Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20552

71 (2017) 95–106
April

Pretreatment of cosmetic wastewater by dissolved ozone flotation (DOF)

Piotr Robert Wiliński*, Piotr Paweł Marcinowski, Jeremi Naumczyk, Jan Bogacki

Faculty of Building Services, Hydro and Environmental Engineering, Warsaw University of Technology, Nowowiejska 20, 00-653 Warsaw, Poland, Tel. +48 (22) 234 74 82; emails: piotr.wilinski@is.pw.edu.pl (P.R. Wiliński), piotr.marcinowski@is.pw.edu.pl (P.P. Marcinowski), jeremi.naumczyk@is.pw.edu.pl (J. Naumczyk), jan.bogacki@is.pw.edu.pl (J. Bogacki)

Received 28 October 2016; Accepted 24 January 2017

ABSTRACT

Dissolved ozone flotation (DOF) treatment method was applied to oxidize soluble substances, i.e., emerging micropollutants that are not completely removed by dissolved air flotation (DAF) in cosmetic wastewater treatment. With the DOF method, solid particles float on the top of the treated solution, and soluble substances are oxidized by ozone. Twelve aluminium-based coagulants were used in the experiments: Al 6010, Al 3010, Al 3030, Al 3035, Al 1019, Al 2019, PAX XL19, PAX16, Flokor 1.3, Flokor 1S, Flokor 1.2a, and Megafloc. Of all the coagulants, the two with the highest efficiency were selected: Al 3010 and Al 6010. The results obtained by both treatment methods, DOF and DAF, show similar chemical oxygen demand (COD) removal 79.1% and 78.8%, respectively, and total suspended solids (TSS) removal 95.2% and 94.4%, respectively, for Brenntag 6010. For Brenntag 3010 removal rate of 81.3% and 81.0% COD was observed, and the same 96.3% TSS removal for both DAF and DOF methods. However, extended removal of micropollutants was observed in the DOF method. The headspace-solid phase microextraction-gas chromatography-mass spectrometry (HS-SPME-GC-MS) analysis was used to identify the compounds in wastewater and to evaluate the effectiveness of both methods that were used. The HS-SPME-GC-MS results confirmed that the DOF process with using coagulant Al 3010 had better removal efficiency compared with DAF. The removal rate of micropollutants including endocrine disruptors for DOF was 96.3% compared with 93.8% when using DAF treatment.

Keywords: Cosmetic wastewater; Dissolved air flotation; Dissolved ozone flotation; Gas chromatography-mass spectrometry; Endocrine disrupting compounds

1. Introduction

The most common physicochemical treatment methods applied in cosmetic wastewater are: coagulation with sedimentation [1,2], membrane processes [3], coagulation with dissolved air flotation (DAF) [4,5], electrocoagulation [6] and advanced oxidation processes (AOPs) as an additional treatment step [7]. Naumczyk et al. [8] observed that coagulation with $Al_2(SO_4)_3$ and pre-hydrolyzed aluminum coagulants in pH 7.0, and subsequent sedimentation result in up to 74.6% chemical oxygen demand (COD) removal. The most effective was a two-step process of coagulation with sedimentation (C/S) followed by photo-Fenton (PF) which resulted in 92.4% COD removal for optimal H_2O_2/Fe(II) doses of 435/45 mg/L. Another study [8], showed that the total effect of COD removal, including primary sedimentation and coagulation, ranged from 63.9 to 90.6% when using aluminium coagulant. In this study, the removal of galaxolide and tonalide was also measured with the first being in 87.3%–92.2% and the latter in range 86.5%–95.8%. Boroski et al. [6] obtained 92% of COD removal after 90 min of treating of cosmetic wastewater by using electrocoagulation at pH 6.0 with ferrous electrodes and 763 $A*m^{-2}$ current density. Michel et al. [9] observed 75.6% COD removal efficiency from cosmetic wastewater using a DAF full scale unit with the capacity of 4 m^3/h wastewater flow and $FeCl_3$ as coagulant for the process at pH 7.5. They also observed an

---

* Corresponding author.

1944-3994/1944-3986

increase in biodegradability by using DAF from a 0.14 to a 0.40 (biochemical oxygen demand [BOD_5]/COD ratio). Despite the high efficiency of abovementioned methods for COD removal, it is important to note that they do not completely remove endocrine disrupting chemicals (EDCs) and pharmaceutical and personal care products (PPCPs).

Currently, flotation with ozone, referred to as DOF, combines two methods of treatment, DAF and ozonation, in one treatment unit. Ozone is used instead of air with the DOF method. The substitution of the carrier gas (from air to ozone) makes it possible to obtain two processes in one treatment unit: the separation of solids and emulsions by gas bubbles (same as in conventional flotation) and oxidation of soluble organic compounds using a strong oxidizing agent – ozone. Synergy of these two processes (separation and oxidation) leads to a better treatment effect. Flotation with ozone has several positive effects such as decreasing the dosage of coagulants and flocculants, the removal of pathogens, improvement in wastewater biodegradability and the removal of micropollutants (EDCs and PPCPs). As the generation of ozone gas has become less expensive, this method might be of interest for many different industrial wastewater sectors for the enhancement the micropollutants removal. Gottschalk et al. [10] reported that the typical energy consumption of 10 kWh/kgO_3 generated whereas some researchers discovered novel ozone generation methods with low energy consumption of 2.5 kWh/kgO_3 generated. However, improvement in energy consumption is still needed.

Until now, the research on conventional flotation with ozone as a feeding gas was used for municipal wastewater [11–14], livestock wastewater [15] and as a method of algae removal [16,17]. In the treatment of municipal wastewaters, DOF was compared with traditional mechanical diffuser ozone injection [11]. With DOF at a 6.1 mgO_3/L ozone dose in a pH 6.55 and temperature of 20°C, the following removal rates were obtained: 86.9% turbidity, 81% total suspended solids (TSS), 72.6% colour, 82.4% BOD_5 and 92% total phosphorus (T-P). However, low removal efficiencies of 42.9% and 33.4% were obtained for COD and total Kjeldahl nitrogen (TKN), respectively. The authors noticed a complete coliform bacteria removal from initial 860 MPN/mL concentration detected in raw wastewater. The DOF method removed all bacteria with an ozone concentration of 2.4 mg/L and higher [11].

Jin et al. [12] compared the DOF method with an existing tertiary treatment by chlorine for water reuse in a wastewater treatment plant. The effect obtained with DOF, with ozone dose of 1.6 mgO_3/L and powdered activated carbon 50 mg/L, indicates a 71%–85% colour removal, compared with 14%–57% removal by chlorine. The DOF method produced a total odour removal, as compared with conventional chlorine treatment that produced a slightly uncomfortable smell. Moreover, DOF was 4–6 times faster, compared with DAF, which decreases significantly the hydraulic retention time of wastewater. Other parameters, such as BOD_5, COD, TSS, turbidity and coliforms, were decreased at a similar removal rate for both DOF and DAF and by chlorination. Lee et al. [13] compared DAF and DOF efficiency for treatment of secondary effluent from a wastewater treatment plant. The DOF system was applied for effluent in a secondary wastewater treatment plant, and the results were compared with those of the DAF system. Long-term pilot plant trials (6 months) showed that the ozone dose of 2.5 mgO_3/L used in the flotation process enhanced 13.6% of TSS, and 20% of turbidity removal rates; 7.7% of T-P and 3.3% of TKN were enhanced in their removal rates: 7.4% more COD was removed by the DOF system than by the DAF system. The enhancement of the removal rates of colour and coliform bacteria were even more evident, with an extra 41.5% of colour and 54% of coliform bacteria removal when DOF method was applied.

