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Treatability of hazardous substances in industrial wastewater: case studies for textile manufacturing and leather production sectors

B. Hande Gursoy-Haksevenler · **Elif Atasoy-Aytis** · **Mehmet Dilaver** ·
Yakup Karaaslan

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Abstract Hazardous substances used and produced by different industrial activities pose a potential risk to the environment and to human health. Different physicochemical and/or biological processes are used in industrial wastewater treatment; these methods, however, may not be effective in removing these substances. This study was carried out to comparatively evaluate the removal of hazardous substances through conventional wastewater treatment processes that are used by major industries in Turkey. A four-season monitoring study was carried out in textile manufacturing and leather production sectors, representing industrial activities in Turkey. Samples were analyzed for 45 priority substances defined by the European Union and 250 specific pollutants listed in the Turkish Regulation on Surface Water Quality. For both wastewaters, where biological treatment was performed after pretreatment, their characteristics showed that organics were almost completely removed. except for dichloromethane (44–51% removals) and dioxin and dioxin-like compounds (64–69% removals). Additionally, different removal ratios (16–97%) were obtained for metals; the poorer removal was observed for B, Ba, Ag, Sb, and Si. The remaining metals (Cu, Pb, Sb, V, Si for textile; Cr, Cu, Sb, Si for leather effluents) in the treated wastewaters were still higher than environmental quality standards (EQS) of receiving water bodies. The study revealed that existing treatment processes were not adequate for efficient hazardous substance removal and there is an urgent need to improve them. Finally, advanced treatment technologies were suggested for specific pollutants together with their unit treatment costs.

Keywords Conventional treatment processes · Hazardous substances · Leather production · Textile manufacturing · Treatment efficiency

Introduction

With rapid industrialization and population growth, the amount and types of hazardous substances released into the aquatic environment are increased. Hazardous substances mostly used in or produced by many different industrial activities are resistant to biodegradation;

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B. H. Gursoy-Haksevenler (✉)
Department of Political Science and Public Administration, Faculty of Political Science, Marmara University, 34820 Beykoz, Istanbul, Turkey
e-mail: hande.gursoy@marmara.edu.tr

E. Atasoy-Aytis · M. Dilaver
Environment and Cleaner Production Institute, TUBITAK Marmara Research Center (MRC), Kocaeli, Turkey

Y. Karaaslan
General Directorate of Water Management, Ministry of Agriculture and Forestry, Ankara, Turkey

hence, they affect the ecological balance and pose a potential risk for human health. Thus, it is crucial to treat wastewater before discharging it into a water body. However, many industrial wastewater treatment plants (WWTPs) generally consist of physical, chemical, and biological units and are not designed particularly for the removal of hazardous substances. Therefore, these substances reach the receiving aquatic environment without being treated due to their persistence and complex structures (Lofrano et al., 2013; van Wezel et al., 2018; Yaseen & Scholz, 2019). Recently, advanced treatment technologies such as membrane filtration (Arzate et al., 2019), adsorption (Vatankhah et al., 2019), and advanced oxidation (Liu et al., 2019) have presented effective and promising methods for the removal of hazardous substances. However, even if successful removal results have been obtained, these treatment alternatives may not be economical. Additionally, most of the performed studies are on a laboratory scale, and different results can be obtained when moving to large scale (Beier et al., 2011; Blackbeard et al., 2016; Hollender et al., 2009; Kennedy et al., 2015; Kharel et al., 2020; Kruithof et al., 2007; Margot et al., 2013; Trinh et al., 2012).

In addressing pollution from hazardous substances, The Water Framework Directive (WFD, 2000/60/EC) adopted by the European Union (EU), was accepted as the first regional effort toward hazardous substances (European Commission, 2010, 2013). The WFD (2000/60/EC) requires compliance with all environmental quality standards (EQS) recognized for priority substances at the European level, and specific pollutants at the national level. In developing countries, even though considerable progress in improving water quality has been made, further efforts are still needed, especially for controlling hazardous substances coming from industries (Haider et al. 2015). In Turkey, the Turkish By-law on Surface Water Quality (RSWQ, 2016) has identified EQSs for 45 priority substances that were adapted from 2013/39/EU and 250 national specific pollutants and has imposed the implementation of these EQSs. However, to implement the regulation, not only is the removal of hazardous substances required, but also, their detection and monitoring (Bolong et al., 2009; Gursoy-Haksevenler et al., 2020). This mainly depends on having appropriate institutional capacity and adequate infrastructure. However, most developing countries are not equipped to control this wide variety of hazardous substances. For this reason, it is a priority to determine which substances come from which industrial production. Then, a roadmap can be drawn for the removal of the detected substances.

There are comprehensive studies that aim to minimize the negative effects of hazardous substances, and to determine their source, fate, and toxicity. The number of studies on conventional treatment processes for removal of hazardous substances, especially, has been rapidly increasing. However, most of these studies focus on the removal of these substances from municipal wastewater (Bui et al., 2016; Luo et al., 2014; Margot et al., 2015); only a few have focused on their determination and removal in industrial wastewater (Talouizte et al., 2020; Yadav et al., 2019). The purpose of this study is to shed light on the questions of which hazardous substances may come from industrial wastewaters, to what extent the existing treatment systems can be effective for their removal, and which treatment systems can be suitable for their removals. In order to do so, effluents of Specialized Textile Industrial Zone (STIZ) and Specialized Leather Industrial Zone (SLIZ) were examined, since huge volumes of wastewater originate from these facilities and their wastewaters may contain high concentrations of many types of hazardous substances (Lofrano et al., 2013; Yaseen & Scholz, 2019). Thus, seasonal samples were taken from these facilities during 2016–2017, and their untreated and treated samples were examined through 45 priority substances (WFD, 2013/39/EU) and 250 national-specific pollutants (RSWQ, 2016).

Materials and methods

Study area

In this study, the presence of hazardous substances and their removal efficiencies through conventional treatment processes in WWTPs were examined by monitoring untreated wastewater and treated wastewater of STIZ and SLIZ, by collecting samples in November 2015, February 2016, May 2016, and August 2016. Wastewater treatment plant (WWTP) of STIZ that collects the wastewaters of 339 textile manufacturing facilities is located in Uşak, Turkey,

Table 1 Monitored facilities in the study

Facility (sector)	Wastewater amount	Wastewater treatment
Specialized Textile Industrial Zone (STIZ) (339 facilities)	10,000 m^3/day (capacity: 12,000 m^3/day)	Chemical (coagulation and flocculation by $Ca(OH)_2$ and $Al_2(SO_4)_3$) + biological (extended aeration activated sludge)
Specialized Leather Industrial Zone (SLIZ) (30 facilities)	600 m^3/day (capacity: 1000 m^3/day)	Physical + chemical (coagulation and flocculation by $Al_2(SO_4)_3$ and NaOH) + biological (activated sludge)

while WWTP of SLIZ that collects the wastewaters of 30 leather production facilities is located in Manisa, Turkey. The features of the monitored WWTPs in the study are given in Table 1, and their flow diagrams are displayed in Figs. 1, 2.

