient for compounds such as naphthalene, mono-*n*-butylphthalate, and di-sec-octylphthalate.

Keywords: Endocrine-disrupting chemicals; Textile finishing industry wastewaters; Nanofiltration; Phthalates; Octamethylcyclotetrasiloxane; Polycyclic aromatic hydrocarbons

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1. Introduction

An endocrine-disrupting chemical (EDC) is defined as "an exogenous substance or mixture that changes the function of the endocrine system and which results in adverse health effects on a healthy organism or its offspring or (lower) populations" [1]. It has been noted that no compromise has been reached with regard to the use of threshold values for damage characterization (potency, significance, prominent toxicity, reversibility) and low dose effects or non-monotonic dose–response relationships in the identification of EDCs [2]. Therefore, the discharge of EDCs to surface water bodies should be prevented at the highest possible level.

Membrane processes have a practicable potential in industrial areas for water treatment, recycle process water, reuse, and by-product recovery. Various membrane separation processes with different characteristics are used in water, municipal, and industrial wastewater treatment, and these processes are known to play a significant role in the elimination of pharmaceuticals, hormones, EDCs, and their metabolites from wastewaters [3]. Membrane separation can be carried out as a continuous process providing constant and automatic operation or can be operated as a batch process at a particular time of the day, providing a significant advantage, especially in industrial wastewater treatment and reclamation. The ability to design these systems modularly eliminates size limitations. In addition, these systems have significant advantages such as less space requirement, the possibility of mobile operation due to portability, and less shock loading impacts. Nanofiltration (NF) membranes can reject particles between 200 and 1,500 Da molecular weight cutoff and are considered to be ideal for the removal of divalent ions, organics, color, bacteria, and viruses. They are also used in integration with either reverse osmosis (RO) or ultrafiltration (UF) membranes for primary or secondary treatment of wastewaters [4].

Membrane filtration technology is used for water recovery applications as well as for controlling the micropollutants, including EDCs [5–9]. NF and RO membranes are more effective in retaining the micropollutants than microfiltration (MF) and UF membranes due to their small pore size. According to studies cited in the literature, hybrid systems that are formed by the addition of powdered activated carbon in MF or UF increase the treatment efficiency of micropollutants. Retention mechanisms of the micropollutants by polymeric membranes are membrane penetration, electrical repulsion, adsorption, sorption–diffusion, interaction with other dissolved substances, and membrane clogging as cited in the literature [10,11].

Membrane bioreactors are one of the promising applications of membrane filtration. In a study, the occurrence and removal of polycyclic aromatic hydrocarbons (PAHs) were investigated in a combination process of anoxic baffled reactor (ABR)-hybrid coagulation/membrane bioreactor (HCMBR) for real textile dyeing wastewater treatment. The combination process achieved over 88% removal for all the PAHs. It was postulated that low molecular weight PAHs might be mainly removed by volatilization, adsorption, and sedimentation in the ABR treatment unit. In contrast, high molecular weight PAHs might be mainly removed by adsorption and sedimentation processes after coagulation and solid–liquid separation in the HCMBR treatment unit [12].

Another study was carried out to investigate the effects of cross-flow velocity, transmembrane pressure, and organic matter presence in the wastewater on the treatment of estrone and estradiol in NF and low-pressure RO process. The results of the study showed that the rate of retention of estrone and estradiol on the membrane was similar, the presence of organic matter in the wastewater increased the retention of hormones on the membrane, the cross-flow configuration provided more efficient removal than the dead-end flow, and cross-flow velocity had no effect on the removal of hormones [13].

It is difficult to obtain a high removal efficiency by using conventional drinking water treatment (DWT) technologies such as sand filtration, coagulation/flocculation, and chlorination for the removal of persistent micropollutants from drinking water. On the other hand, high treatment performance on micropollutants removal can be achieved by advanced treatment techniques such as advanced oxidation and activated carbon. In addition, pressurized membrane processes such as NF and RO have recently gained importance for the removal of micropollutants. In many scientific studies, these two pressurized membrane filtration methods have been shown to work efficiently in separating many organic and inorganic micropollutants from the water [14].