In another study, Lee et al. [15] used ozone in doses of 200–250 mgO_3/L in a DAF unit for the pretreatment of livestock wastewater. The results from this industrial scale experiment showed 81.1% COD removal, and 92% TSS removal. The highest removal rate was obtained for T-P 94.6% and the lowest, 67.7%, for TKN.

Kim et al. [18] used dissolved ozone flotation–pressurized ozone oxidation (DOF–PO_2) after sequential batch reactor (SBR) treatment to fulfill required the parameters as the separate SBR process did not reach discharge limits. COD was removed from 421 to 171 mg/L (by 59.4%) and a further 76% removal to 41 mg/L after the DOF–PO_2 process. The overall removal rate was over 90% with the DOF–PO_2 process. The BOD of 185.3 mg/L was decreased to 31.5 mg/L by the SBR process. The effluent in the SBR process was further decreased to a BOD of 12.2 mg/L (93.4% removal rate), which fulfilled the discharge quality standard of 20.0 mg/L.

Jin et al. [14] studied the influence of ozone dosage using the DOF method for tertiary wastewater treatment. The dose of ozone 0.8 mg/L showed the best TOC removal rate of 58%, and the rate did not increase when applying higher ozone doses, up to 1.6 mg/L. However, the best disinfection results were obtained with the highest dose of ozone (1.6 mg/L) for *Escherichia coli* removal. The highest colour removal (90%) and highest UV_{254} absorption decrease (60%) was obtained for the highest ozone dose of 1.6 mg/L.

Ya-Ling et al. [16,17] applied the DOF method to assess its ability of harvesting algae from water. A small amount of ozone of 0.2–0.5 mgO_3/mg applied to an algae biomass as a feeding gas produced a positive effect of algae cells agglomeration and better flotation on the top of the solution afterwards.

A laboratory-scale DAF/DOF pressure vessel was used to compare the treatment effect of cosmetic wastewater treatment by flotation with and without ozone. To the best of authors' knowledge, this is a novel approach and has not been done before. The study was aimed: (i) to measure overall treatment effect by DAF and DOF methods and (ii) to measure the removal of micropollutants using headspace-solid phase microextraction-gas chromatography-mass spectrometry (HS-SPME-GC-MS).

2. Materials and methods

2.1. Sample collection and determination methods

Cosmetic wastewater samples were collected from an equalization tank at a cosmetic factory that manufactures primarily lipsticks, serum, creams and UV filters. The following parameters were determined in the raw wastewater samples according to the EN or ISO Standards: COD, COD_{dis} (for a sample filtered with 0.45 μm filter; ISO 6060), TSS (EN 872), pH (EN ISO 10523), petroleum ether extractable organics (Standard Methods) and anionic surfactants (EN 903).

2.2. Coagulation

The experiments were carried out with 1 L wastewater samples. For the coagulation step, 13 different coagulants were used in a jar test. The following aluminum-based coagulants were used: Brenntag coagulants – 6010, 3010, 1019, 2019, 3030, and 3035; from Kemipol – PAX19XL and PAX16; from Dempol-Eco – Flokor 1.3, Flokor 1S, and Flokor 1.2a; Megafloc; and one iron-based coagulant, Brenntag Brentafloc F3. Coagulants' parameters are presented in supplementary data, Table S1. For each coagulant used, the applied doses varied from 0.25 to 1.25 mL/L. After the addition of the coagulants, a pH correction to 7.0 was made, with 1 M HCl or 3 M NaOH. The pH 7.0 was determined to be optimal in the preliminary jar test experiments. Reagents were added during a 5 min fast stirring (400 rpm, revolutions per minute). Afterwards 12 mg/L with concentration of 0.05% of selected anionic flocculant AN913SH was dosed with a slow 30 s stirring at 40 rpm (the optimal dose was set during the initial experiments). After observed flocculation, the wastewater was transferred into the laboratory DAF/DOF unit, with the hose, to avoid breaking the agglomerates.

2.3. Dissolved ozone flotation (DOF)

Wastewater sample was saturated with ozone under 4 bar pressure in the laboratory DOF unit of 1 L operational capacity (cylindrical, 56 mm inner diameter and 1,080 mm height). The DOF procedure was applied according to the laboratory DAF bench-scale testing method [19]. Ozone gas was produced by an Atlas 30 (Absolute Ozone®) ozone generator with a maximum capacity of 30 g/h from bottled 99.9% pure oxygen. Ozone gas was injected to pressure vessel at 4 bar pressure during a 2 min purging with gas flow of 240 L/min. Afterwards, the flotation cell was gently stirred and placed in the horizontal position to obtain the highest gas–liquid interphase surface exchange area. After 5 min retention, the flotation cell was emptied with a constant pressure of 4 bar. Wastewater was then transferred to the separation reactor in which the treated wastewater was separated from the sludge under pressure lowered to the atmospheric pressure. Samples for analysis were taken from the sampling port from the bottom of the flotation chamber after 3 min, when sludge was floated on the top.

Dissolved ozone concentration was measured in the flotation cell by an amperometric microsensor type A (AMT Analysenmesstechnik GmbH). Ozone concentration was measured in the water phase during 1,100 s of dissolution. Before the wastewater experiments, the ozone dissolution rate was measured in distilled water at 20°C. The layout of the laboratory DAF unit for treatment process is presented in Fig. 1. Ozone off-gas from flotation cell was sent to ozone destruction unit with a Carulite bed (cylindrical, 110 mm inner diameter, total volume 4.4 L).

2.4. Dissolved air flotation (DAF)

DAF procedure followed the same steps as DOF procedure described above with the only difference being the use of air instead of ozone. Samples for determination of COD were taken 3 min after the completion of the flotation process. The experiments were made in room temperature (ca. 20°C).

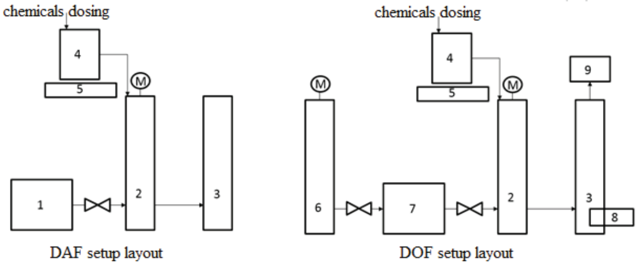

Fig. 1. Experimental setup of laboratory DAF and DOF unit.
Note: 1 – compressor, 2 – pressure vessel, 3 – flotation cell, 4 – coagulation jar, 5 – mixer, 6 – oxygen bottle, 7 – ozone generator, 8 – dissolved ozone sensor, 9 – ozone off gas destruction unit, and M – manometer.