Analysis of effluents

Amber glass or plastic bottles were used for collecting samples. Samples were carried to the laboratory at + 4 °C and kept at − 20 °C until their analysis. The collected samples were analyzed for 45 priority substances identified by the European Union (WFD, 2013/39/EU; Online Resource1) and 250 specific pollutants listed in the RSWQ, Annex 5 Table 4 (RSWQ, 2016; Online Resource 2) at TUBITAK MRC's accredited laboratories. ICP-MS, GC–MS, GC–MS/MS, and LC–MS/MS instruments were used for the analyses of these substances (Online Resource 1 and 2). The analysis results were assessed based on the presence of substances, (> limit of detection, LOD) as well as annual average concentration (AAC) and maximum allowable concentration (MAC) of the EQS mentioned in the RSWQ. While calculating the removal efficiency, all values recorded under the LOD were halved as suggested in the document titled "Chemical Analysis and Monitoring of Water Status, 2009/90/EC" and taken as measured data (European Commission, 2009).

Results and discussion

Determination of hazardous substances and their removals by conventional WWTPs

Textile manufacturing wastewater

The textile industry is known as one of the most polluting industries (Savin & Butnaru, 2008; Sharma et al., 2007). Since it consumes a high amount of

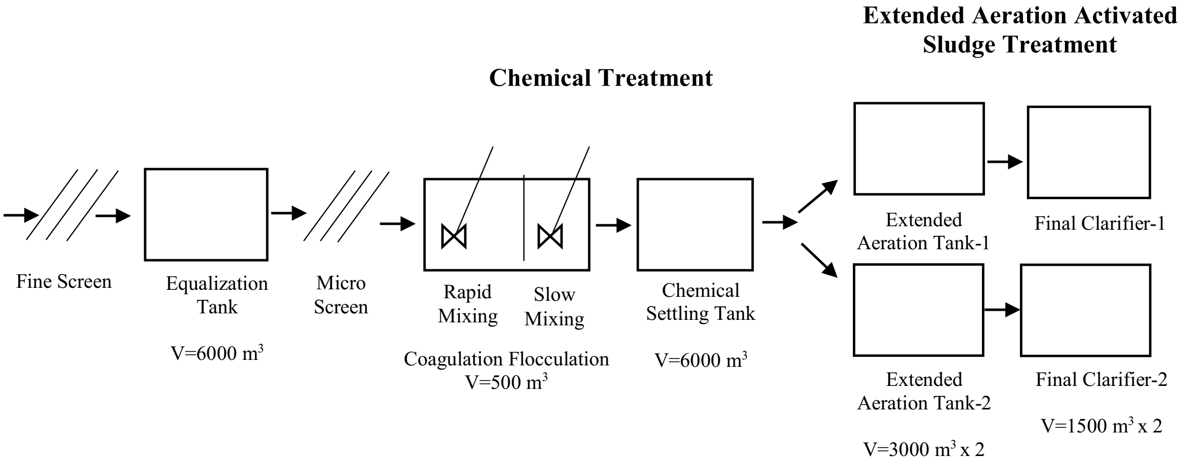

Fig. 1 Flow diagram of STIZ's WWTP

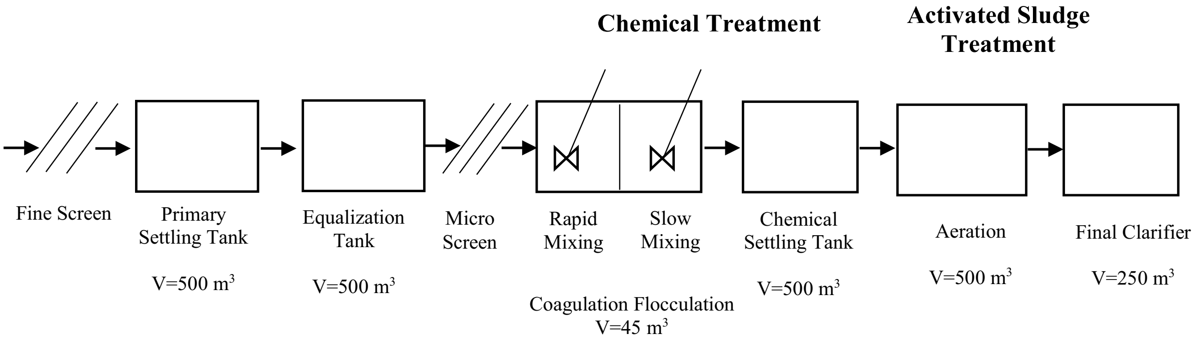

Fig. 2 Flow diagram of SLIZ's WWTP

water and generates considerably polluted wastewater, it is of great importance in terms of its impact on the environment. During production, 230–270 L of water is used for the treatment of 1 kg finished product (Keskin et al., 2021). The characteristics of the textile effluent are variable depending on the type of fiber, the processes applied, and the chemicals used. Chemical reagents used in the textile industry contain a wide variety of inorganic and organic structures. Wastewater produced from the textile industry (especially dyeing wastewater) contains organic dyes, auxiliary substances, detergents, metals, salts, mineral oils, and high chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspended solids (TSS), and total dissolved solids (TDS) (Yaseen & Scholz, 2019).

In our study, wastewater of the STIZ, which collects the wastewaters of 339 textile manufacturing facilities, was analyzed. Twenty-four out of 295 parameters analyzed were detected in the wastewater (Table 2). The determined substances appeared to be organic substances, specifically, dioxin and dioxin-like compounds (of which some textile dyes and pigments may be significant sources), trichloromethane (used as a stabilizer for textiles dyestuffs), dichloromethane (used as a carrier solvent), 2,4-d; (2,4-dichlorophenoxyacetic acid) (a widely used herbicide, especially in cotton production that can be used during cotton growth), and some metals. The obtained metals, Pb, Cr, Cd, and Cu are usually used in the stages of dyeing, printing, and production of color pigments of textile dyes. These metals can be found naturally in textile structures or can penetrate textile fibers during production, dyeing, or storage. Characteristic ranges of these metals in a textile effluent were defined as 2–5 mg/L for Cr, 3–6 mg/L for Zn, 2–6 mg/L for Cu, 0.07–2 mg/L for Cd, 0.03–2.0 mg/L for Fe, and 0.5–3 g/L for Ni (Priya & Selvan, 2017). The identified hazardous substances in monitored STIZ wastewater and their removals by conventional WWTP were presented in Table 2. The values exceeded EQS were displayed with dark color.

