The Applicability of an Advanced Oxidation Process for Textile Finishing Waste Streams & Fate of Persistent Organic Pollutants

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ABSTRACT: The trend of sustainable use of available water resources encourages textile finishing enterprises to implement efficient wastewater treatment technologies that enable water recycling, and not just it's discharging into the local wastewater treatment plants (WWTP). This paper presents the results obtained from the H_2O_2/UV treatment of wastewater from Slovene textile finishing company. Laboratory scale decolouration experiments were performed on the most representative wastewater samples, collected in three months period. In general 80 % decolouration and 86 % total organic carbon (TOC) reduction was achieved. On the other hand, the use of ultraviolet (UV) radiation to degrade and destroy organic pollutants in textile wastewater could lead to the formation of toxic dioxins and dioxin-like compounds, groups of persistent organic pollutants, especially due to the presence of halogenated compounds in textile finishing processes. For these reasons, textile wastewater samples were analysed for any content of dioxins before and after the treatment with H_2O_2/UV .

Key words: Textile wastewater, Advanced oxidation process, H₂O₂/UV, Ecological parameters, Dioxins

INTRODUCTION

Industrial wastewater may adversely affect the water bodies when not appropriately treated (Ajibola and Ladipo, 2011; Chen et al., 2011; Rameshraja and Suresh, 2011; Houda et al., 2011; Naim et al., 2011; Mesci and Elevli, 2012; Daniel and Prabhakara Rao, 2012). The textile finishing industry is considered to be a water-intensive sector, as the nature of textile processes require several washing and rinsing cycles (EPA, 1997). The major environmental concern is, therefore, the amount of produced wastewater and its pollutants' load. Those major pollutants specific for textile wastewater are suspended solids, highrecalcitrant chemical oxygen demand, dyes that are responsible for colour, and some other soluble substances (Chaolin et al., 2011). In addition, many inorganic substances are present that contribute to a high-conductivity of textile wastewater (Savin and Butnaru, 2008). Throughout Europe, 108 million tons of water is produced on a yearly basis and 36 million tons of chemicals and auxiliaries have to be removed from textile wastewater (Volmajer Valh and Majcen Le Marechal, 2009). The price for the wastewater treatment varies, on average, from 0.5-2.5 €/m³ and it is expected that the price will increase in the future (estimated value is from $3-5 \notin (M^3)$ (Water Framework Directive, 2000).

Most of the wastewater produced by the textile industry is coloured. The presence of very small quantities of dyes in water (less than 1 ppm) is highly visible due to their brilliance. So, the removal of colour from wastewater is often very costly, but a stringent environmental legislation does stimulate the textile sector towards developing wastewater-treatment plants (Vandervivere, 1998). Advance Oxidation Processes (AOP) employing hydrogen peroxide together with UV radiation, ozone or Fenton's reagent, have been found quite effective for the decolouration of wastewater, by using a formation of hydroxyl radicals during oxidation (Arslan-Alaton, 2004; Tuhkanen, 2004) which are highly powerful oxidizing species with an oxidation potential of 2.8 V (Kurbus, 2003). The advantages of this process are among others that no additional disposal problems are involved after treatment because the organics in the water are almost completely destroyed whilst removing the colour (Volmajer Valh et al., 2011; Slokar and Majcen Le Marechal, 1998; Riga et al., 2007). On the other hand, the use of ultraviolet (UV) light to degrade and destroy organic pollutants within textile wastewater could be a source of toxic dioxin and dioxin-like compounds. Dioxin (Fig. 1) is the term for a group of chemical compounds with 75 polychlorinated dibenzo-p-dioxins

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(PCDDs) and 135 polychlorinated dibenzofuranes (PCDFs) (Ballschmiter and Bacher, 1996). Dioxins are related to halogens (Palm et al., 2004; Halsall, 2004), they are persistent and toxic pollutants (Stephens et al., 1995). Exposure to even low doses of dioxins can lead to cancer, damage to the nervous system, immunesystem diseases, and reproductive disorders (Mitrou et al., 2001). Textile wastewater might contain wellknown dioxin precursors such as pentachlorophenol and chloranil (Križanec and Majcen Le Marechal, 2006). Chloranil is used as a starting compound during the production of some dioxazine dyes and pigments, and chloranil is produced from chlorinated phenols, PCDD/ Fs as by-products are formed during synthesis (Wiliams et al. 1992; Križanec, 2007; Santl, 1994). The future formation of PCDD/Fs can occur via dyeing and textile finishing processes with conditions favourable for the generation of PCDD/Fs (high-temperatures (Stanmore, 2004), alkaline conditions, UV radiation or other radical starters).