Table 1
Typical values of selected parameters in cosmetics wastewater [21]

Parameter	Typical values	Value
COD, mgO_2/L	1,089–77,600	2,680
COD_{dis}, mgO_2/L	512–2,296	1,760
BOD/COD	0.132–0.462	0.18
TSS, mg/L	57.5–41,866	268
Anionic surfactants, mg/L	<0.2–33	260
Substances extracted by petroleum ether, mg/L	463–897	97

2.5. Chromatographic analysis

Identification and quantitative analyses of the organic components in the raw wastewater samples treated with DAF and DOF processes were performed using HS-SPME-GC-MS. The HS-SPME-GC-MS procedure was previously described by Liu et al. [20]. Microsorption was performed using 10 mL of the sample at 75°C for 15 min with a Supelco PDMS 100 μm fibre. Desorption was performed in a chromatograph injector at 280°C for 2 min. The analysis was performed with a Finnigan GCQ chromatograph with a Restek RTX-5MS and 30 m, 0.25 mm and 0.25 μm column. The following temperature program was applied: 50°C for 2 min and 5°C min^{-1} up to 300°C before maintaining at 300°C for 10 min. A mass spectrometer was used as a detector in the Electron Ionization (EI) mode, at 70 eV and 185°C across a range of 50–650 amu. Identification of compounds was based on two factors. Firstly, it was knowledge of the production profile and specific compounds used during the production process. Secondly, it was comparison of obtained mass spectra with library of our mass spectrometer and with NIST 98.L published spectra. Xcalibur Qual Browser v.1.2 was used for data acquisition and handling.

3. Results and discussion

3.1. Characteristics of raw wastewater

Raw wastewater samples were compared with typical values occurring in cosmetic wastewater (Table 1), which were described by Bogacki et al. [21]. A BOD/COD ratio (0.18) of wastewater was very low. COD was 2,680 mg/L, and COD_{dis} was of 1,760 mg/L. These values were not high compared with typical values observed in cosmetic wastewater with an average COD of 7,984 mg/L and median 3,800 mg/L. The pH value of raw wastewater was 7.54, which was very close to the average 7.21. The temperature was 19.2°C. The amount of TSS was 268 mg/L with very low amount of 0.5 mL/L ESS (easily settleable solids). This amount was low compared with an average of 3,252 mg/L and a median of 424.5 mg/L for typical cosmetic wastewater [21]. The wastewater sample was also characterized by a very high concentration of anionic surfactants for this kind of wastewater with a value of 260 mg/L where typical values are in the range of 0.2–33.0 mg/L. However, Michel et al. [9] observed also high anionic surfactants concentration for cosmetics wastewater with an average value 245 mg/L. Substances extracted by petroleum ether were on the low level of 97 mg/L, where the average for cosmetic wastewater is typically above 400 mg/L.

There were 76 peaks detected. The analysis of peaks led to identification of 53 compounds. There were a few emerging pollutants that should be marked as potential risk for aquatic environment: 3-(4-*tert*-butylphenyl)-2-methylpropanal (lilial) – lotion, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[*g*]-2-benzopyran (galaxolide1) and 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[*g*]-2-benzopyran (galaxolide2), both polycyclic musks, which are classified as endocrine disrupting compounds [22]. The other detected compounds were fragrances, i.e., 1-methyl-4-(1-methylethenyl)cyclohexene (*p*-mentha-1,8-diene), (isolimonene), 3,7,7-trimethylbicyclo[4.1.0]hept-3-ene (3-carene) or 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (beta-lanone); cosmetics bases, i.e., 2,2-dimethyl-3-methylenebicyclo[2.2.1]heptane (camphene) or hexadecamethylheptasiloxane; solvents, i.e., 2,2-dimethylhexane or decamethyltetrasiloxane; and UV filters, i.e., 2-ethylhexylester,3-(4-methoxyphenyl)-2-propenoic acid (Parsol MCX).

3.2. Ozone dissolution in distilled water and wastewater

The flotation was conducted for a duration of 5 min, and theoretically, 11 mgO_3/L might be dissolved during this period (in pure distilled water). However, due to organic matter present in wastewater, ozone is immediately consumed before it is dissolved in wastewater. Linear dissolution rate was observed during 1,100 s of experiment (Fig. 2).

The dissolution of ozone in water is a process that occurs very slowly, far slower than the dissolution of air in water [10]. What is more, as a result of various reactions occurring in the aqueous phase between the ozone and therein contained pollutants, ozone concentration could even decrease. Changes in the concentration of dissolved ozone in the aqueous phase mean that the equilibrium has not been reached. On the other hand, based on the thermodynamical data, time required to reach the equilibrium is far too long to perform the experiment, because of that non-equilibrium experiment has been performed.

Ozone gas can be dissolved up to 11 mg/L of ozone gas under 4 bar pressure (Fig. 2). However, ozone in wastewater is immediately consumed for oxidation processes. There was no residual ozone detected in wastewater after flotation. That confirms that two main processes occur in wastewater: dissolution of O_2/O_3 in wastewater and direct oxidation of pollutants contained in wastewater by ozone and created radicals.

3.3. Wastewater treatment with DAF and DOF

Brenntag 3010 and 6010 coagulants were selected for the flotation experiments. DOF and DAF treatment efficiency is shown in Table 2. The selection was done during preliminary experiments, and the choice was based on the lowest COD value (COD was measured for effluent taken from the top of the graduated cylinder), turbidity of pretreated wastewater and the volume and quality of sludge generated. Results of the experiments are shown in the supplementary data. During the jar tests, the optimal dose of coagulants (3010 and 6010) was set at 1.0 mL/L. After coagulation, wastewater samples

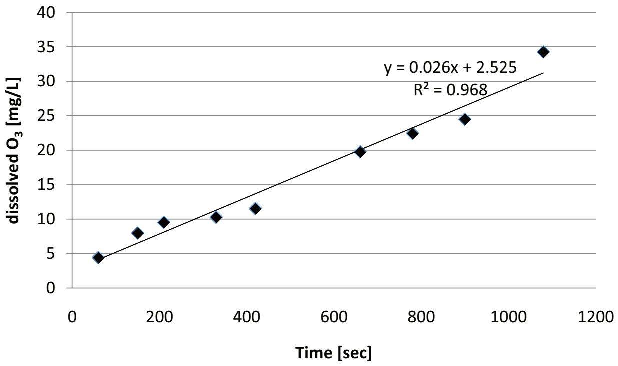

Fig. 2. Concentration of ozone in 4 bar pressure vessel after time in 20°C distilled water.