After treatment, metals were removed by 23–93%, whereas organics were almost completely removed except for dichloromethane (its removal was 51%) (Table 2). However, even after treatment, the concentrations of Cu, Pb, Sb, Si, and V were still higher than EQS values. The high concentration of Si, Sb, and As are thought to be caused by natural background concentrations, in addition to those caused by production processes. In the analyses made in the STIZ feed water, the value of Si, Sb, and As was approximately 18 and 4.2, and 1.4 times, higher, respectively, than their EQSs (Table 2). Si is known as one of the most abundant elements on earth (Cornelis et al., 2011). As concentration in natural waters in Turkey were found in the range of 0.05–7750 µg/L (Baskan & Pala, 2009); this can be explained by its abundance in the earth's crust and its dissolving when underground water passes through the soil. It may be a question mark why these pollutants, which are expected to have a relatively high levels due to its natural abundance, are monitored. The "specific substances" list of RSWQ 2016 (Annex 5, Table 4; Online Resource 2), which includes As, Si and Sb, has been determined by considering entire basins of Turkey (there are 25 basins). Presence and concentrations of these substances may show regional differences. For this reason, studies on determining basin-based natural background concentrations are needed to be done, but currently there are limited studies (Gursoy-Haksevenler

Table 2 The identified hazardous substances in monitored STIZ wastewater and their removals by conventional WWTP (the EQS exceeded values are displayed with dark color)

Hazardous substances	**(µg/L)**						**%**
	AA-EQS*	**MAQ-EQS***	**LOD**	**Feed water**	**Untreated textile effluent**	**Treated textile effluent**	**Removal efficiency**
Dichloromethane (CAS: 75–09-2)	20		2	6.23	7.92	3.86	51
Dioxin			0.000005	< 0.000005	0.000116	0.000014	88
Dioxin-like compounds			0.000010	< 0.00001	0.000059	< 0.00001	100
Trichloromethane (CAS: 67–66-3)	2.5		0.1	< 0.1	**12.5**	< 0.1	100
2,4-d; (2,4-dichlorophenoxyacetic acid) (CAS: 94–75-7)	5.3	583	0.025	< 0.025	**0.272**	< 0.025	95
Ag (CAS: 7440–22-4)	1.5	1.5	0.021	0.148	1.36	1.05	23
Al (CAS: 7429–90-5)	2165	2189	0.512	35	**1550**	885	43
As (CAS: 7440–38-2)	53	53	0.209	**75**	**114**	43	62
B (CAS: 7440–42-8)	1792	1792	0.067	252	459	372	19
Ba (CAS: 7440–39-3)	680	680	0.447	155	183	61	67
Be (CAS: 7440–41-7)	2.5	3.9	0.037	< 0.037	0.226	< 0.037	92
Cd (CAS: 7440–43-9)	0.70	1.50	0.059	0.496	**0.909**	0.346	62
Co (CAS: 7440–48-4)	1.96	2.6	0.026	0.241	1.86	0.596	68
Cr (CAS: 7440–47-3)	14	142	0.2	2.81	**78**	9.98	87
Cu (CAS: 7440–50-8)	21	23	0.263	14	**127**	**69**	45
Fe (CAS: 7439–89-6)	3832	3897	2.172	55	1445	176	88
Ni (CAS: 7440–02-0)	33	34	0.073	4.96	15	4.80	68
Pb (CAS: 7439–92-1)	5.31	14	0.066	1.16	**17**	**8.62**	49
Sb (CAS: 7440–36-0)	7.8	103	0.12	**33.05**	**412**	**272**	34
V (CAS: 7440–62-2)	11	97	0.021	4.85	**35**	**21**	40
Zn (CAS: 7440–66-6)	79	231	0.667	47	**478**	74	84
Si (CAS: 7440–21-3)	1830	1830	20	**15,330**	**32,330**	**11,360**	65
Ti (CAS: 7440–32-6)	246	262	7.67	< 7.67	17	< 7.67	77
Free CN (CAS: 57–12-5)	1.2	6	1	< 1	**6.74**	< 1	93

*Turkish Regulation on Surface Water Quality Annex 5 Tables 4 and 5 (RSWQ 2016; Online Resource 2)

et al., 2019). The region where the monitoring study was carried out has a geothermal structure that the high As and Si values may be originated (as can be seen as feed concentrations in Table 2). Similarly, high As and Si values were also obtained in groundwater monitoring studies conducted by State Hydraulic Works in the same region (State Hydraulic Works, 2016).

When studies on textile wastewater in the literature are examined, it appears that hazardous substances from textile production are rarely reported. In a study by Castillo et al. (1999), phenol, nonylphenol isomers, and phthalate esters were found as the main pollutants in the wastewater of the textile industry in Portugal (Castillo et al., 1999). Some studies investigated the degradation products of azo dyes and found N-(3,4-bishydroxymethylphenyl) acetamide, 6-acetylamino3-aminonaphthalene-2-sulfonic acid, aromatic amines, and anilines in the textile wastewater (Bilgi & Demir, 2005; Pinheiro et al., 2004). High amounts of polyethoxylate decylalcohol, polyethylene glycol, and linear alkylbenzene sulphonates have also been reported as the main components in textile wastewater. High concentration levels have been obtained for some benzene and naphthalene sulphonates used as dye bath auxiliaries in the textile industry as well (Castillo & Barceló, 2001). In a recently published study by Talouizte et al. (2020), chemically characterized specific micropollutants were found from textile wastewater in Morocco. In the study, three different wastewater samples were collected from different textile manufacturing facilities and were analyzed. Main organic compounds that were detected by GC/MS analysis were "2-amino-4-hydroxy-6-p-cyanophenylpropylpteridine; benzoic acid, 2,3-dimethyl-6-(3-methyl-1-oxobutyl); phenol, 4-[2-[2-(chloromethyl)-1,3 dioxolan-2-yl]ethyl]; naphtho [2,3-d]-1,3-dioxol-5-ol, 3a,4,9,9a-tetrahydro-2,2-dimethyl-, cis; and benzene, 1-chloro-2-diethoxymethyl." Additionally, the concentrations of metals in the wastewater samples were found to be considerably low (lower than both their national standards and WHO standards) (Talouizte et al., 2020).

For the treatment of textile wastewater, biological processes have been used for many years. For biological processes, the metabolic abilities of microorganisms are used to oxidize or reduce organic and inorganic compounds. Biological processes are assumed to be relatively cost-effective compared to other treatment processes. However, biological processes can only transform biodegradable compounds and do not function in the presence of toxic substances, which limits the scope of their use in treatment. Physicochemical pretreatment (coagulation/flocculation, advanced oxidation processes) processes are often employed to convert biologically resistant compounds into more biodegradable compounds. In the literature, it appears that biological treatment with both pure cultures (Mohamad-Hanapi et al., 2021) and activated sludge (which is composed of heterotrophic bacteria; Pavlíková, 2020) have been examined. However, on the industrial scale, the activated sludge (AS) process is mainly applied. The microorganisms present in AS can form flocs during treatment and provide removal of pollutants in wastewater by sedimentation. Furthermore, these microorganisms can survive under aerobic, anoxic, and anaerobic conditions. Color can also be removed by anaerobic processes, while organic compounds can be removed by aerobic processes. It is concluded that although more than 90% of both the color and COD can be removed by biological processes, the treated wastewater often still cannot reach the desired standard (Paździor et al., 2019).