In a study using NF and RO membranes, the effects of physicochemical properties and initial concentrations on the removal efficiencies of nine micropollutants, including bisphenol-A, were evaluated. According to the results of this research, the negatively charged materials were generally removed by 90% and the removal efficiencies were not related to the micropollutants physicochemical properties; whereas, the uncharged materials had lower removal efficiencies (Bisphenol-A; NF: 45%, RO: 99%) and the removal rate was in proportion to their molecular sizes. Finally, it has been identified that low initial concentrations were reduced up to the membrane rejection capacity [15].

The removal rate of some chemicals, including natural and synthetic estrogens, has been observed in South Korea's Gwangju and Seoul cities' DWTPs. While the Seoul DWTP was operated with coagulation, UF, and granular activated carbon (GAC), the Gwangju DWTP had conventional DWTP units such as coagulation, sand filtration, and chlorination. As a result of the study, it was determined that conventional DWTP was ineffective in the removal of EDCs and that GAC removed EDCs and other pharmaceuticals by 99%. Finally, it was mentioned that using RO or NF with GAC and MF ensures higher removal efficiencies of EDCs and other micropollutants [16].

Membrane processes using NF/RO membranes have also been studied for indirect potable reuse applications. Jacob et al. [17] investigated the retention of pesticides, PAHs, metals, and microorganisms in real membrane bioreactor (MBR) permeate matrix and in ultrapure water matrix by NF/RO process. The impact of their retention on NF/RO membrane fouling was also investigated. The NF 90 and ESPA2 membranes were chosen for this work. The RO membrane (ESPA2) showed high retention for most of the molecules tested; whereas the NF 90 membrane exhibited

some variation in the retention of pesticides. The presence of PAHs in the MBR permeate increased the permeability of the RO membrane. However, a similar effect was not observed for pesticides, metals, and microorganisms.

The textile industry is one of the most important sectors in Turkey, and appropriate treatment is required for textile industry wastewaters to protect the receiving water environment. In addition to the conventional pollutants, textile discharges also include micropollutants such as EDCs. This study aims to investigate the effectiveness of NF for the removal of EDCs from textile finishing effluents. NF of a biologically treated textile finishing wastewater was investigated. At first, the wastewater from a textile finishing industry was characterized employing a seasonal monitoring program and the occurrence of 299 EDCs in the effluent to and from the already existing biological treatment plant of the textile factory was investigated. Then, the NF treatment of EDCs that were found to exist in the effluent from the biological wastewater treatment plant was investigated. Before NF, UF was applied as pretreatment.

2. Materials and methods

The investigated textile finishing industry produces upholstery fabrics, curtain fabrics, bed fabrics, and home textiles. The plant operates under "13.30-Finishing of textiles", "13.92-Manufacture of made-up textile articles, except apparel" and "13.96-Manufacture of other technical and industrial textiles" NACE (statistical classification of economic activities in the European Community) Rev 2 codes. The raw materials used in the production are supplied both from the domestic and international markets. Production schedule varies from time to time due to fluctuations in the hardness level of the municipal water supply; however, no seasonal/periodical difference in production is of concern that would be an important aspect in discharge sampling. Water is supplied from the municipal line and wastewater forms due to fabric dyeing and chemical finishing activities (for non-flammability, stain-proofing, as anti-bacterial, etc.) during production. The industry owns an industrial wastewater treatment plant (WWTP) with a capacity of 1,000 m^3/d, and presently produces an average amount of 220 m^3/d of wastewater.

Wastewater is initially subjected to secondary (biological) treatment. Treated wastewater overflowing from the final sedimentation tank is transferred to the municipal WWTP via the discharge line for final polishing. The WWTP flow diagram of the plant is given in Fig. 1.

Wastewater samples were taken from the influent and effluent of the WWTP of the textile industry at four different times in a year. A seasonal sampling program has been adopted to follow the quality changes in the receiving water body.