Table 2
Characteristics of raw wastewater and after DAF and DOF treatment

Parameter	Raw wastewater	Brenntag 6010		Brenntag 3010	
		DAF	DOF	DAF	DOF
COD, mgO_2/L (% removal)	2,680 (–)	567 (78.8)	559 (79.1)	509 (81.0)	501 (81.3)
TSS, mg/L (% removal)	268	15 (94.4)	13 (95.2)	10 (96.3)	10 (96.3)
Anionic surfactants, mg/L (% removal)	260 (–)	27 (89.6)	24 (90.8)	7 (97.3)	11 (95.8)
Substances extracted by petroleum ether, mg/L (% removal)	97 (–)	12 (87.6)	10 (89.7)	10 (89.7)	7 (92.8)

were transferred to a DAF or DOF pressure vessel. The treated wastewater was then taken for the analyses. The results obtained for both DOF and DAF pretreatment were very similar: 79.1% and 78.8% COD removal and 95.2% and 94.4% TSS removal for Brenntag 6010 and 81.3% and 81.0% COD and 96.3% TSS removal for Brenntag 3010 (Figs. 3 and 4). The results were close to the results obtained by Michel et al. [9] that showed a 75% COD removal efficiency when using PIX 111 and El-Gohary et al. [4] who observed 77.5% COD removal from personal care products wastewater when using $Al_2(SO_4)_3$. Smogarzewski et al. [5] obtained COD removal efficiency in range from 45.6% up to 97.6%. In this case high COD removal above 95% might be explained by much higher amount of TSS (1,455 mg/L) and low COD_{dis} (960 mg/L) in raw wastewater.

Anionic surfactants removal was higher when Brenntag 3010 was used. With DAF, 90.0% of the anionic surfactants were removed with Brenntag 6010 and 97.4% with Brenntag 3010 (Fig. 5). DOF allowed removal of 91.1% for Brenntag 6010 and 96.0% for Brenntag 3010. Substances extracted by petroleum ether were removed with 87.6% efficiency for DAF and 89.7% with DOF by using Brenntag 6010 and with 89.7% efficiency for DAF and 92.8% with DOF by using Brenntag 3010. The removal efficiencies obtained in DAF and DOF were at a similar level for these two parameters. This might be related to the ozone dissolution rate that was in low range of 0.7%–1.8% measured during initial ozone dissolution experiments in distilled water. Ozone reacts faster with certain aromatic and aliphatic compounds, i.e., carrying hydroxyl or amine group that was observed by Gottschalk et al. [10]. Therefore, chromatographic analysis was made to compare the effect of the DAF flotation and DOF method for removing micropollutants.

Removal efficiency of substances identified by HS-SPME-GS-MS was based on the difference in the peak's area in raw wastewater and after treatment with DAF and DOF. The chromatograms of raw and DAF or DOF treated wastewater samples are shown in Fig. 6.

The main compound was dodecamethylcyclohexasiloxane, which is cosmetic base. DAF and DOF removed more than 99.0% of the compound using both for Brenntag 3010 and 6010. The chromatograms from DAF and DOF with Brenntag 3010 showed total removal of 12 from 53 compounds, which were not detected after both processes, which were: 2,2-dimethylhexane, decamethyltetrasiloxane, unknown, dodecamethylpentasiloxane, 6-methylundecane, 2,3,4-trimethylheptane, tetradecamethylhexasiloxane, 2,4,6,8-tetramethylcyclotetrasiloxane, hexadecamethylheptasiloxane, and 3a,6,6,9a-tetramethyldodecahydronaphtha[2,1-*b*]furan (Ambrox). The other 41 compounds were removed with higher efficiency by DOF method compared with DAF. The biggest differences were observed for 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[*g*]-2-benzopyran

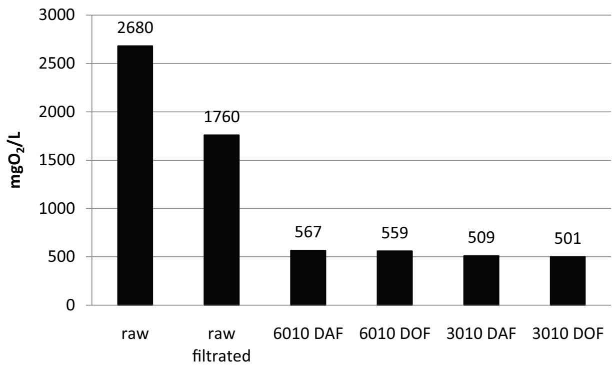

Fig. 3. COD in raw and DAF/DOF treated wastewater and after treatment by DAF and DOF method with coagulants 6010 and 3010.

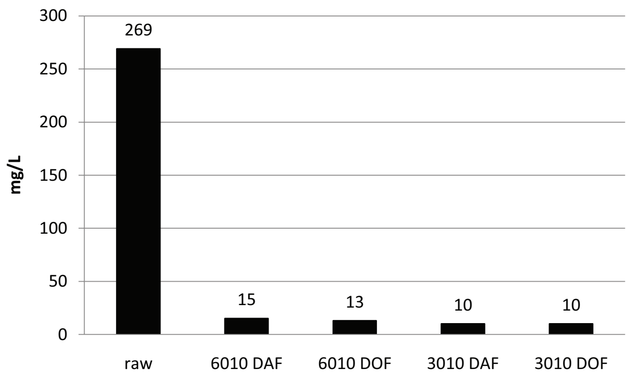

Fig. 4. TSS in raw and DAF/DOF treated wastewater with coagulants 6010 and 3010.

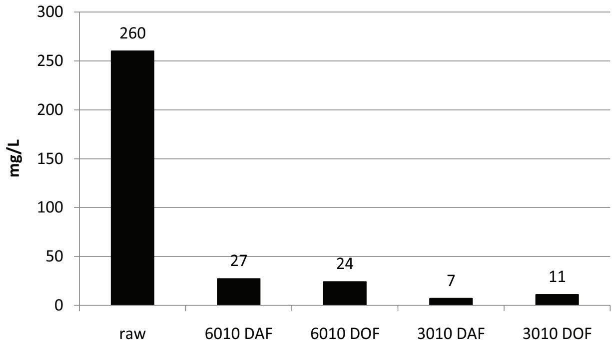

Fig. 5. Surfactants in raw and DAF/DOF treated wastewater with coagulants 6010 and 3010.

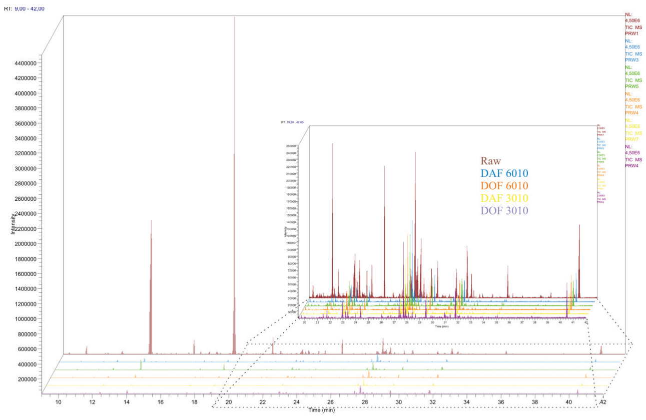

Fig. 6. Chromatograms of PPCPs removal by DAF and DOF wastewater treatment.