Studies related to textile wastewater treatment mostly focused on the removals of COD, BOD_5, SS, and color (Donkadokula et al., 2020). There are only a few studies on hazardous substances removal in textile wastewater. Of these few, most studies examine the removals of metals from textile effluent. For instance, Zeiner et al. (2012) investigated Cr, Mn, and Co removals from synthetic textile wastewater by microbial biofilms. They obtained 100% Cr, 94% Co, and 69% Mn removals (Zeiner et al., 2012). Basha and Rajaganesh (2014) examined microbial bioremediation of metals using isolated bacterial strains, namely *Escherichia coli*, *Salmonella typhi*, *Bacillus licheniformis*, and *Pseudomonas fluorescence.* Among these strains, *Bacillus licheniform* was found to be the most efficient bacterial strain for heavy metal removal. The lowest obtained removal ratios were 92% for Cd, 87% for Pb, and 92% for Zn (Basha & Rajaganesh, 2014).

Leather production wastewater

Strong environmental regulations, intensive labor effort, and high labor costs resulted in the move of leather production from industrialized/developed countries to developing countries such as China, India, Latin America, and Turkey (International Council of Leathers, 2021). Leather industries are one of the top polluters, due to the complex nature of their wastewater (Dixit et al., 2015; Montalvão et al., 2017; Schrank et al., 2009). During leather production, large volumes of water and various chemicals are used to convert raw leather into leather products, resulting in large volumes of high-strength wastewater. Leather industry wastewater contains organic matter (COD, typically 1800–11,000 mg/L; BOD_5, typically 600–3000 mg/L), dissolved solids (TDS, typically 6800–37,000 mg/L) and suspended solids (SS, typically 900–5000 mg/L), oil-grease, as well as chromium (III) (30–260 mg/L), sulfur, and phenol originating from the chemicals used (Lofrano et al., 2013). The produced wastewater varies in the range of 10–100 L/kg hide due to processed raw material and production processes (Tunay et al., 1995).

In this study, wastewater of the SLIZ, which collects the wastewaters of 30 leather production facilities, were monitored. According to the obtained results, 31 out of 295 possible parameters were detected in wastewater (Table 3). The detected organic substances were dichloromethane (used as a carrier solvent), 1,2,4-trichlorobenzenes (used as dyeing carriers or leveling agents for dyeing, printing, and coating), dioxin and dioxin-like compounds (released by leather dyeing with chloranil and finishing with alkaline extraction), 1,2,4-trimethylbenzen and 1,3,5-trimethylbenzene (used in the production of dyes), isopropylbenzene (used in leather tanning), xylene musk, m-xylene, and o-xylene, (used as solvents for tissue processing), 2,4-d; (2,4-dichlorophenoxyacetic acid), clopyralid and ciromazine (herbicides and insecticide that

Table 3 The identified hazardous substances in monitored SLIZ wastewater and their removals by conventional WWTP (the EQS exceeded values are displayed with dark color)

Hazardous substances	**(µg/L)**						**%**
	AA-EQS*	**MAQ-EQS***	**LOD**	**Feed water**	**Untreated leather effluent**	**Treated leather effluent**	**Removal efficiency**
Dichloromethane (CAS: 75–09-2)	20		2	6.56	**8.19**	4.58	44
1,2,4-Trichlorobenzenes (CAS:120–82-1)			0.1	< 0.1	**3.99**	< 0.1	99
Dioxin			0.000005	0.000021	0.000042	0.000013	69
Dioxin-like compounds			0.00001	0.000019	0.000108	0.000039	64
1,2,4-trimethylbenzene (CAS: 95–63-6)	7.4	516	0.1	< 0.10	**30**	< 0.1	100
1,3,5- trimethylbenzene (CAS: 108–67-8)	9	150	0.1	< 0.10	7.65	< 0.1	99
Isopropylbenzene (CAS: 98–82-8)	35	260	0.1	< 0.10	1.84	< 0.1	97
m-Xylen (CAS: 108–38-3)	24	273	0.1	< 0.10	3.53	< 0.1	99
o-Xylen (CAS: 95–47-6)	24	585	0.1	< 0.10	6.11	< 0.1	99
Xylene mix (CAS: 81–15-2)	5.6	56	0.1	< 0.10	**9.64**	< 0.1	99
2,4-d; (2,4-dichlorophenoxyacetic acid) (CAS: 94–75-7)	5.3	583	0.025	< 0.025	4.22	0.831	80
Clopyralid (CAS: 1702–17-6)	200	200	0.002	0.196	0.133	< 0.002	92
Ag (CAS: 7440–22-4)	1.5	1.5	0.021	1.004	1.18	0.993	16
Al (CAS: 7429–90-5)	2165	2189	0.512	38.2	**17,677**	640	96
B (CAS: 7440–42-8)	1792	1792	0.067	76	**2776**	1622	42
Ba (CAS: 7440–39-3)	680	680	0.447	108	115	67	42
Be (CAS: 7440–41-7)	2.5	3.9	0.037	< 0.037	0.14	< 0.037	87
Co (CAS: 7440–48-4)	1.96	2.6	0.026	0.186	**2.2**	1.101	50
Cr (CAS: 7440–47-3)	14	142	0.201	2.56	**11,668**	**403**	97
Cu (CAS: 7440–50-8)	21	23	0.263	14.5	**77**	**22**	71
Fe (CAS: 7439–89-6)	3832	3897	2.17	76.2	980	336	66
Ni (CAS: 7440–02-0)	33	34	0.073	1.01	20	7.76	61
Pb (CAS: 7439–92-1)	5.3	14	0.066	1.23	**5.34**	2.44	54
Sb (CAS: 7440–36-0)	7.8	103	0.12	6.46	**77**	**54**	30
V (CAS: 7440–62-2)	11	97	0.021	4.03	**22.91**	10.81	53
Zn (CAS: 7440–66-6)	79	231	0.667	56	**185**	46	75
Si (CAS: 7440–21-3)	1830	1830	20	**12,150**	**7310**	**5093**	30

*Turkish Regulation on Surface Water Quality Annex 5 Table 4 (RSWQ, 2016; Online Resource 2)

can be generated from the rawhide). The obtained metals mainly originate from dyeing and finishing processes that are used as fastening agents or tanning agents. The most commonly used tanning material is chromium; hence, the high values of chromium in untreated effluent may be derived from this process (almost 40% of the used chromium) (Saha & Orvig, 2010). The identified hazardous substances in monitored SLIZ wastewater and their removals by conventional WWTP were presented in Table 3. The values exceeded EQS were displayed with dark color.