Samples were collected as grab samples from the equalization tank (influent) and final sedimentation tank discharge (effluent) of the WWTP by using borosilicate glass sample collectors. Samples were taken in 1-L pre-rinsed amber glass bottles tightly closed with PTFE caps. They were then transported to a laboratory in a cold and dark medium. Based on the standard operating procedure, one of the samples should be taken into two separate bottles; one bottle for analysis and the second for possible repetition of the analysis. It is also advisable to take a spare bottle in case of any accidents (breakage, spillage, etc.) and to prepare a three-bottle set for each measure. As soon as the samples were taken, pH was measured, and they were preserved in a cooler environment with sufficient ice/ice boxes for immediate delivery to the laboratory to be analyzed within 24 h. The analysis of all EDCs was carried out in almost 48 h after their acceptance to the laboratory. Preservation conditions for all samples were determined and applied in accordance with TS EN ISO 5667-3 standard [18].

After a year of monitoring, the presence of EDCs in the textile industry wastewater, upon the detection of many EDCs in WWTP effluent, 4th sampling effluent was used to specify the treatment efficiency of NF. The basic characterization of the sample used in the study is given in Table 1.

In the UF experiments applied as pretreatment to NF, the "Philos ES10B (Republic of Korea)" UF membrane was used to prevent rapid fouling on the NF membrane. Following this phase, the commercial Filmtech NF 270 (Dow Chemical Michigan, United States) membrane was compacted before the filtration test to stabilize membrane flux for about 1 h. Compaction was performed at 20 bar, and 80% recovery rate was used. The NF test was performed at 20 bar with a Sterlitech (WA, United States) HP4750 filtration cell. The apparatus used for the test is similar to those used in previous studies for testing the performance of membranes in industrial wastewater treatment [19–21]. Samples taken prior to filtration test and from the final permeate were mixed at 500 rpm at room temperature.

Table 1
Characterization of the wastewater sample used in laboratory work

pH	7.60
TDS, mg/L	1,087
Electrical conductivity, μS/cm	2,149
Salinity, %	1.10
Dissolved oxygen, mg/L	2.20

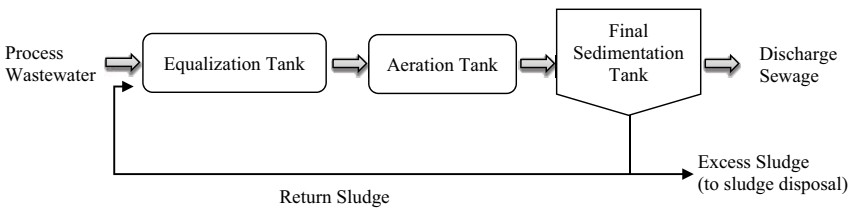

Fig. 1. Textile WWTP flow diagram.

The permeability (P) of a membrane is defined as the amount of water passing through the unit membrane area per unit time and pressure using the following formula:

$$P = \frac{J}{\Delta P} \quad (1)$$

where P: permeability (L/m^{2}h.bar); J: flux (L/m^{2}h); ΔP: pressure (bar).

EDCs analyses were performed with LC-MS/MS, GC-MS/MS, GC/MS-HS, GC/MS-P&T, GC-MS, and ICP-MS according to standard methods such as ASTM D7065, ISO 17294-1/2 (2006/2016), Ionization Tandem Mass Spectrometry, EPA Method 1694, EPA Method 8270D, EPA Method 3510C, EPA Method 8260D, EPA Method 5030C, EPA Method 535, EPA Method 536, and EPA Method 6020B, and developed in-house methods. The details and method references are given as supplementary material (Table S1).

The characteristics of the membrains used in this study are given in Table 2.