(galaxolide2) not detected after DOF and 48.7% removal after DAF; 2,5-dimethyl-3-vinyl-1,4-hexadiene (santolina triene) not detected after DOF and 52.3% removal after DAF; 2,2-dimethyl-3-methylenebicyclo[2.2.1]heptane (camphene) not detected after DOF and 58.8% removal after DAF. Only 3,7,7-trimethylbicyclo[4.1.0]hept-3-ene (3-carene) was removed more efficiently by using DAF (not detected) as compared with DOF (92%). All results for DAF and DOF using Brenntag 3010 are shown in Table S2.

The chromatograms from DAF and DOF with Brenntag 6010 showed a total removal of 10 of the 53 compounds, which were not detected after both processes. These compounds were: 2,2-dimethylhexane, decamethyltetrasiloxane, unknown, dodecamethylpentasiloxane, 6-methylundecane, 2,3,4-trimethylheptane, tetradecamethylhexasiloxane and 2,4,6,8-tetramethylcyclotetrasiloxane. For 11 of the 43 compounds better removal rate was obtained by using DAF as compared with DOF. It concerns the following chemical compounds: decamethylcyclopentasiloxane,1-(3-methylbutyl)cyclopentene, dodecamethylcyclohexasiloxane, cyclodecane, nonylester 3-cyclopentylpropionic acid, 2-(phenylmethylene)-octanal (alpha-hexylcinnamalaldehyde), 1-methylethylester tetradecanoic acid (isopropyl myristate), oxacycloheptadec-8-en-2-one (ambrettolid), 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[*g*]-2-benzopyran (galaxolide1), 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[*g*]-2-benzopyran (galaxolide2) and 1-ethyethylester hexadeconoic acid (isopropyl palmitate). The other 32 compounds were removed with a higher efficiency by the DOF method as compared with DAF. The biggest differences were observed for 3a,6,6,9a-tetramethyldodecahydronaphtha[2,1-*b*]furan (Ambrox) not detected after DOF and 26.1% removal after DAF; 2,5-dimethyl-3-vinyl-1,4-hexadiene (santolina triene) not detected after DOF and 32.8% removal after DAF; and 2,2-dimethyl-3-methylenebicyclo[2.2.1]heptane (camphene) not detected after DOF and 38.8% removal after DAF. Total removal of micropollutants from raw wastewater was at high level for both processes and for both coagulants, and entire peaks area decreased by 93.5% for DAF and 93.0% for DOF with Brenntag 6010 and by 93.8% for DAF and 96.3% for DOF with Brenntag 3010. All results from DAF and DOF using Brenntag 6010 are shown in Table S3. Several studies conducted by Carballa et al. [23] showed efficiency in the removal of fragrances by conventional aerobic treatment plant between 70% and 90% (88% removal of galaxolide and 90% of tonalide), and the removal efficiency for galaxolide in this study was 100% (for galaxolide2). Carballa et al. [24] used flotation to study the removal of selected PPCPs from urban wastewater. Musks were removed at the highest rate (35%–60%), followed by pharmaceutical compounds removed at a lower rate (10%–50%). In another study, Carballa et al. [25] used ozonation for sludge pretreatment and stabilization before anaerobic treatment and studied PPCPs removal. More than 60% removal of galaxolide and tonalide was observed and a lower efficiency for some pharmaceuticals, i.e., ibuprofen 20%–50% and ~20% of iopromide. Monsalvo et al. [3] observed high efficiency (>99.9%) in removing trace organic compounds using a full-scale membrane bioreactor with the presence of some trace amount of fragrances in the permeate: bicycle-4,10-hept-2-ene-3,7-dimethyl; 2-phenylethanolphenethyl (a floral odour); eucalyptol (a spicy aroma and taste); 1,6-octadien-3-ol-3,7-dimethyl synthetic linalool (a thick green sweet wood green flavour); and 1-undecanol (a citrus-like odour).

Ozonation is considered by Esplugas et al. [26] as one of the most efficient methods to remove EDCs and PPCPs from water. For some pharmaceuticals 100% removal rate was reached when treatment conditions were optimal. However, most of the experiments were carried out with distilled, drinking, Milli-Q or deionized water, not with industrial wastewaters as in this study.

Proper selection of coagulant and addition of ozone to flotation gave ability to obtain high EDCs removal in comparison with existing studies of other authors.

4. Conclusions

The pretreatment of cosmetic wastewater by DAF and DOF showed that the removal of COD, TSS, surfactants and substances extracted by petroleum ether was at a similar level with a negligible difference to the advantage of DOF. HS-SPME-GC-MS analysis showed that the highest removal of micropollutants was observed for the DOF method with the coagulant Brenntag 3010 leading to 96.3% removal of all micropollutants. Three compounds from EDCs list [22]: (4-*tert*-Butylphenyl)-2-methylpropanal (lilial) – lotion, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[*g*]-2-benzopyran (galaxolide1) and 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[*g*]-2-benzopyran (galaxolide2) were removed with much higher efficiency when using DOF method 87.7%, 64.9% and 100%, respectively, as compared with DAF efficiency: 64.8%, 42.2% and 48.7%. Results showed a very efficient removal of emerging pollutants (which are potentially harmful substances) from EDC list with the use of DOF method.

HS-SPME-GC-MS analysis provided more detailed treatment efficiency results when compared with standard measured base factors like COD, TSS or surfactants, and should be considered as important tool for assessment of technology and efficiency of the processes.

The removal effects for COD, TSS, surfactants and substances extracted by petroleum ether and PPCPs should be enhanced by using more efficient ozone dissolution system with micro and nanobubbles instead of pressurized vessel.

Acknowledgement

The authors gratefully acknowledged the financial support provided by the Faculty of Environmental Engineering (grant no. 504M/1110/0007/000 "Application of micro and nanoflotation with ozone for industrial wastewater treatment in cosmetics industry") and scholarship no. 111 granted from The Office of the Marshal of the Mazowieckie Voivodeship in Warsaw called: Science development – region development – scholarships and accompanying support for Mazovian PhD fellows (8.2.2. PO KL).

References

[1] J. Bogacki, J. Naumczyk, P. Marcinowski, M. Kucharska, Treatment of cosmetic wastewater using physicochemical and chemical methods, Chemik, 65 (2011) 94–97.

[2] J. Naumczyk, J. Bogacki, P. Marcinowski, P. Kowalik, Cosmetic wastewater treatment by coagulation and advanced oxidation processes, Environ. Technol., 35 (2014) 541–548.

[3] V.M. Monsalvo, J. Lopez, A.F. Mohedano, J.J. Rodriguez, Treatment of cosmetic wastewater by a full-scale membrane bioreactor (MBR), Environ. Sci. Pollut. Res. Int., 21 (2014) 12662–12670.