In our study, the generated leather effluent is treated by physicochemical and biological processes, and, after treatment, it is discharged to the receiving environment. With this treatment, 44% dichloromethane, 64–69% dioxin, and dioxin-like compounds were removed, and almost complete removal was achieved for other organic substances. For metals, the removal

Table 4 Seasonal values of detected hazardous substances in treated STIZ and SLIZ wastewaters

STIZ-treated wastewater (μg/L)

Parameter	AA-EQS	Season 1	Season 2	Season 3	Season 4	Average	Standard deviation
Dichloromethane (CAS: 75–09-2)	20	4.92	3.52	3.14	3.88	3.86	0.76
Trichloromethane (CAS: 67–66-3)	2.5	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
Dioxin		0.000049	< 0.000005	< 0.000005	< 0.000005	0.0000141	-
Dioxin-like compounds		< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	-
2,4-d; (2,4-dichlorophenoxyacetic acid) (CAS: 94–75-7)	5.3	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	-
Ag (CAS: 7440–22-4)	1.5	0.18	**1.79**	0.98	1.25	1.05	0.67
Al (CAS: 7429–90-5)	2165	1055	841	752	891	885	127
As (CAS: 7440–38-2)	53	**58**	38	40	35	43	10.3
B (CAS: 7440–42-8)	1792	388	342	378	381	372	20.5
Ba (CAS: 7440–39-3)	680	84	65	51	43	61	18.0
Be (CAS: 7440–41-7)	2.5	< 0.037	< 0.037	< 0.037	< 0.037	< 0.037	-
Cd (CAS: 7440–43-9)	0.70	0.27	0.41	0.39	0.34	0.35	0.06
Co (CAS: 7440–48-4)	1.96	1.41	0.45	0.33	0.21	0.60	0.55
Cr (CAS: 7440–47-3)	14.00	**17.60**	8.20	8.75	5.39	9.98	5.28
Cu (CAS: 7440–50-8)	21	40	**72**	**84**	**79**	**69**	20
Fe (CAS: 7439–89-6)	3832	418	108	95	82	176	162
Ni (CAS: 7440–02-0)	33	9.27	2.79	4.05	3.08	4.80	3.03
Pb (CAS: 7439–92-1)	5.31	**6.15**	**11.50**	**7.23**	**9.61**	**8.62**	2.40
Sb (CAS: 7440–36-0)	7.80	**97.93**	**242**	**324**	**425**	**272**	138
V (CAS: 7440–62-2)	11.0	**13.2**	**25.5**	**23.4**	**22.4**	**21.0**	5.39
Zn (CAS: 7440–66-6)	79	**99**	**81**	62	55	74	19.8
Si (CAS: 7440–21-3)	1830	**14,145**	**11,520**	**10,687**	**9086**	**11,360**	2114
Ti (CAS: 7440–32-6)	246	< 7.67	< 7.67	< 7.67	< 7.67	< 7.67	-
Free CN (CAS: 57–12-5)	1.2	< 1	< 1	< 1	< 1	< 1	-

SLIZ-treated wastewater (μg/L)

Parameter	AA-EQS	Season 1	Season 2	Season 3	Season 4	Average	Standard Deviation
Dichloromethane (CAS: 75–09-2)	20	1.02	7.52	4.13	5.65	4.58	2.75
Trichloromethane (CAS: 67–66-3)		< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
Dioxin		0.000006	0.000018	0.000019	0.000006	0.000013	0.000007
Dioxin-like compounds		0.000019	0.000052	0.000039	0.000046	0.000039	0.000014
1,2,4-trimethylbenzene (CAS: 95–63-6)	7.4	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
1,3,5-trimethylbenzene (CAS: 108–67-8)	9	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
Isopropylbenzene (CAS: 98–82-8)	35	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
m-Xylen (CAS: 108–38-3)	24	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
o-Xylen (CAS: 95–47-6)	24	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
Xylene mix (CAS: 81–15-2)	5.6	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
2,4-d; (2,4-dichlorophenoxyacetic acid) (CAS: 94–75-7)	5.3	0.0125	1.26	0.961	1.09	0.831	0.559

Table 4 (continued)

STIZ-treated wastewater (μg/L)

Parameter	AA-EQS	Season 1	Season 2	Season 3	Season 4	Average	Standard deviation
Clopyralid (CAS: 1702–17-6)	200	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	-
Ag (CAS: 7440–22-4)	1.5	0.215	0.861	1.23	**1.662**	0.993	0.613
Al (CAS: 7429–90-5)	2165	1041	821	298	401	640	350
B (CAS: 7440–42-8)	1792	**2654**	**1971**	1021	843	1622	848
Ba (CAS: 7440–39-3)	680	49.8	71.5	68.2	76.9	67.0	11.7
Be (CAS: 7440–41-7)	2.5	< 0.037	< 0.037	< 0.037	< 0.037	< 0.037	-
Co (CAS: 7440–48-4)	1.96	**2.325**	0.544	0.951	0.584	1.101	0.836
Cr (CAS: 7440–47-3)	14	**1020**	**120**	**254**	**218**	**403**	415
Cu (CAS: 7440–50-8)	21	**29.8**	18.9	20.7	18.7	**22**	5.29
Fe (CAS: 7439–89-6)	3832	541	281	205	317	336	144
Ni (CAS: 7440–02-0)	33	17.05	6.44	3.39	4.15	7.76	6.33
Pb (CAS: 7439–92-1)	5.3	**6.18**	2.09	0.95	0.55	2.44	2.58
Sb (CAS: 7440–36-0)	7.8	3.56	**81**	**67**	**63**	**54**	34
V (CAS: 7440–62-2)	11	**23.6**	9.15	5.28	5.23	10.81	8.72
Zn (CAS: 7440–66-6)	79	**101**	25	29	30.5	46	36.5
Si (CAS: 7440–21-3)	1830	**7090**	**4250**	**3514**	**5519**	**5093**	1568

rates were in the range of 16 to 97%. Among them, Ag, B, Ba, Sb, and Si were removed at rates less than 50% (Table 3). The concentrations of Cr, Cu, Sb, and Si, however, still exceeded AA-EQS after treatment.

According to studies on characterizing leather effluent in the literature, the main pollutants were defined as chromium salts, tannins or synthetic tannins (syntans), phenolics, phthalates, and azo dyes (Kumar et al., 2008; Lofrano et al., 2013; Dixit et al., 2015; Bharagava & Mishra, 2018). These are mostly used for the transformation of raw leather into commercial goods; however, they are not entirely attached to the leather and mostly remain in the wastewater. Tannins and syntans were characterized as refractory groups since they consist of an extended range of chemicals such as naphthalene-, phenol-, formaldehyde- and acrylic resins, and melamine-based syntans (De Nicola et al., 2007; Lofrano et al., 2013) A study done by Yadav et al. (2019) characterized the wastewater from leather production and determined the presence of benzoic acid, 3-[4,-(T-butyl) phenyl] furan-2–5-dione, benzeneacetamide, resorcinol, dibutyl phthalate, and benzene-1,2,4-triol (Yadav et al., 2019). Along with these organic substances, metals such as Co, Cu, Pb, and Zn in untreated leather production effluent were also identified in studies done by Vidya and Usha (2007), Deepali and Gangwar (2010), and Sugasini and Rajagopal (2015).