3. Results and discussion

The monitoring study has shown that several EDCs were present in the influent of the WWTP in all the four samples, and some of these EDCs could not be treated in the WWTP. As shown in Tables 3 and 4, 53 EDCs in total, have been detected in the influent and 45 in the effluent of the WWTP have been determined above the limit of detection (LOD) values in all the samples. In addition, four compounds (benzo(g,h,i)perylene, β-HCH, mirex, and dutasteride) have been detected in the effluent of the WWTP during monitoring although they were not detected in the influent. Consequently, a total of 57 different EDCs were detected in the textile industry wastewaters. Eight compounds were commonly detected in the influent, and in the effluent. Seven of these compounds detected in both the influent and the effluent were fluorene, naphthalene, phenanthrene, dicyclohexyl phthalate (DCHP), diethyl phthalate (DEP), boric acid, and octamethylcyclotetrasiloxane (D4). Also, fluoranthene was detected only in the influent, and mono-2-ethylhexylphthalate (MEHP) only in the effluent for all the samples.

Five of the EDCs detected in the influent for all samples (fluoranthene, naphthalene, dicyclohexyl phthalate [DCHP], diethyl phthalate [DEP] and octamethylcyclotetrasiloxane [D4]) were found to be treated with average efficiencies ranging from 14% to 54%. However, it has been observed that the effluent concentrations of three EDCs detected in each sample (fluorene, phenanthrene, and boric acid) were higher than their influent concentrations. Treatment efficiencies of the EDCs detected in all the four influent samples of the WWTP are given in Fig. 2.

Nanofiltration studies were performed for the effluent of the 4th sample where 17 different EDCs were detected. Corresponding removal efficiencies of the effluent in NF is illustrated in Fig. 3.

The NF studies have shown that 10 of the 17 EDCs (benzo(g,h,i)perylene, fluorene, phenanthrene, mono-2-ethylhexylphthalate [MEHP], dicyclohexyl phthalate [DCHP], diethyl phthalate [DEP], di-*n*-butylphthalate [DBP], octamethylcyclotetrasiloxane [D4], mirex, and saccharin) determined in the textile WWTP effluent could be treated below their LOD values. Three of the tested 13 compounds (fluorene,

Table 2
Characteristics of the membranes

	ES10B	NF270
Manufacturer	Philos	Dow Filmtec
Polymer structure	Polyethersulfone	Thin film polyamide
pH range	2–10	2–11
MWCO (Da)	10,000	~200–400
Pore radius (nm)	15,000	0.43
Rejection (% $MgSO_4$)	–	99.2
Zeta potential at pH 7.9 (mV)	–24 ± 4	–28 ± 1
Contact angle, °	69 ± 0.5	30 ± 3
Isoelectric point	–	5.2
Charge (at pH above isoelectric point)	Negative	Negative

Table 3
Number of detected compounds in the WWTP influent and effluent of the textile industry WWTP

	Number of detected compounds				Number of common compounds for 4 samples	Number of total compounds for 4 samples	Number. of detected compounds in influent and effluent
	1st sample	2nd sample	3rd sample	4th sample			
WWTP influent	22	22	33	23	8	53	57
WWTP effluent	20	17	35	17	8	45	

Table 4
Detected compounds in the influent and effluent of the textile industry WWTP