[4] F. El-Gohary, A. Tawfik, U. Mahmoud, Comparative study between chemical coagulation/precipitation (C/P) versus coagulation/dissolved air flotation (C/DAF) for pre-treatment of personal care products (PCPs) wastewater, Desalination, 252 (2010) 106–112.

[5] M. Smogarzewski, P. Marcinowski, J. Bogacki, J. Naumczyk, Application of coagulation and dissolved air flotation for cosmetic wastewater treatment, J. Civ. Eng. Environ. Arch., 62 (2015) 369–381.

[6] M. Boroski, A.C. Rodrigues, J.C. Garcia, L.C. Sampaio, J. Nozaki, N. Hioka, Combined electrocoagulation and TiO_2 photoassisted treatment applied to wastewater effluents from pharmaceutical and cosmetic industries, J. Hazard. Mater., 162 (2009) 448–454.

[7] P. Marcinowski, J. Bogacki, J.H. Naumczyk, Cosmetic wastewater treatment using the Fenton, photo-Fenton and H_2O_2/UV processes, J. Environ. Sci. Health., Part A, 49 (2014) 1531–1541.

[8] J. Naumczyk, P. Marcinowski, J. Bogacki, P. Wiliński, Cosmetic wastewater treatment by coagulation, Arch. Environ. Prot., 15 (2013) 873–891.

[9] M. Michel, T. Siwiec, M. Tytkowska, L. Reczek, Analysis of flotation unit operation in coagulation of wastewater from a cosmetic factory, Przem. Chem., 94 (2015) 2000–2005.

[10] C. Gottschalk, J.A. Libra, A. Saupe, Ozonation of Water and Waste Water, Willey-WCH, New Jersey, USA, 2009, pp. 13–26.

[11] B.H. Lee, W.C. Song, B. Manna, J.K. Ha, Dissolved ozone flotation (DOF) – a promising technology in municipal wastewater treatment, Desalination, 225 (2008) 260–273.

[12] P.K. Jin, X.C. Wang, G. Hu, A dispersed-ozone flotation (DOF) separator for tertiary wastewater treatment, Water Sci. Technol., 53 (2006) 151–157.

[13] B.H. Lee, W.C. Song, H.Y. Kim, J.H. Kim, Enhanced separation of water quality parameters in the DAF (dissolved air flotation) system using ozone,Water Sci. Technol., 56 (2007) 149–155.

[14] X. Jin, J. Pengkang, W. Xiaochang, A study on the effects of ozone dosage on dissolved-ozone flotation (DOF) process performance, Water Sci. Technol., 71 (2015) 1423–1428.

[15] B.H. Lee, W.C. Song, High Concentration of Ozone Application by the DAF (Dissolved Ozone Flotation) System to Treat Livestock Wastewater, WIT Transactions on Ecology and the Environment, Vol. 95 (2006) pp. 561–569.

[16] C. Ya-Ling, J. Yu-Chuan, L. Guan-Yu, H. Shih-Hsin, Y. Kuei-Ling, C. Chun-Yen, C. Jo-Shu, L. Jhy-Chern, L. Du-Jong, Dispersed ozone flotation of *Chlorella vulgaris*, Bioresour. Technol., 101 (2010) 9092–9096.

[17] C. Ya-Ling, J. Yu-Chuan, L. Guan-Yu, T. Pei-Wen, H. Shih-Hsin, Y. Kuei-Ling, C. Chun-Yen, C. Jo-Shu Chang, L. Jhy-Chern, C. Wen-Ming, L. Duu-Jong, Harvesting of *Scenedesmus obliquus* FSP-3 using dispersed ozone flotation, Bioresour. Technol., 102 (2011) 82–87.

[18] J.H. Kim, H.S. Ki, B.H. Lee, Combination of sequential batch reactor (SBR) and dissolved ozone flotation-pressurized ozone oxidation (DOF-PO) processes for treatment of pigment processing wastewater, Environ. Eng. Res., 16 (2011) 97–102.

[19] L.K. Wang, N.K. Shammas, W.A. Selke, D.B. Aulenbach, Flotation Technology, Handbook of Environmental Engineering, Vol. 12, Humana Press, Springer Science, New York, USA, 2010.

[20] H. Liu, L. Liu, Y. Xiong, X. Yang, T. Luan, Simultaneous determination of UV filters and polycyclic musks in aqueous samples by solid-phase microextraction and gas chromatography – mass spectrometry, J. Chromatogr. A, 1217 (2010) 6747–6753.

[21] J. Bogacki, P. Marcinowski, P.R. Wiliński, J. Naumczyk, Cosmetics wastewater characteristics, Gas, Water and Sanitation Technique, 90 (2016) 8–13.

[22] TEDX List of Potential Endocrine Disruptors. Available at: http://endocrinedisruption.org/endocrine-disruption/tedx-list-of-potential-endocrine-disruptors/overview

[23] M. Carballa, F. Omil, J.M. Lema, M. Llompart, C. Garcıa-Jares, I. Rodrıguez, M. Gomez, T. Ternes, Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant, Water Res., 38 (2004) 2918–2926.

[24] M. Carballa, G. Manterola, L. Larrea, T. Ternes, F. Omil, J. Lema, Influence of ozone pre-treatment on sludge anaerobic digestion: removal of pharmaceutical and personal care products, Chemosphere, 67 (2007) 1444–1452.

[25] M. Carballa, F. Omil, J.M. Lema, Removal of cosmetic ingredients and pharmaceuticals in sewage primary treatment, Water Res., 39 (2005) 4790–4796.

[26] S. Esplugas, D.M. Bila, L.G.T. Krause, M. Dezotti, Ozonation and advanced oxidation technologies to remove disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents, J. Hazard. Mater., 149 (2007) 631–642.

Supplementary data

Tables S1
Parameters of applied coagulants

Parameter	Coagulants												
	PAX16	PAX19XL	Al 6010	Al 3010	Al 1019	Al 2019	Al 3030	Al 3035	Flokor 1S	Flokor 1.2a	Flokor 1.3A	Brentafloc F3	Megafloc
Al_2O_3, %	15.5 ± 0.4	16.0 ± 0.9	13.5 – 14.5	>18.9	23.0 – 24.2	23.0 – 24.2	>17.01	>17.0	22.6 ± 0.9	22.6 ± 0.9	21.6 ± 0.9	–	No data available
Al^{3+}, %	8.2 ± 0.2	8.5 ± 0.3	no data	>10.0	12.2 – 12.8	12.2 – 12.8	>9.0	>9.0	12 ± 0.5	12 ± 0.5	11.5 ± 0.5	–	
Fe^{3+}, %	–	–	–	<0.02	–	–	–	–	–	–	–	12.8 – 14.0	
Chlorides, %	8.0 ± 2.0	5.5 ± 0.5	8.0 – 14.0	<6.5	7.0 – 11.0	7.5 – 9.5	<6.0	<6.0	9.0 ± 0.5	6.5 ± 0.5	8.5 ± 0.5	26 – 28	
Density, kg/m^3	1,250 – 1,280	1,220 ± 20	1,270 – 1,300	<1,260	1,310 – 1,390	1,310 – 1,370	1,200	1,150 – 1,250	1,300 ± 0.05	1,290 ± 0.05	1,300 ± 0.05	1,350 – 1,500	
pH	<1	4.0 ± 0.5	1.5 – 2.5	>4.1	3.1 – 3.9	3.1 – 3.9	3.8	3.7	3.5 ± 0.5	4.2 ± 0.5	3.5 ± 0.5	<1	
Alkalinity, %	<40	85 ± 5	>60	>70	80 – 90	80 – 90	>70	>90	80 ± 5	80 ± 5	80 ± 5	–	