Leather production effluent is generally treated by using physicochemical and/or biological processes. Since it is more economic than chemical oxidation, biological treatment is usually preferred to reduce organic content (Dogruel et al., 2006). However, poorly biodegradable compounds, such as metals and tannins, can display inhibitory effects to the biological treatment. A study done by Stasinakis et al. (2002) reported that in the presence of 10 mg/L Cr (VI), heterotrophic growth was significantly inhibited. To prevent this inhibitory effect of these substances, a sequencing batch reactor (SBR) has been found to be a suitable method, depending on the enhancement of particular microbial species (Farabegoli et al., 2004; Ganesh et al., 2006). Naphthalenesulfonates and their substituted analogs, which are widely implemented for tanning of hides, have been reported to be resistant to degradation (Stolz, 1999). These sulfonated structures in wastewater can be degraded by several bacterial groups; however, xenobiotic organosulfonates are generally subject to desulfonation (Song & Burns, 2005). In some studies, applying chemical treatment before biological treatment is preferred to remove organic content (particularly COD reduction), suspended solids (SS), and chromium by using coagulants of ferric chloride ($FeCl_3$), ferrous sulphate ($FeSO_4$), aluminum sulphate ($AlSO_4$), as well as newer forms of coagulants. According to the obtained results, 30–70% COD, 30–40% SS, and 70–99% chromium were reduced by different types of coagulants under differing conditions, such as pH and coagulant dosage (Chowdhury et al., 2013; Lofrano et al., 2006; Pire-Sierra et al., 2016; Song et al., 2004).

Considering that leather production wastewater is generally treated with physicochemical and biological processes, it can be said that the treatment efficiency is poor for hazardous substances, even if it is efficient for conventional parameters (such as COD and TSS). However, the studies found in the literature rarely investigate the fate of hazardous substances in the leather production wastewater. A study done by Bharagava et al. (2018) characterized and identified recalcitrant organic pollutants present in biologically treated leather production wastewater. According to their results, butyl octyl phthalate, benzyl chloride, 2,6-dihydroxybenzoic acid 3TMS, dibutyl phthalate, benzyl butyl phthalate, benzyl alcohol, 4-chloro-3-methyl phenol, 2′6′-dihydroxyacetophenone, phthalic acid, diisobutyl phthalate, 4-biphenyltrimethylsiloxane, di-(-2ethy hexyl) phthalate, 1,2-benzenedicarboxylic acid, dibenzyl phthalate, and nonylphenol were still existent in the treated leather effluent (Bharagava et al., 2018).

Treatability of hazardous substances by conventional WWTPs

A wide range of hazardous substances are produced by industries and arrive at WWTPs. The fate of these pollutants is based on their physicochemical characteristics. Biodegradability, hydrophobicity, and volatility are the main properties that determine their removal mechanisms. For instance, relatively hydrophobic pollutants (such as heavy metals, persistent organic pollutants-POPs, polycyclic aromatic hydrocarbons-PAHs, and several household chemicals like several personal care products and brominated flame retardants) can be removed by sorption mechanisms using hydrophobic interactions between pollutants and suspended solids or electrostatic interactions between positively charged groups of the pollutants and negatively charged surfaces of microorganisms and the organic content of effluent. For relatively hydrophilic and organic pollutants (such as surfactants, plastic additives, hormones, several personal care products, and some pharmaceuticals), biodegradation can be the major removal mechanism, using the processes of metabolic or co-metabolic reactions. During metabolic reactions, organic pollutants are used as a growth substrate by microorganisms, while during co-metabolic reactions, pollutants are biologically transformed through side reactions. For volatile micropollutants, depending on their Henry's law constant, the transfer from effluent to air can occur during wastewater treatment. Volatile organic compounds (VOCs) like benzene, toluene, ethylbenzene, xylene, and styrene (BTEXS group) can be removed by surface volatilization (by stripping during aeration).

In our pilot study carried out in STIZ and SLIZ, primarily, a few organic substances and metals were observed in their effluents. In the examined wastewaters, the organic substances were determined to be dichloromethane, trichloromethane, 1,2,4-trichlorobenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, isopropylbenzene, dioxin, dioxin-like compounds, xylene musk, m-xylene, o-xylene, clopyralid, and 2,4-d; (2,4-dichlorophenoxy) acetic acid. After treatment, pollutants at concentrations exceeding relevant AA-EQS values in treated STIZ and SLIZ wastewaters were presented in Table 4 regarding their seasonal variation. As seen in Table 4, the values of obtained treated pollutants vary in each season. This variation generally depends on seasonal changes in production and using different chemicals in processes during production. On the other hand, this variation may be the result of biological treatment's characteristic since its performance alters due to the variability of incoming effluent (Ribeiro et al., 2017). Considering the average values of the pollutants detected after treatment, the following results were obtained. Among these, dichloromethane removals were significantly lower (44% for textile and 51% for leather wastewater) than other organics. For dioxin and dioxin-like compounds that were identified in both wastewaters, the removals were 69% and 64% in leather wastewater, respectively (88% and 100% in textile wastewater, respectively). The remainder of the identified organic substances were almost completely removed after treatment.

Since dichloromethane has a volatile nature, its removal is achieved by air stripping (99%) and adsorption (90%) (Shestakova & Sillanpää, 2013). For dichloromethane, removals with aerobic activated sludge systems were achieved in the range of 49–66% (WHO, 1996). During the aeration stage of aerobic treatment, 38% of dichloromethane was stripped into the atmosphere (Wu et al., 2009). Dioxins and dioxin-like compounds (such as biphenyls and polychlorinated dibenzofurans) are stable and highly toxic pollutants. On average, their removal was typically reported as 75% in conventional WWTPs (Katsoyiannis & Samara., 2004). Due to their hydrophobicity and poor biodegradability, they are mostly removed by sorption (Blanchard et al., 2004; Katsoyiannis & Samara, 2004). 2,4-Dichlorophenoxyacetic acid and clopyralid are widely used herbicides that are non-volatile and highly soluble in water. Because of their high solubility, they do not bind with suspended particles and are mostly degraded by microbial activities in conventional WWTPs (Hura, 2019). 1,2,4-Trimethylbenzene is one of the three isomers of trimethylbenzene and is classified as an aromatic hydrocarbon removed through volatilization (60%) and biodegradation (35%). Its typical effluent concentration in municipal WWTPs was 340 µg/L, and its removal ratio was 82% (Fatone et al., 2011). Another organic substance observed in the effluents was musk xylene which is a synthetic musk fragrance used in a wide variety of products. Its removal mechanism depends on sorption directly. Its typical value present in municipal wastewater was defined as 17 µg/L, and its removal ratio was reported as 54% (Bester et al., 2008). On the other hand, obtained m-xylene and o-xylene, which are isomers of xylene, classify as volatile organic compounds, and their removals mainly depend on volatilization (60%) and biodegradation (35%). Their typical removal ratios in municipal WWTPs are 97% and 70%, respectively (Fatone et al., 2011).