No	Chemical name	WWTP influent samples				WWTP effluent samples			
		1st	2nd	3rd	4th	1st	2nd	3rd	4th
1	PCB 28-2,4,4′-trichlorobiphenyl	–	+	–	–	–	–	–	–
2	Nonylphenols	–	–	+	–	–	–	+	–
3	Octylphenols	–	–	+	–	–	–	+	–
4	Acenaphthene	–	+	+	–	–	+	+	–
5	Anthracene	+	–	+	–	+	–	+	–
6	Acenaphthylene	–	+	+	–	–	+	+	–
7	Benzo(g,h,i)perylene	–	–	–	–	–	–	–	+
8	Benzo(a)anthracene	+	–	–	–	+	–	–	–
9	Benzo(k)fluoranthene	+	–	–	–	–	–	–	–
10	Chrysene	+	–	+	–	+	–	+	–
11	Fluoranthene	+	+	+	+	+	+	+	–
12	Fluorene	+	+	+	+	+	+	+	+
13	Naphthalene	+	+	+	+	+	+	+	+
14	Phenanthrene	+	+	+	+	+	+	+	+
15	Pyrene	+	+	+	–	+	+	+	–
16	β–HCH	–	–	–	–	+	–	–	–
17	Mono-2-ethylhexylphthalate (MEHP)	–	+	+	+	+	+	+	+
18	Mono-*n*-butylphthalate	–	+	+	+	–	–	+	+
19	Dicyclohexyl phthalate (DCHP)	+	+	+	+	+	+	+	+
20	Diethyl phthalate (DEP)	+	+	+	+	+	+	+	+
21	Dimethyl phthalate	–	–	+	–	–	–	+	–
22	Di-*n*-butylphthalate (DBP)	–	+	+	+	+	–	+	+
23	Di-*n*-octyl phthalate (DnOP)	–	–	+	+	–	–	+	+
24	Di-sec-octylphthalate (DEHP) (DOP)	+	–	+	+	+	–	+	+
25	Benzylbutylphthalate (BBP)	–	–	+	+	–	–	+	+
26	Endrin	–	–	–	+	–	–	–	–
27	Chloroalkanes C10–13 (Short chain chlorinated paraffins)	+	+	+	–	+	+	+	–
28	Benzene	–	–	–	+	–	–	–	–
29	Cypermethrin	+	–	–	–	+	–	–	–
30	Dichlobenil	–	–	+	–	–	–	+	–
31	Endosulfan (alpha/beta)	–	–	–	+	–	–	–	–
32	Hexachlorobenzene (HCB)	–	+	–	–	–	–	+	–
33	Imidacloprid	–	+	–	–	–	+	–	–
34	Pendimethalin	–	+	–	–	–	–	–	–
35	Pentachlorobenzene	–	–	+	–	–	–	+	–
36	Tebuconazole	–	+	–	–	–	+	–	–
37	Triclosan	+	–	–	+	–	–	–	–
38	Trifluralin	+	–	–	–	+	–	–	–
39	Nonylphenol ethoxylates	–	–	+	–	–	–	–	–
40	Total dithiocarbamates (Mancozeb, Maneb, Metam–Sodium, Metiram, Thiram, Zineb, Ziram)	–	–	+	–	–	–	–	–
41	3,4-Dichloroaniline	+	–	+	–	–	–	+	–
42	4-Hydroxybiphenyl (4-phenylphenol)	–	–	+	–	–	–	+	–
43	4-Nitrotoluene	–	–	–	+	–	–	–	+
44	Boric acid	+	+	+	+	+	+	+	+
45	Iodine	+	+	–	–	–	+	–	–

(continued)

Table 4 Continued

No	Chemical name	WWTP influent samples				WWTP effluent samples			
		1st	2nd	3rd	4th	1st	2nd	3rd	4th
46	Methyl-tert-butyl ether (MTBE)	–	–	–	+	–	–	–	–
47	Octamethylcyclotetrasiloxane (D4)	+	+	+	+	+	+	+	+
48	*o*-Phenylphenol	–	–	+	–	–	–	+	–
49	Mirex (Perchloropentacyclodecane)	–	–	–	–	–	–	–	+
50	*p*-Hydroxybenzoic acid	+	–	+	–	+	–	+	–
51	Dydrogesterone	–	–	+	–	–	–	+	–
52	Drospirenone	–	–	+	–	–	–	+	–
53	Dutasteride	–	–	–	–	–	–	+	–
54	Methimazole	+	–	–	–	–	–	–	–
55	Propylthiouracil	–	–	–	+	–	–	–	–
56	Saccharin	–	+	–	+	–	+	+	+
57	Ulipristal	–	–	–	+	–	–	+	–