The aim of our study was to examine the applicability of H₂O₂/UV treatment for reduction of main ecological parameters from wastewater, produced in Textile Finishing Company in Slovenia. In addition, we also investigated the presence of dioxins in textile wastewater and their fate during H₂O₂/UV treatment. The annual consumption of process water within the company is about 87,000 m³ (240 L/kg of product). The company uses two different water sources: the municipal water supply and its own well. The main water consumers are the steam boiler-house and the dye-house. Before entering into the process, water is chemically treated to remove hardness. Dye-house wastewater is the major source of pollutants. Effluents from the dye-house contain high-concentrations of inorganic and organic chemicals. The source of inorganic pollutants within the dye-house is auxiliary chemicals. Other effluents represent wastewater from the steam-boiler house, wastewater from the regeneration of the ionic exchangers, sanitary wastewater, wastewater from the pump's cooling-



X + Y = 1-8 (75 congeners)

Polychlorinated dibenzo-p-dioxins

system, and meteoric wastewater. The annual consumption of dyestuffs is 4,300 kg and the annual consumption of other auxiliary chemicals is 48,000 kg.

MATERIALS & METHODS

Representative wastewater samples were taken directly from the company twice a week over the measuring-period of 11 weeks. Samples were taken from two measuring-places: measuring- place 1 represented wastewater after neutralisation and measuring-place 2 represented wastewater after cooling (Fig. 2). The wastewater samples after neutralisation were a dark brown colour, and the colour of the wastewater samples after cooling was brighter.

On the sampling days, 100 % PES and 100 % PAS sewing threads were dyed with disperse and metalcomplex dyes. Such dyeing requires usage of the following auxiliaries: tenzides, dispersing agents, acetic acid, sodium hydroxide, sodium hydrosulphite etc.

The measured wastewater parameters were chosen according to Slovenian environmental legislation (OGRS, 2007) and as the most disputable part of their monitoring procedures. *pH value* was measured electrochemically. Absorbance was measured at three defined wavelengths, namely, 436, 525, and 620 nm, using a Cary 50 spectrophotometer. The results are expressed as *SAC*, and were calculated according to the equation:

$$SAC_{\lambda} = \frac{A}{l}f \tag{1}$$

Where:

1

 SAC_{λ} is the spectral absorption coefficient in m⁻¹ A is the absorbance at wavelength λ

is the optical pathlength of the cell in mm

f is the factor used to give the spectral

coefficient (f=1000).

Chemical oxygen demand (COD) was measured using the open-reflux method using a CR 2010 Thermoreactor, following the ISO 6060 standard.



X + Y = 1-8 (135 congeners)

Polychlorinated dibenzofurans

Fig. 1. Molecular structures of polychlorinated dibenzo-p-dioxins and dibenzofurans



Fig. 2. Schematic view of the wastewater network within the Company at marked measuring-places

Total organic carbon (TOC) was measured on DC – 190 TOC analyzer, Dhorman. (5000A Shimadzu analyzer).

Determination of PCDD/Fs during sample extraction was carried out using high-resolution gas chromatographic (HRGC) separation on a HP 6890 GC (Hewlett-Packard, Palo Alto, CA, USA) coupled to s Finnigan MAT 95XP (Thermo Finnigan, Bremen, Germany) high resolution mass spectrometer (HRMS). The samples were analyzed for PCDD/Fs concentrations using the isotope dilution method based on US EPA 1613 protocol (USEPA method 1613, 1994). The wastewater samples (0.5 L) were transferred in separate funnels and spiked with an internal standard mixture containing ¹³C-labelled isomers of analytes. Hexane (100 mL) was used as the liquid-liquid extraction solvent. Separation of the organic and water phases was achieved after an addition of ethanol (250 mL), which prevents the occurrence of emulsion. The cleanup of organic (hexane) extract was performed on a mixed column (layers: silica gel/sulphuric acid, silica gel/ KOH, and silica gel) followed by additional cleaning using size exclusion chromatography (SEC) and adsorption chromatography on a graphitised carbon column. 30% H₂O₂ was used from Belinka during all the decolouration experiments.