Regarding the metals detected in the investigated wastewaters, their removal mainly depends on the sorption mechanism as mentioned above. In conventional wastewater treatment, the removal of metals is generally associated with TSS removal. Even if a relationship is established between suspended solids and metal removal in wastewater, conventional treatment usually has a poor effect (< 60%), as metals are mostly present in their dissolved forms (within the exception of Al and Fe). The achieved metal removal results were 19–93% for textile and 16–97% for leather effluents. Poor removals were observed for metals of B, Ag, Sb, Si, and Ni. Considering the average values of detected pollutants in treated wastewater, their treatability by conventional treatment processes is given in Table 5.

Table 5 Removals of hazardous substances by conventional treatment processes of STIZ and SLIZ (by considering the average values of detected pollutants in treated wastewater)

Hazardous substances	**Removals (%)**	
	STIZ	**SLIZ**
Dichloromethane (CAS: 75–09-2)	51	44
Trichloromethane (CAS: 67–66-3)	100	-
Dioxin	88	69
Dioxin-like compounds	100	64
m-Xylen (CAS: 108–38-3)	-	99
o-Xylen (CAS: 95–47-6)	-	99
Xylene mix (CAS: 81–15-2)	-	99
1,2,4-Trichlorobenzenes (CAS:120–82-1)	-	99
1,2,4-trimethylbenzene (CAS: 95–63-6)	-	100
1,3,5- trimethylbenzene (CAS: 108–67-8)	-	99
Isopropylbenzene (CAS: 98–82-8)	-	97
4-d; (2,4-dichlorophenoxyacetic acid) (CAS: 94–75-7)	95	80
Clopyralid (CAS: 1702–17-6)	-	92
Ag (CAS: 7440–22-4)	23	16
Al (CAS: 7429–90-5)	43	96
As (CAS: 7440–38-2)	62	-
B (CAS: 7440–42-8)	19	42
Ba (CAS: 7440–39-3)	67	42
Be (CAS: 7440–41-7)	92	96
Cd (CAS: 7440–43-9)	62	-
Co (CAS: 7440–48-4)	68	50
Cr (CAS: 7440–47-3)	87	97
Cu (CAS: 7440–50-8)	45	71
Fe (CAS: 7439–89-6)	88	66
Ni (CAS: 7440–02-0)	68	61
Pb (CAS: 7439–92-1)	49	54
Sb (CAS: 7440–36-0)	34	30
V (CAS: 7440–62-2)	40	53
Zn (CAS: 7440–66-6)	84	75
Si (CAS: 7440–21-3)	65	30
Ti (CAS: 7440–32-6)	77	-
Free CN (CAS: 57–12-5)	93	-

Enhancing removal of hazardous substances in WWTPs

Conventional treatment processes

Currently, conventional WWTPs mainly consist of primary, secondary, and tertiary treatment units, and are not designed to remove hazardous substances. They are mostly designed for the removal of suspended solids, organic content which is easily biodegradable, and nutrients (such as nitrogen and phosphorus). However, many hazardous substances existing in the effluent are influenced by physical, chemical, and biological processes that occur during treatment. Margot et al. (2015) reviewed the fate of these substances in municipal WWTPs and determined that metals, PAHs, POPs, several household chemicals known as being relatively hydrophobic, were well removed (> 70%) in municipal WWTPs; plastic additives, surfactants, hormones, several personal care products, and some pharmaceuticals, which are known to be easily biodegradable, could be biodegraded/transformed in municipal WWTPs, while some VOCs could be also removed by volatilization (Margot et al., 2015). However, for relatively hydrophilic (polar) and non-biodegradable compounds such as pharmaceuticals, pesticides/biocides, and some household chemicals, only poor removals (< 50%) could be obtained by conventional WWTPs. Furthermore, the concentrations of hazardous substances, which are found to be relatively removed in conventional WWTPs (such as heavy metals and surfactants), can be still high at the end of the treatment and can adversely affect aquatic life.

According to our results, current conventional treatment technologies were effective in removing most of the detected substances, while insufficient for some of them (especially for some metals). To reduce hazardous substances' concentration in the effluent, it is necessary to enhance the treatment. The removal efficiency of these compounds can be increased with (i) optimization of conventional treatment technologies and (ii) applying advanced treatment technologies. The presence of the substances at the outlet of the WWTP depends on the high persistence of the compound (its hydrophilicity and biodegradability) as well as the lack of sufficient hydraulic retention time for complete biodegradation and the lack of sufficient diverse bacterial communities to metabolize/co-metabolize the substance or insufficient sorption mechanisms. Hence, optimization of conventional treatments can improve the removal of hazardous substances. For instance, increasing TSS removal will reduce the concentration of substances characterized as hydrophobic, such as heavy metals, PAHs, PCBs, whereas increasing BOD and ammonium removal will reduce biodegradable substances, such as estrogen and ibuprofen triclosan (Margot et al., 2015).

Advanced treatment technologies

In the case of hardly biodegradable and hydrophilic substances, such as some pharmaceuticals, pesticides, and corrosion inhibitors, optimization of existing conventional treatments seems to be inadequate. Advanced treatment technologies are the most suitable and promising alternatives for these substances' removal. Among advanced treatment methods, adsorption (Vatankhah et al., 2019), membrane filtration (such as nanofiltration-NF and reverse osmosis-RO), and oxidation with OH radicals (Arzate et al., 2019), UV/H_2O_2 (Liu et al., 2019), and ozone (Cruz-Alcalde et al., 2019; Vatankhah et al., 2019) were mostly applied for hazardous substances' removal. Published studies on advanced treatment processes for textile manufacturing wastewater (Topare & Bokil, 2021; Azerrad & Kurzbaum 2021; Othman et al., 2021) and leather production effluent (Bhaduri, 2021; Korpe & Rao, 2021) have increased recently. However, the removal of hazardous substances was not discussed in these studies.

According to the results we obtained, the hazardous substances detected in STIZ and SLIZ's wastewater were organic substances and metals; their removal mainly depends on oxidation and sorption mechanisms, respectively. Membrane filtration, activated carbon adsorption, and ozonation can be promising alternatives for identified substances for both textile and leather production industries. Adsorption on activated carbon that widely used for industrial wastewater treatment has advantageous due to its easy application and operation, no need for chemicals, and no by-product formation. However, used activated carbon needs to be replaced, and this replacement cost limits its use if the treated wastewater has a low

COD concentration. High treatment performance can be also obtained by membrane filtration, but its pretreatment requirement, energy consumption, removal of retained pollutants, and the need for qualified personnel can increase its operating costs. Oxidation processes have only potential for degrading pollutants, but unknown and toxic byproduct generation can be observed as a result of partial oxidation (Wu et al., 2019). According to their treatment performance, high removals for hazardous substances can be obtained by membrane filtration. Activated carbon's efficiency is better for pollutants with large particles; however, it is less effective on pesticides and organometallics. Ozonation has better performance for the removal of some drugs, pesticides, and polycyclic aromatic hydrocarbon (Peyrelasse et al., 2021).