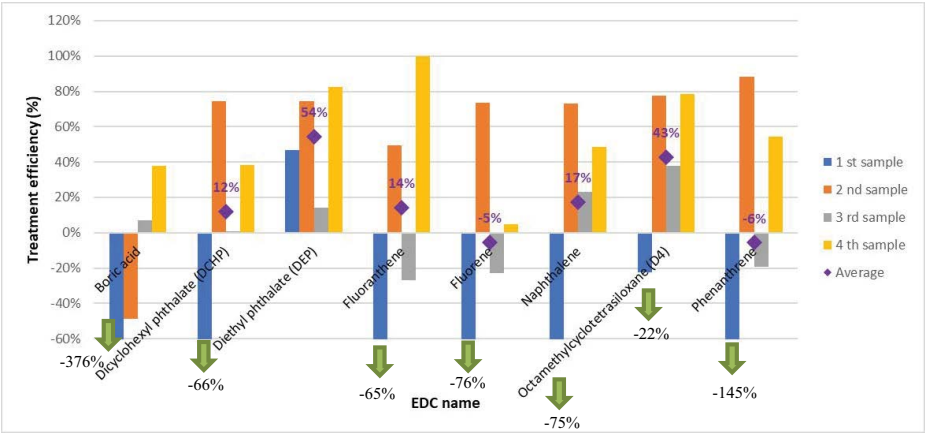

Fig. 2. Textile WWTP treatment efficiencies.

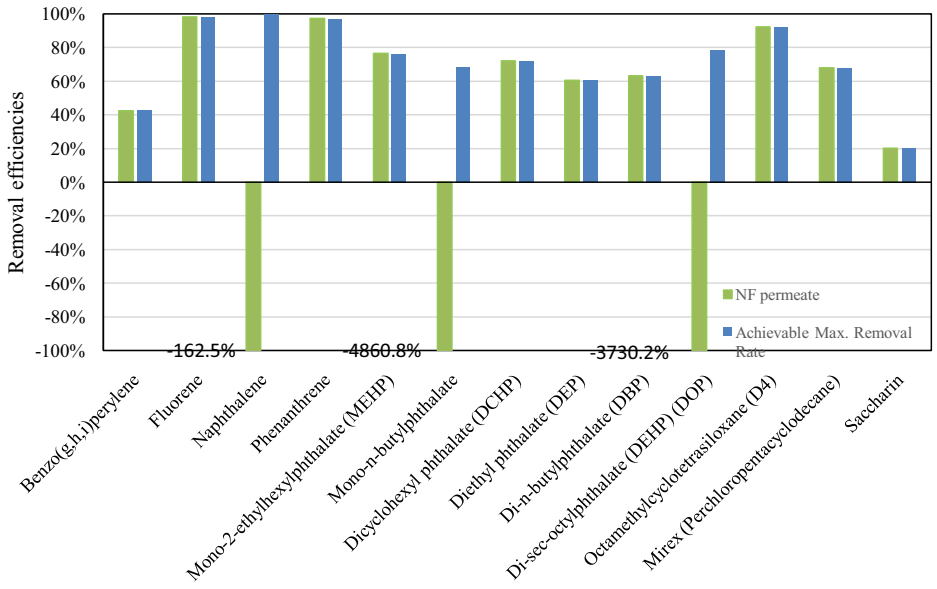

Fig. 3. Textile WWTP effluent NF removal efficiencies. DnOP, BBP, 4-nitrotoluene and boric acid could not be analyzed due to insufficient sample volume.

phenanthrene, and octamethylcyclotetrasiloxane [D4]) were removed by over 90%. The removal rates were determined to be 20% for saccharin and between 40% and 80% for the other six EDCs. It should be noted that the removal efficiencies were limited to the ratio of the monitored concentration of the relevant EDCs over their LOD levels. Thus, the treatment efficiency evaluations have also been made according to the achievable maximum removal rate (AMRR) of each particular EDC. AMRR values of each individual EDCs are also shown in Fig. 3. As can be seen from Fig. 3, the removal rates of 10 of the 17 EDCs were comparatively higher than AMRR values. Naphthalene, mono-*n*-butylphthalate, and di-sec-octylphthalate (DEHP) (DOP) removal rates were detected as negative. The negative trends in treatment yields resulted mainly from experimental errors. The reason for the experimental errors could be either due to the low concentration level close to LOD values or to the possible matrix effect in case the number and concentration of EDCs were higher in the WWTP influent.