Table S2
Chromatographic data for raw wastewater and wastewater after DAF and DOF treatment with coagulant Brenntag 3010

Name of the identified compound	Peak area for raw wastewater	Function	Peak area for DAF (% removal)	Peak area for DOF (% removal)
2,2-Dimethylhexane	11,498	Solvent	n.d.	n.d.
Unknown	11,248	–	n.d.	n.d.
Unknown	68,367	–	n.d.	n.d.
1-Methyl-4-(1-methylethenyl)cyclohexene (*p*-mentha-1,8-diene), (isolimonene)	306,890	Fragnance	21,284 (93.1)	16,999 (94.5)
Decamethyltetrasiloxane	33,835	Solvent	n.d.	n.d.
2-Methyl-6-methylene-2-octanol (dihydro mycenol)	56,847		25,028 (56.0)	14,024 (75.3)
3,7-Dimethyl-3-octanol (linalool tetrahydride)	135,448		66,150 (51.2)	58,830 (56.6)
Decamethylcyclopentasiloxane	11,866,989		111,870 (99.1)	40,231 (99.7)
2,4-Dimethoxyphenol	46,456		20,356 (56.2)	10,482 (77.4)
5-Methyl-2-(1-methylethyl)cyclohexanol (methol)	31,370	Extraction solvent	15,539 (50.5)	13,040 (58.4)
2,5-Dimethyl-3-vinyl-1,4-hexadiene (santolina triene)	15,974		7,617 (52.3)	n.d.
2,2-Dimethyl-3-methylenebicyclo[2.2.1]heptane (camphene)	41,149	Fragnance base	16,946 (58.8)	n.d.
9-Ethylbicyclo[3.3.1]nonan-9-ol	41,657		10,649 (74.4)	6,310 (85.0)
Unknown	13,023		n.d.	n.d.
3,7-Dimethyl-3-octanol (linalool tetrahydride)	66,284		7,891 (88.1)	6,106 (91.0)
Dodecamethylpentasiloxane	500,608		n.d.	n.d.
3,7,7-Trimethylbicyclo[4.1.0]hept-3-ene (3-carene)	97,275	Fragrance	n.d.	7,750 (92.0)
6-Methylundecane	19,132		n.d.	n.d.
Methylcyclooctane	129,307		45,386 (64.9)	41,085 (68.2)
1-Methoxy-4-(1-propenyl)benzene (*p*-propenylanisole)	94,885		22,211 (76.6)	n.d
1-(3-Methylbutyl)cyclopentene	38,050		7,105 (81.3)	5,513 (85.5)
Dodecamethylcyclohexasiloxane	13,588,584	Solvent	82,118 (99.4)	49,258 (99.6)
2,3,4-Trimethylheptane	55,627		n.d.	n.d.
1-Methyl-3-(2-methyl-1-propenyl)cyclopentane	60,610		13,393 (77.9)	7,084 (88.3)
Tetradecamethylhexasiloxane	569,807		n.d.	n.d.
1,2,3,4,5,6-Hexahydro-1,1,6-trimethylnaphthalene	40,197		22,301 (44.5)	15,204 (62.2)
6,6-Dimethyl-,acetate bicyclo[3.1.1]hept-2-ene-2-ethanol (nopylacetate)	119,235		31,613 (73.5)	21,659 (81.8)
Unknown	18,434		7,346 (60.1)	5,126 (72.2)
2,4-Dimethyl-2-decene	17,757		5,032 (71.7)	4,860 (72.6)
2,4,6,8-Tetramethylcyclotetrasiloxane	35,968		n.d.	n.d.
Cyclodecane	379,597		129,462 (65.9)	69,209 (81.8)
4-(2,6,6-Trimethyl-2-cyclohexen-1-yl)-3-penten-2-one	106,446		38,191 (64.1)	27,866 (73.8)
4-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (beta-lanone)	225,976	Fragnance	60,219 (73.4)	35,305 (84.4)
1-(5,6,7,8-Tetrahydro-2,8,8-trimethyl-4H-cyclohepta[*b*] furan-5-yl)ethanone	117,309		19,770 (83.2)	11,421 (90.3)
3-(4-*tert*-Butylphenyl)-2-methylpropanal (lilial)	159,742	Skin care lotion	56,233 (64.8)	19,722 (87.7)
Hexadecamethylheptasiloxane	481,929	Base	n.d.	n.d.
1-(3,6,6-Trimethyl-1,6,7,7a-tetrahydrocyclopenta[*c*] pyran-1-yl)ethanone	30,949		23,208 (25.0)	18,194 (41.2)
Unknown	23,423		9,605 (59.0)	n.d.
Unknown	37,581		10,721 (71.5)	n.d.

(*Continued*)

Table S2 (*Continued*)

Name of the identified compound	Peak area for raw wastewater	Function	Peak area for DAF (% removal)	Peak area for DOF (% removal)
3-Oxo-2-pentyl, methylester cyclopentaneacetic acid (methyldihydrojasmonate)	144,225		117,369 (18.6)	81,106 (43.8)
1-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-1-penten-3-one (methyl-beta-lanone)	768,192		348,918 (54.6)	254,792 (66.8)
Nonylester 3-cyclopentylpropionic acid	426,393	Preservative	25,899 (93.9)	9,679 (97.7)
4-(2,6,6-Trimethyl-2-cyclohexen-1-yl)-3-methyl-3-buten-2-one (isomethylionane)	88,003		49,811 (43.4)	39,481 (55.1)
2-(Phenylmethylene)-octanal (alpha-hexylcinnamalaldehyde)	176,650		127,675 (27.7)	78,242 (55.7)
3a,6,6,9a-Tetramethyldodecahydronaphtha[2,1-*b*]furan (Ambrox)	15,397	Fragnance	n.d.	n.d.
1-Methylethylester tetradecanoic acid (isopropyl Myristate)	170,694	Softener/ opacifier	24,301 (85.8)	17,971 (89.5)
Unknown	10,155		7,014 (30.9)	n.d.
Oxacycloheptadec-8-en-2-one (Ambrettolid)	45,835	Fragnance	18,568 (59.5)	12,158 (73.5)
1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[*g*]-2-benzopyran (galaxolide1)	357,537	Polycyclic musk	206,578 (42.2)	125,456 (64.9)
1-(3-Ethyl-5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-ethanone	15,448		10,230 (33.8)	6,970 (54.9)
1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[*g*]-2-benzopyran (galaxolide2)	15,638	Polycyclic musk	8,025 (48.7)	n.d.
1-Methyethylester hexadeconoic acid (isopropyl palmitate)	128,389		6,168 (95.2)	n.d.
2-Ethylhexylester,3-(4-methoxyphenyl)-2-propenoic acid (Parsol MCX)	470,934	UV filter	182,067 (61.3)	106,548 (77.4)

Note: n.d. means not detected.