 H_2O_2/UV experiments were carried out in a batch photoreactor using a medium-pressure mercury UV lamp emitting at 254 nm (Berson UV-technik) (Fig. 3). The wastewater samples were taken from measuringplaces 1 and 2. For each experiment, 6 L of the effluent was pumped into the reservoir; the dosage of hydrogen peroxide was 4.5 mL L⁻¹, the UV lamp ($\lambda = 254$ nm) was set at 1400 W, and the treatment time was 1 h. Samples were taken every 10 minutes during the treatment. Ecological parameters such as pH, COD, TOC, and absorbance at three wavelengths (436, 525 and 620 nm) were measured for all the taken samples during the process and for the samples after decolourisation.

Experiments were performed in batch mode using glass beaker as reactor. 10 g of activated sludge from local municipal wastewater treatment plant (Dogoše, Maribor) was added in the reactor filled with 250 mL of wastewater sample. The system has been mixed for 1 hour. The addition of 100 mL 1% solution of $Al_2(SO_4)_3$ was followed. After centrifugation wastewater sample have been prepared for determination of *PCDD/Fs*.

RESULTS & DISCUSSION

The characteristics of the wastewater samples from measuring-places 1 and 2 are shown in the Tables 1 and 2. High fluctuations in measured parameters were found, reflecting frequently changeable production, typical for textile finishing processes. Almost all the wastewater parameters at both measuring points were too high under Slovenian regulations. According to the Slovenian environmental legislation called Decree on substances, and emissions during the removal of wastewater from objects and devices for the production, modification, and treatment of textile fibres pH=6.5-9, TOC = 60 mg/L, COD = 200 mg/L, SAC(436) = 7.0 m⁻¹, SAC(525) = 5.0 m⁻¹, SAC(620) = 3.0 m⁻¹.



Fig. 3. Computer-controlled H₂O₂/UV pilot plant

S am ple	nH	SAC (m ⁻¹)			TOC	COD
	pm	436	5 2 5	620	(mg/L)	(mg/L)
Sample-1	10	23.6	11.6	7.8	284	-
Sample-2	8.7	54.1	27.3	16.9	429	1627
Sample-3	9.2	79.8	55.3	44.5	596	3603
Sample-4	8.9	59.0	38.2	25.5	727	4049
Sample-5	8.9	87.6	43.3	20.5	656	3805
Sample-6	8.7	77.3	39	26.3	500	3282
Sample-7	9.9	53.1	35.5	22.6	565	3395
Sample-8	9.4	36.2	18.3	12.2	436	2685
Sample-9	7.6	21.1	12.5	8	483	3295
Sample-10	7.6	30.0	19.1	13.7	305	3208
Sample-11	7.4	20.8	10.1	7.5	306	2920
*	6.5-9	7.0	5.0	3.0	60	200

Table 1. Characteristics	of waste stream at	t measuring-place 1
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*Concentration limits of emission into water

Table 2. Characteristics of waste stream at measuring-place 2

Sample	nH	SAC (m ⁻¹)			TOC	COD
	рп	436	525	620	$(\mathbf{m} \mathbf{g}/\mathbf{L})$	(mg/L)
Sample-1	8	55.4	45	45.5	573	3150
Sample-2	12	3.3	2.5	2.1	140	1724
Sample-3	7.3	21.4	12.3	9.7	146	5215
Sample-4	8.2	26.4	15	10.5	85	4270
Sample-5	7	12.8	7.9	5.2	84	659
Sample-6	12.5	9	3.2	2.3	109	1639
*	6.5-9	7.0	5.0	3.0	60	200

