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Effect of sodium hypochlorite on conversions of octyl-dimethyl-*para*-aminobenzoic acid

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ABSTRACT

The stability of octyl-dimethyl-*para*-aminobenzoic acid (OD-PABA) in water samples has been studied under the action of UV radiation and sodium hypochlorite (NaOCl). It was shown that OD-PABA is unstable in the presence of UV. It undergoes demethylation and decomposition to *para*-aminobenzoic acid. However, in the presence of NaOCl, chloro-organic derivatives are formed. The experiment was carried out on water samples with the known amounts of OD-PABA introduced. Irradiation of samples was performed by the use of a medium-pressure mercury lamp TQ 150 W. The products were identified using a gas chromatograph coupled with a mass spectrometry detector (GC–MS). Samples for analysis were prepared by a liquid–liquid technique. The mixture of ethyl acetate/*n*-hexane was applied as an eluant.

Keywords: UV filters; Octyl-dimethyl-*para*-aminobenzoic acid; Water samples; Chloro-organic products; Gas chromatography; Mass spectrometry

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1. Introduction

Awareness of the need to protect our skin from harmful UV rays caused an increase in production of protective preparations. These preparations contain chemical compounds that absorb, reflect, or disperse radiation reaching the Earth (290–320 nm for UVB and 320–400 nm for UVA) [1]. These compounds are commonly called the UV filters. They are added to personal care products (suntan creams, lipsticks, shampoos and others) as well as to paints and plastics.

UV filters contained in sunscreen formulations can be organic (chemical compounds) or inorganic (mineral compounds). Organic UV filters comprise various classes of compounds, with the most common being benzophenones, cinnamates, salicylates, camphor derivatives, benzimidazoles, and *para*-aminobenzoates. In general, these compounds possess one benzenic moiety (or several), conjugated with an electron-releasing–electron-accepting group in either *ortho* or *para* positions, therefore allowing for an efficient electronic delocalization and rendering them a specific maximum absorbance wavelength. They very often also have attached hydrophobic groups like long

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alkane chains to prevent aqueous dissolution. Whereas there are only two inorganic UV filters known to exist: titanium dioxide (TiO_2) and zinc oxide (ZnO).

Because of their widespread use in personal care products as well as in other applications (plastics, textiles, and agricultural products), UV filters have been significantly introduced into the environment [2–4]. In recent years, it has been shown that UV filters are present in surface water, in swimming pools [5], wastewater [4], sludge [6], and they have also been identified in fish from lakes used for bathing [7]. More recently, UV filters have also been detected in human breast milk and human urine [8].

UV filters are released into environment directly (direct release from skin in swimming pools and sunbathing areas, and industrial wastewater) and indirectly (during showering, cloths washing, and urine excretion) [7].

The increased release of UV filters into the environment has prompted them to be considered to be a new class of organic pollutants called emerging contaminations. Several studies have demonstrated that same organic UV filters possess estrogenic properties and can behave as endocrine disrupting chemicals in the environment [9,10,]. Therefore, the investigation of UV filters behavior in natural surface water is of great importance for understanding its fate and aquatic risk on an ecological system. There are many reports in the literature stating that the composition of surface waters affects the conversion of organic pollutants [11–14]. It was shown that dissolved organic matter, iron ions (Fe^{3+}), and nitric ions (NO_3^{2-}) participate in the photolysis processes. Components of matrix, taking part in reactions with participation of light, form reactive forms of oxygen, which in turn react with organic contaminants. Then, the competitive processes of photolysis occur, which at first slows down degradation of pollutants and the products of these conversions react with organic compounds. It consequently causes an increase in conversion rate of pollutants. Zhou et al. [11] described an effect of dissolved organic matter on photodegradation of *para*-aminobenzoic acid. They pointed out that it is unstable and when exposed to light in an aqueous solution it contributes to formation of singlet molecular oxygen and intermediate products, which cause dermatologic side effects. Therefore, its use was limited by replacing it with a derivative of octyl-dimethyl-*para*-aminobenzoic acid (OD-PABA). In Europe, the permissible level of OD-PABA added to cosmetics is about 8%. Therefore, monitoring of the presence of organic pollutants in the aquatic environment is important, especially when there is a risk of formation of conversion products which adversely affect human health.