There are several studies in the literature related to the cost of the removal of hazardous substances (Wahlberg et al., 2011; Lofrano et al., 2013; Paździor et al., 2019). Mendret et al. (2019) reported the cost of the ozonation process as 100 \$ $g^{-1}O_3$ h for a capacity of 1.15 kgO_3 h^{-1}, based on feedback from ozone generator suppliers and manufacturers. The cost of activated carbon is usually between 1 and 4 € kg^{-1}, while the reactivation cost is 0.6–0.7 € kg^{-1} (without transport), and the elimination cost is 0.4–0.5 € kg^{-1} (Peyrelasse et al., 2021). NF and RO investment costs as determined by IRH company are estimated to be around 1500–1750 € m^{-3} d (when flow rate is 200–300 m^3 d^{-1}) and 7500 € m^{-3} d (when flow rate is less than 10 m^3 d^{-1}). In addition, 25 to 30% additional costs for installation, commissioning, etc. should be considered (IRH, 2010). A comprehensive literature review on urban wastewater treatment plants that remove hazardous substances and operate at different flow rates was carried out by Ates (2019). In his study, unit installation cost as well as operation and maintenance cost functions were defined, and applied to different treatment alternatives of ozonation, activated carbon adsorption, and membrane filtration. In our study, these defined functions were used to reveal the cost analysis for the proposed alternatives (Table 6). When the calculated costs for textile and leather wastewater are examined, as expected, the cost decreases as the wastewater flow increases. Among the proposed treatment alternatives, the NF process has the highest installation, operation, and maintenance cost while adsorption has the lowest cost. While deciding the most effective treatment alternative, not only its cost but also its technical and environmental criteria are of great importance. Peyrelasse et al. (2021) designed a methodology for comparing RO, ozonation, and activated carbon processes for the treatment of an industrial effluent which had recalcitrant COD. According to their results, reverse osmosis had the highest environmental impact due to energy and material consumption during operation. Intermediate results were obtained with ozonation as a result of its high costs (when the organic concentration of the wastewater is high) and the formation of potentially toxic oxidation by-products (from not complete mineralization of organic matter). The activated carbon was obtained as having the lowest cost when reactivation was applied to the spent carbon (Peyrelasse et al., 2021).

As presented, activated carbon adsorption seems both cost effective and has less environmental impact when compared with other alternatives. However, its removal efficiency should be investigated. This depends on not only treatment alternative applied but also wastewater characteristics such as pollutant type and its concentration. In the study conducted by Ates

Table 6 Cost analysis for proposed treatment alternatives for STIZ and SLIZ effluents

Cost		**PAC adsorption**	**Nanofiltration**	**Ozonation**
Unit installation cost function* (\$)		$y = -3.726\ln(x) + 45.821$	$y = -251\ln(x) + 3981.5$	$Y = -39.8\ln(x) + 562.44$
Unit operation and maintenance cost function* (\$)		$y = -6.773\ln(x) + 107.6$	$y = -7.894\ln(x) + 862.55$	$y = -7.3691\ln(x) + 139.25$
STIZ (10,000 m^3/day)	Installation cost	20	2.248	288
	Operation and maintenance cost	61	808	99
SLIZ (1000 m^3/day)	Installation cost	12	1.670	196
	Operation and maintenance cost	45	790	99

*Cost functions were taken from Ates (2019)

(2019), a strategy was drawn for deciding treatment alternatives according to wastewater characteristics. The results showed that if metal concentrations were high, membrane filtration was the best option. If metal concentrations were relatively low, activated carbon was determined to be the most effective. For the wastewater included both metals and organic substances, membrane filtration (NF and RO) and ozonation were suggested as the alternative options (Ates, 2019). According to our results obtained for textile and leather effluents, a significant amount of metals was observed after conventional treatment; in this case NF seems appropriate for an advanced treatment for textile and leather effluents. It should be kept in mind that even membrane technologies are promising and appropriate option for the treatment of metal and other organic substances, membrane concentrate streams must be considered for further treatment. NF membranes and other pressure-driven membrane filtration have 40 to 90% concentrate volume ratio of feed volume (Van Der Bruggen et al., 2003). These concentrate streams have higher amount of pollutions compared to feed and permeate streams. A recent study investigated membrane concentrate treatment options such as two stage RO, RO + NF, electrodialysis, evaporation, RO + electrodialysis + crystallization with their cost analysis (Çelebi et al., 2021). Based on their works, membrane concentrates can be treated in line with chemical coagulation/precipitation-ceramic microfiltration and NF with approximately 0.47 US$/m^3. Despite all these disadvantages, the mentioned alternatives are the last known techniques used in the removal of hazardous materials. Otherwise, insufficiently treated wastewater may be discharged into water systems and cause serious environmental problems.

Conclusion

Although the number of studies on the effectiveness of traditional treatment processes for the removal of hazardous substances is increasing in the literature, most of these studies focus on the removal of hazardous substances in domestic wastewater; only a limited number of studies have focused on their identification and removal in industrial wastewater. The contribution of the present study was to determine which hazardous substances come from textile and leather production sectors with high polluting effect and their treatability by conventional treatment processes. In addition, even the number of studies on the removal of textile and leather wastewater with advanced treatment techniques has increased recently, the removal of hazardous substances has not been discussed much in these studies. Also, this study has another importance for being the first study in Turkey, that is, a comprehensive wastewater monitoring program was performed for 45 priority pollutants identified by the EU WFD and 250 river basin specific pollutants listed in the Turkish Regulation on Surface Water Quality. In this context, this study attempted to determine the hazardous substances in textile manufacturing and leather production wastewaters and their removal by current conventional processes.

According to the seasonal monitoring of these effluents, of the 295 parameters monitored, 24 were detected in textile manufacturing wastewater, whereas 31 were detected in leather production wastewater. By current conventional treatment processes, more than 90% removal was achieved for organic substances (trichloromethane, 2,4-trichlorobenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene isopropylbenzene, xylene musk, m-xylene, o-xylene, clopyralid, and 2,4-d; (2,4-dichlorophenoxy) acetic acid), with the exception of dichloromethane (44–51%), dioxin (69% for textile effluent), and dioxin-like compounds (64% for textile effluent). Metals were removed in the range of 19–93% for textile and 16–97% for leather effluents. Poor removals were observed for metals of B, Ag, Sb, Si, and Ni. Additionally, the concentrations of some other metals were still higher than the limit values. Even if some of these pollutants could be removed with the current conventional WWTPs, it was not enough to be safely discharged into the receiving environment. For improving treatment efficiency, it is recommended to make a long-term analysis for each facility to identify which substances are formed and to what extent they are removed by the current treatment processes. The treatment process should then be improved in relation to the characteristics of pollutants. In our study, adsorption, nanofiltration, and ozonation processes were found to be the most appropriate advanced treatment alternatives considering the characteristics of the hazardous substances. When the costs of these processes were compared, the most suitable process was seen as adsorption; when the removal efficiencies of the detected hazardous substances were compared, the most appropriate treatment seen was as nanofiltration.

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