*Concentration limits of emission into water

All the measured parameters were lowered after treatment at the laboratory scale H₂O₂/UV plant. Figs. 4 to 7 show the trends of the ecological parameters (COD, TOC, pH, SAC) regarding the textile wastewater samples from measuring-place 1 (neutralization pool) taken every 10 minutes during the experiments' $H_2O_2/$ UV treatment. From the initial COD and TOC values, a wide variation in the pollution levels of the wastewater can be observed, reflecting very heterogeneous textile processes during company's production. The COD parameter varied from 1500 to 4000 mg/L and consequently, TOC from 300 mg/L to 750 mg/L. The use of oxidation treatment technology (UV/H₂O₂) successfully diminished the main parameters of interest, except for 4 samples (3, 4, 5 and 7), which were heavily charged with organic pollution and intense colour in the first place. In the case of sample Nr. 5 the COD

value after 60 minutes of treatment was still 1685 mg/L, over the limit value for discharge. A similar trend was found for the TOC parameter. The pH parameter had constantly decreased over the treatment-time and, reached a final value around 6 for all samples. The initial SAC values at the defined wavelengths (436, 525 and 620 nm), for all the tested samples, were spread and very high (up to 90) indicating intensive colour pollution. UV/H₂O₂ treatments, in most cases, efficiently reduced the absorbance and related SAC values, except for samples 3, 4, 5, and 7 where 82 %, 54.4 %, 61.5 % and 53.9 % decolouration at 436 nm were achieved. The intensive colour of wastewater reduces the transmission of UV light through the sample. No correlation was found between the production process on the sampling day and the characteristics of the previously-mentioned samples.



Fig. 4. COD trends for wastewater samples during the AOP treatment at measuring-place 1



Fig. 5. TOC trends for wastewater samples during the AOP treatment at measuring-place 1



Fig. 6. Trends of pH for wastewater samples during the AOP treatment at measuring-place 1



Fig. 7a-c. Trends of SAC values at three different wavelengths (436 nm, 525 nm and 620 nm) for wastewater samples during the AOP treatment at measuring-place 1

Sample	лЦ	SAC (m ⁻¹)			тос	COD
	рп	436	525	620	- 100	COD
Sample-1	6.4	7.1	0.9	0.4	6	6
Sample-2	6.2	6.4	0.3	0	14	52
Sample-3	6.3	14.1	5.4	3.6	75	588
Sample-4	6.0	26.9	13.7	6.7	200	1054
Sample-5	6.0	33.7	13.4	7.8	212	1685
Sample-6	6.2	11.8	4.4	2.4	26	248
Sample-7	6.0	24.5	10.3	6.8	121	1026
Sample-8	6.2	11.1	1.5	3.7	13	128
Sample-9	5.9	1.9	1.2	0.7	24	198
Sample-10	5.9	4.7	4.1	3.1	19	37
Sample-11	6.1	5.2	0.5	0.8	11	71
*	6.5-9	7.0	5.0	3.0	60	200

Table 3. H,O,/UV treatment efficiencies for wastewater samples at measuring-place 1

*Concentration limits of emission into water

The UV/H₂O₂ treatment efficiencies after 60 minutes for samples at measuring-place 1 are shown in Table 3. SAC values on average dropped to within a range of 73-82 % at all three wavelengths. The final decolouration efficiency after 60 minutes was almost equal to that after 30 minutes of treatment. The wastewater samples were more polluted but nevertheless, on average, we achieved the 50-70 % decolouration. The COD reduction was on average 84 %. TOC reduction was on average 86 %. Even at high COD and TOC loading rates considerable removal efficiencies were obtained for both parameters. Figs. 8 to 10a-c show the trends of ecological parameters (COD, pH, SAC) during the treatment of textile wastewater samples from measuring-place 2, taken every 10 minutes. The initial COD pollution level of the samples from this reservoir varied significantly but constantly decreased during UV/H2O2 treatment.

The wastewater samples from measuring-place 2 were not as dark coloured as the wastewater from measuring-place 1. UV/H₂O₂ treatment efficiency after 60 minutes for the samples at measuring-place 2 is shown in the Table 4. After one hour of treatment the SAC values on average, decreased for 82 %. It is interesting to note that the SAC values at 436 nm decreased under the limit of detection after 10 minutes of treatment. The TOC values were on average, 189 mg/L and 32 mg/L after treatment. For water samples from this measuring point there is more uniform tendency in COD decrease with treatment time. The COD reduction was on average 95 %.