4. Conclusions

Nanofiltration studies conducted on textile WWTP effluent have resulted in significant treatment efficiencies for most of the EDCs, and even some EDCs were detected below their LOD values. This study has shown that NF can be effectively used as a post-treatment technology to remove EDCs from the biologically treated textile finishing wastewater. Although high removal efficiencies were observed in NF post-treatment, it has been revealed that the treatment performance depends on the specific EDCs under concern. Therefore, complete removal of all EDCs might require other post-treatment technologies such as advanced oxidation and activated carbon adsorption.

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Supplementary information

Table S1. Analysis method details for compounds

Chemical name	CAS No	In-house method	Method reference	LOD µg/L (ppb)	LOQ µg/L (ppb)
		Group compounds			
Polychlorinated biphenyls (PCB)					
PCB 28-2,4,4′-trichlorobiphenyl	7012-37-5	Method for determination of polychlorinated biphenyls (PCBs) By GC/MS-MS	Camino-Sánchez et al. [S1]	0.003	0.009
Nonylphenols	186825-36-5	Method for determination of organic pollutants (pharmaceuticals and personal care products) by LC/MS-MS	EPA Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS [S2]	0.3	0.9
	17404-66-9				
	104-40-5				
	142731-63-3				
	52427-13-1				
	30784-30-6				
	90481-04-2				
	26543-97-5				
	84852-15-3				
	25154-52-3				
Octylphenols	1806-26-4			0.1	0.3
	140-66-9				
	27193-28-8				
Polyaromatic hydrocarbons (PAH)					
Acenaphthene	83-32-9	Method for determination of PAHs by GC/MS-MS	Camino-Sánchez et al. [S1]	0.003	0.009
Anthracene	120-12-7			0.003	0.009
Acenaphthylene	208-96-8			0.003	0.009
Benzo(g,h,i)perylene	191-24-2			0.001	0.003
Benzo(a)anthracene	56-55-3			0.003	0.009
Benzo(k)fluoranthene	207-08-9			0.003	0.009
Chrysene	218-01-9			0.001	0.003
Fluoranthene	206-44-0			0.003	0.009
Fluorene	86-73-7			0.003	0.009
Naphthalene	91-20-3			0.003	0.009
Phenanthrene	85-01-8			0.003	0.009
Pyrene	129-00-0			0.003	0.009
Hexachlorocyclohexane (HCH)					
β-HCH	319-85-7	Method for determination of pesticides by GC/MS-MS	Camino-Sánchez et al. [S1]	0.003	0.009
Cyclodiene pesticides			EPA Method 8270D: Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) [S3]		
Endrin	72-20-8			0.003	0.009
Phthalates					
Mono-2-ethylhexylphthalate (MEHP)	4376-20-9	Method for determination of semi-volatile organic compounds by GC/MS	EPA Method 8270D: Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) [S3] EPA Method 3510C: Preliminary procedures for water samples [S4]	0.06	0.18
Mono-*n*-butylphthalate	131-70-4			0.06	0.18
Dicyclohexyl phthalate (DCHP)	84-61-7			0.06	0.18
Diethyl phthalate (DEP)	84-66-2			0.06	0.18
Dimethyl phthalate	131-11-3			0.06	0.18
Di-*n*-butylphthalate (DBP)	84-74-2			0.06	0.18
Di-*n*-octyl phthalate (DnOP)	117-84-0			0.06	0.18
Di-sec-octylphthalate (DEHP) (DOP)	117-81-7			0.06	0.18
Benzylbutylphthalate (BBP)	85-68-7			0.06	0.18