Table S3
Chromatographic data for raw wastewater and wastewater after DAF and DOF treatment with coagulant Brenntag 6010

Name of the identified compound	Peak area for raw wastewater	Peak area for DAF (% removal)	Peak area for DOF (% removal)
2,2-Dimethylhexane	11,498	n.d.	n.d.
Unknown	11,248	n.d.	n.d.
Unknown	68,367	n.d.	n.d.
1-Methyl-4-(1-methylethenyl)cyclohexene (*p*-mentha-1,8-diene), (isolimonene)	306,890	34,531 (88.7)	34,189 (88.9)
Decamethyltetrasiloxane	33,835	n.d.	n.d.
2-Methyl-6-methylene-2-octanol(dihydromycenol)	56,847	40,772 (28.3)	19,682 (65.4)
3,7-Dimethyl-3-octanol (linalool tetrahydride)	135,448	115,191 (15.0)	80,066 (40.9)
Decamethylcyclopentasiloxane	11,866,989	131,550 (98.9)	349,886 (97.1)
2,4-Dimethoxyphenol	46,456	28,567 (38.5)	13,277 (71.4)
5-Methyl-2-(1-methylethyl)cyclohexanol (methol)	31,370	23,346 (25.6)	17,315 (44.8)
2,5-Dimethyl-3-vinyl-1,4-hexadiene (santolina triene)	15,974	10,732 (32.8)	n.d.
2,2-Dimethyl-3-methylenebicyclo[2.2.1]heptane (camphene)	41,149	25,185 (38.8)	n.d.
9-Ethylbicyclo[3.3.1]nonan-9-ol	41,657	12,983 (68.8)	9,867 (76.3)
Unknown	13,023	n.d.	n.d.
3,7-Dimethyl-3-octanol (linalool tetrahydride)	66,284	12,415 (81.3)	10,717 (83.8)
Dodecamethylpentasiloxane	500,608	n.d.	n.d.
3,7,7-Trimethylbicyclo[4.1.0]hept-3-ene (3-carene)	97,275	25,383 (73.9)	6,518 (93.3)
6-Methylundecane	19,132	n.d.	n.d.
Methylcyclooctane	129,307	66,697 (48.4)	58,574 (54.7)
1-Methoxy-4-(1-propenyl)benzene (p-propenylanisole)	94,885	29,529 (68.9)	13,484 (85.8)
1-(3-Methylbutyl)cyclopentene	38,050	7,426 (80.5)	7,570 (80.1)
Dodecamethylcyclohexasiloxane	13,588,584	108,722 (99.2)	223,189 (98.4)
2,3,4-Trimethylheptane	55,627	n.d.	n.d.
1-Methyl-3-(2-methyl-1-propenyl)cyclopentane	60,610	14,001 (76.9)	12,753 (79.0)
Tetradecamethylhexasiloxane	569,807	n.d.	n.d.
1,2,3,4,5,6-Hexahydro-1,1,6-trimethylnaphthalene	40,197	23,990 (40.3)	20,873 (48.1)
6,6-Dimethyl-,acetate bicyclo[3.1.1]hept-2-ene-2-ethanol (nopylacetate)	119,235	38,649 (67.6)	32,623 (72.6)
Unknown	18,434	9,660 (47.6)	8,815 (52.2)
2,4-Dimethyl-2-decene	17,757	6,624 (62.7)	6,356 (64.2)
2,4,6,8-Tetramethylcyclotetrasiloxane	35,968	n.d.	n.d.
Cyclodecane	379,597	96,193 (74.7)	134,863 (64.5)
4-(2,6,6-Trimethyl-2-cyclohexen-1-yl)-3-penten-2-one	106,446	38,609 (63.7)	31,980 (70.0)
4-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (beta-lanone)	225,976	67,335 (70.2)	41,408 (81.7)
1-(5,6,7,8-Tetrahydro-2,8,8-trimethyl-4H-cyclohepta[*b*]furan-5-yl)ethanone	117,309	22,097 (81.2)	17,721 (84.9)
3-(4-*tert*-Butylphenyl)-2-methylpropanal (lilial)	159,742	68,423 (57.2)	47,757 (70.1)
Hexadecamethylheptasiloxane	481,929	6,819 (98.6)	5,973 (98.8)
1-(3,6,6-Trimethyl-1,6,7,7a-tetrahydrocyclopenta[*c*] pyran-1-yl)ethanone	30,949	19,280 (37.7)	18,543 (40.1)
Unknown	23,423	10,318 (55.9)	8,041 (65.7)

(*Continued*)

Table S3 (*Continued*)

Name of the identified compound	Peak area for raw wastewater	Peak area for DAF (% removal)	Peak area for DOF (% removal)
Unknown	37,581	11,639 (69.0)	10,865 (71.1)
3-Oxo-2-pentyl, methylester cyclopentaneacetic acid (methyldihydrojasmonate)	144,225	113,911 (21.2)	100,754 (30.1)
1-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-1-penten-3-one (methyl-beta-lanone)	768,192	371,673 (51.6)	322,199 (58.1)
Nonylester 3-cyclopentylpropionic acid	426,393	n.d.	38,399 (91.0)
4-(2,6,6-Trimethyl-2-cyclohexen-1-yl)-3-methyl-3-buten-2-one (isomethylionane)	88,003	57,365 (34.8)	42,029 (52.2)
2-(Phenylmethylene)-octanal (alpha-hexylcinnamalaldehyde)	176,650	104,627 (40.8)	116,934 (33.8)
3a,6,6,9a-Tetramethyldodecahydronaphtha[2,1-*b*] furan (Ambrox)	15,397	15,397 (26.1)	n.d.
1-Methylethylester tetradecanoic acid (isopropyl Myristate)	170,694	28,494 (83.3)	39,329 (77.0)
Unknown	10,155	8,724 (14.1)	6,360 (37.4)
Oxacycloheptadec-8-en-2-one (Ambrettolid)	45,835	16,742 (63.5)	21,231 (53.7)
1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[*g*]-2-benzopyran (galaxolide1)	357,537	156,035 (56.4)	180,925 (49.4)
1-(3-Ethyl-5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-ethanone	15,448	n.d.	10,499 (32.0)
1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[*g*]-2-benzopyran (galaxolide2)	15,638	6,542 (58.2)	11,377 (27.2)
1-Methyethylester hexadeconoic acid (isopropyl palmitate)	128,389	10,440 (91.9)	12,349 (90.4)
2-Ethylhexylester,3-(4-methoxyphenyl)-2-propenoic acid (Parsol MCX)	470,934	143,252 (69.6)	139,572 (70.4)