In order to summarize the proposed UV/H_2O_2 treatment technology, all measured parameters were reduced to the legislation limit for discharge, being the majority of samples taken over the 3 month test



t/min

Fig. 8. COD trends for wastewater samples during AOP treatment at measuring-place 2



Fig. 9. Trends of pH for wastewater samples during AOP treatment at measuring-place 2



Fig. 10a-c: Trends of SAC values at three different wavelengths (436 nm, 525 nm and 620 nm) for wastewater samples during AOP treatment at measuring-place 2

Sample	n U	SAC (m ⁻¹)			тос	COD
	pn	436	525	620	- 100	COD
Sam ple- 1	6.4	1.1	4.2	3.1	75	351
Sam ple-2	10.2	0.1	0.1	0.4	41	227
Sam ple-3	6.7	9.7	3.1	1.5	9	6
Sample-4	6.6	9.8	3.5	2.1	1	10
Sam ple-5	6.7	0	0	0	7	55
Sam ple-6	11.9	4.6	0.03	0.5	58	66
*	6.5-9	7.0	5.0	3.0	60	200

Table 4. H₂O₂/UV treatment efficiency for wastewater samples at measuring-place 2

*Concentration limits of emission into water

period. Some samples were unsusceptible regarding oxidation treatment and exceeded the limit values of parameters for discharge. Nevertheless, with the implementation of simple treatment technology on-site, such as the proposed UV/H_2O_2 technology, the company will be able to reduce their expenses relating to the taxes for discharging their wastewater to local WWTP.

The influence of H_2O_2/UV treatment on the formation of persistent organohalogen compounds was studied on two real-wastewater samples from the above-mentioned textile company. The wastewaters polluted by the disperse and methal complex dyes, were taken directly from the dyeing machine. The obtained results are presented in Table 5, and show that the use of H_2O_2/UV treatment had no significant influence on the formation of PCDD/Fs. With additional HRGC/HRMS measurments we observed some dechlorination of polychlorinated biphenyls (PCBs) and debromination of polybrominated diphenylethers (PBDEs), which are less persistent compounds than PCDD/Fs.

As expected, according to our previous results, a considerable level of PCDD/Fs was found in those wastewater samples polluted with disperse dyes (Križanec *et al.*, 2005). The dominant PCDD/F congener in the disperse dyes wastewater sample is 2,3,4,6,7,8-HxCDF (Fig. 11), which contribute to a Toxic Equivalent (TEQ) using International Toxic Equivalency Factors (I-TEFs) (Bhavsar, 2008) of more than 85 %. Concentration of PCDD/F in wastewater with disperse dyes exceed the limit 0.3 ng TEQ/L as determined by the European regulation for wastewaters from incineration plants.

Simulation of processes taking place in central wastewater treatment plant in Maribor was realized in the laboratory in order to verify the behaviour of dioxins during such treatment, when wastewater is polluted with disperse dyes. Procedure includes the use of activated sludge as an adsorption agent and 1 %

solution of $Al_2(SO_4)_3$ as coagulation agent (Dos Santos, 2007).

The concentrations for all PCDD/Fs congeners in the water after coagulation/adsorption experiments were relative low. It is important to note, that the concentrations of PCDD/Fs in the samples after coagulation/adsorption experiments cannot be direct comparable with the other concentrations in Table 5, due to the dilution of the wastewater in the cases of the adsorption/coagulation experiments. However, sludge adsorption/coagulation experiments were found to be promising methods for the removal of PCDD/Fs and other organic contaminants from disperse dyes' wastewaters.

The concentrations of PCDD/F in the wastewater before and after treatment with H_2O_2/UV were comparable. It can be concluded that H_2O_2/UV processes under the conditions used in our experiments have no significant influence on the formation or degradation of PCDD/Fs congeners.

CONCLUSION

The results are promising and confirm the suitability of UV/H₂O₂ treatment for decolouration purposes regarding wastewater from this textile finishing company. From both sampling points, a significant reduction in TOC, COD and SAC parameters was achieved using the selected oxidation technology. The final wastewater quality was improved and its effluents mostly met the discharge limits. On the other hand, it was expected that the usage of universal treatment technology for a very complex textile wastewater was difficult to implement. The next steps in our investigation will include the separation of effluents in regard to their pollution levels. This approach will increase the treatability of effluents by UV/H₂O₂ treatment technology and, at the same time, increase reusability options as well.