Chemical name	CAS No	In-house method	Method reference	LOD µg/L (ppb)	LOQ µg/L (ppb)
Nonylphenol ethoxylates	104-35-8 7311-27-5 14409-72-4 20427-84-3 26027-38-3 27942-27-4 34166-38-6 37205-87-1 127087-87-0 156609-10-8 68412-54-4 9016-45-9 51811-79-1	Method for determination of nonylphenol ethoxylates by GC/MS	ASTM D7065-Standard Test Method for Determination of Nonylphenol, Bisphenol A, p-tert-Octylphenol, Nonylphenol Monoethoxylate and Nonylphenol Diethoxylate in Environmental Waters by Gas Chromatography Mass Spectrometry [S5]	0.3	0.9
Total Dithiocarbamates (Mancozeb, Maneb, Metam-Sodium, Metiram, Thiram, Zineb, Ziram)	8018-01-7 12427-38-2 137-42-8 9006-42-2 137-26-8 12122-67-7 137-30-4	Method for determination of dithiocarbamate (DTC) pesticides by GC/MS-HS	Kazos et al. [S6]	10	30
Individual compounds					
Triclosan	3380-34-5	Method for determination of organic pollutants (pharmaceuticals and personal care products) by LC/MS-MS	EPA Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS [S2]	0.10	0.3
Dydrogesterone	152-62-5			0.01	0.02
Drospirenone	67392-87-4			0.01	0.02
Dutasteride	164656-23-9			0.01	0.02
Methimazole	60-56-0			0.003	0.01
Propylthiouracil	51-52-5			0.003	0.01
Saccharin	81-07-2			0.03	0.1
Ulipristal	126784-99-4			0.03	0.1
Cypermethrin	52315-07-8 67375-30-8 65731-84-2 71697-59-1	Method for determination of pesticides by GC/MS-MS	Camino-Sánchez et al. [S1] EPA Method 8270D: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) [S3]	0.001	0.003
Dichlobenil	1194-65-6			0.003	0.009
Endosulfan (alpha / beta)	115-29-7 959-98-8 33213-65-9			0.001	0.003
Hexachlorobenzene (HCB)	118-74-1			0.003	0.009
Pentachlorobenzene	608-93-5			0.001	0.003
Trifluralin	1582-09-8			0.003	0.009
3,4-Dichloroaniline	95-76-1			0.003	0.009
4-Hydroxybiphenyl (4-phenylphenol)	92-69-3			0.003	0.009
4-Nitrotoluene	99-99-0			0.003	0.009
o-Phenylphenol	90-43-7			0.003	0.009
Mirex (Perchloropentacyclodecane)	2385-85-5			0.003	0.009
Benzene	71-43-2	Method for determination of VOCs by GC/MS-P&T	EPA Method 8260D: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry [S7] EPA Method 5030C: Pre-treatments for water samples [S8]	0.3	0.9
Methyl-tert-butyl ether (MTBE)	1634-04-4			0.3	0.9
Octamethylcyclotetrasiloxane (D4)	556-67-2			0.3	0.9

(continued)

Table S1. Continued

Chemical name	CAS No	In-house method	Method reference	LOD µg/L (ppb)	LOQ µg/L (ppb)
Tebuconazole	107534-96-3	Method for determination of organic pollutants (fungicides) by LC/MS-MS	EPA Method 536: Determination of Triazine Pesticides and Their Degradation in Drinking Water by Liquid Chromatography Electrospray Ionization Tandem Mass Spectrometry (LC/ESI-MS/MS) [S9]	0.010	0.03
Pendimethalin	40487-42-1	Method for determination of organic pollutants (herbicides) by LC/MS-MS		0.010	0.030
Imidacloprid	138261-41-3	Method for determination of organic pollutants (insecticides) by LC/MS-MS		0.010	0.030
Chloroalkanes C10-13 (Short chain chlorinated paraffins)	85535-84-8	Method for determination of short chain chlorinated paraffin by GC/MS/MS	Carro et al. [S10]	0.3	0.9
p-Hydroxybenzoic acid	99-96-7	Method for determination of various compounds by LC/MS-MS	EPA Method 535: Measurement of Chloroacetanilide and other Acetamide Herbicide Degradates in Drinking Water by Sollid Phase Extraction and Liquid Chromatography /Tandem Mass Spectrometry (LC/MS/MS) [S11]	0.1	0.3
Boric acid	10043-35-3	Method for determination of boric acid and iodine by ICP/MS	ISO 17294-1/2 (2006/2016): Water Quality-Application of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [S12] and EPA Method 6020B: Inductively Coupled Plasma - Mass Spectrometry [S13]	50	150
Iodine	7553-56-2			10	30

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