The promotion of an integrated-approach to water resources and wastewater reclamation and reuse

	Concentration (ng/L)					
Congener/Group	Wastewater with disperse dyes	Wastewater with disperse dyes treated with H ₂ O ₂ /UV	Wastewater with metal complex dyes	W aste wat er with metal complex dyes tre at ed with H ₂ O ₂ /UV	Wastewater with disperse dyes after coagulation/ adsorbtion	
Tetrachlorodibenzo- <i>p</i> - dioxin (TCDD)	< 0.01	0.04	< 0.01	0.01	< 0.01	
Pentachlorodibenzo- <i>p</i> - dioxin(PeCDD)	0.02	0.03	< 0.01	< 0.01	< 0.01	
Hexachlor odibenzo- <i>p</i> - dioxin(HxCDD)	0.08	0.19	0.01	0.03	0.38	
Heptachlorodibenzo- <i>p</i> - dioxin (HpCDD)	0.20	< 0.01	0.01	0.05	0.78	
Octachlorodibenzo- <i>p</i> - dioxin (OCDD)	0.25	0.51	0.06	0.05	0.30	
Tetrachlodibenzofuran	0.15	1.02	< 0.01	0.06	0.24	
Pentachlodibenzofuran (PeCDE)	0.22	1.54	< 0.01	0.03	0.12	
Hexachlor odibenzo fur an (HxCDF)	3.77	3.05	< 0.01	0.08	0.11	
(HxCDF) Heptachlorodibenzofuran (HpCDF)	0.12	0.10	< 0.01	0.01	0.04	
Octachlorodibenzofuran (OCDF)	0.05	0.03	< 0.01	0.01	0.10	
2.3.7.8-TCDD	< 0.01	0.01	< 0.01	< 0.01	< 0.01	
1.2.3.7.8-PeCDD	< 0.01	0.01	< 0.01	< 0.01	< 0.01	
1,2,3,4,7,8-HxCDD	< 0.01	0.12	< 0.01	< 0.01	0.05	
1,2,3,6,7,8-HxCDD	0.01	0.06	< 0.01	< 0.01	0.04	
1,2,3,7,8,9-HxCDD	0.01	0.03	< 0.01	< 0.01	0.02	
1,2,3,4,6,7,8-HpCDD	0.14	0.58	0.01	0.02	0.70	
1,2,3,4,6,7,8,9-OCDD	0.25	0.51	0.06	0.05	0.30	
2,3,7,8-TCDF	< 0.01	0.07	< 0.01	0.01	< 0.01	
1,2,3,7,8-PeCDF	0.01	0.04	< 0.01	0.01	0.02	
2,3,4,7,8-PeCDF	0.01	0.04	< 0.01	0.01	< 0.01	
1,2,3,4,7,8-HxCDF	0.01	0.02	< 0.01	0.01	< 0.01	
1,2,3,6,7,8-HxCDF	0.04	0.01	< 0.01	0.01	< 0.01	
2,3,4,6,7,8-HxCDF	4.23	4.00	0.01	0.07	0.10	
1,2,3,7,8,9-HxCDF	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
1,2,3,4,6,7,8,-HpCDF	0.09	0.08	< 0.01	0.01	0.03	
1,2,3,4,7,8,9-HpCDF	< 0.01	0.01	< 0.01	< 0.01	0.01	
1,2,3,4,6,7,8,9-OCDF	0.05	0.03	< 0.01	0.01	0.10	
Sum TEQ-ITF	0.44	0.47	< 0.01	0.02	0.03	

Table 5. Mass-balance of PCDD/Fs in wastewater polluted with disperse and metal complex dyes treated with H,O,/UV processes

implementation on a larger scale, will also be strongly supported by the European Union (Bixio *et al.*, 2006), and will help the industry to reduce its expenses for wastewater treatment.

At this stage, the used UV/H_2O_2 treatment process does not produce water suitable for reuse. Hence, when

recycling is the ultimate target, a multi-step treatment system will be necessary. So, our further investigations will be oriented towards the elaboration of an efficient and cost-effective treatment train include, beside the oxidation treatment step, also membrane-filtration technologies.



Fig. 11. HRGC/HRMS selected ion monitoring (SIM) chromatogram of disperse dyes wastewater extract. Hexachloro dibenzofuran group with 2,3,4,6,7,8-HxCDF as dominant congener

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