In order to protect swimmers against pathogenic micro-organisms, swimming pool waters are subjected to disinfection [15]. A commonly known disinfectant is sodium hypochlorite. The presence of a chlorinating agent can play an important role in formation of chloro-organic products. Our previous works showed that octyl-methoxycinnamate in the presence of H_2O_2-HCl system (which among others contributes to formation of HOCl) forms chloro-organic products [16]. In turn, Negreira et al. [17] proposed the degradation path for benzophenone-3 to chloro-organic products in tap water submitted to the action of sodium hypochlorite. The results of studies prove that organic UV filters which get into the aqueous matrix under uncontrolled conditions undergo conversions. The environment matrix is of a significant importance.

Therefore, the aim of our study is to determine which products are formed as a result of OD-PABA conversions under the action of: (a) sodium hypochlorite, (b) UV radiation, and (c) sodium hypochlorite and UV radiation in water samples. The knowledge of intermediate products and the final reactions allow us to predict the pathway of OD-PABA conversions.

2. Materials and methods

2.1. Materials

Octyl-dimethyl-*para*-aminobenzoic acid (98%) was purchased from Sigma-Aldrich (Poland). The solvents used (methanol, ethyl acetate, and *n*-hexane) were of the highest available purity and were obtained from Merck (Poland). Sodium hypochlorite NaOCl with a nominal free chlorine content of 100 g/dm^3 and anhydrous sodium sulfate Na_2SO_3 (pure) were obtained from POCh (Poland).

2.2. Chlorination experiments

Water solution of OD-PABA was introduced into laboratory UV reactor (Heraeus) equipped with a medium pressure mercury lamp TQ of 150 W. Three OD-PABA water solutions with the concentration of 0.36×10^{-3} mol/dm^3 were prepared. In the first stage, OD-PABA was dissolved in a small amount of methanol (about 1 cm^3) and then introduced into deionized water. The first solution was introduced into the laboratory UV reactor (Heraeus) equipped with a medium pressure mercury lamp of TQ of 150 W and subjected to UV radiation. About 1 cm^3 of NaOCl was added to the second solution and it was left in the locker. Then, 1 cm^3 of NaOCl was added to the third solution and whole was introduced into laboratory UV reactor and subjected to UV radiation. After 0.5 and 3 h, 100 cm^3 of solution was sampled from each system and subjected to liquid–liquid extraction. Extraction was performed with 20 cm^3 of ethyl acetate/n-hexane mixture (1:1). The extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure to volumes that are suitable for GC–MS analyses. A vacuum evaporator (Buchi) was used to concentrate the solutions.

2.3. Analytical methods

The extracts were analyzed using the Hewlett Packard 5890 Series II Gas Chromatograph, with a model 5972 mass-selective detector equipped with ZB-5MS column (30 m × 0.25 mm × 0.25 μm) under temperature ranging from 80 to 260℃ at the rate of 10℃/min and from 260 to 300℃ at the rate of 5℃/min.

3. Results and discussion

In the first stage of study, the impact of UV radiation on the OD-PABA stability in water medium was determined. Water solution of OD-PABA was irradiated for 3 h. After this time, the appropriate volume of the sample was extracted and the extract was analyzed by GC–MS. The total ion chromatogram of the sample analyzed was presented in Fig. 1. On the basis of molecular ions (m/z), the following products were identified: (1) ethylhexyl alcohol ($m/z = 130, 112, 98, 57$); (2) octyl *para*-aminobenzoic acid ($m/z = 249, 137, 120$); (3) octyl methyl-*para*-aminobenzoic acid ($m/z = 263, 151, 134$).

In the next step, the OD-PABA behavior in the presence of sodium hypochlorite without participation of UV radiation was checked. The total ion chromatogram of the sample subjected to the action of NaOCl for 3 h is presented in Fig. 2. It was demonstrated that mainly dichloroderivatives of OD-PABA are formed in reaction products. The following compounds were identified by GC–MS method: (1) ethylhexyl alcohol ($m/z = 112, 98, 57$); (4) octyl *para*-3-chlorohydroxybenzoic acid ($m/z = 284, 172, 155$); (5) octyl *para*-dichlorohydroxybenzoic acid ($m/z = 318, 206, 161$); (6) octyl-dimethyl-*para*-dichloroaminobenzoic acid ($m/z = 345, 223, 216$); (7) octyl *para*-dichloroaminobenzoic acid ($m/z = 317, 205, 188$); (8) octyl methyl-*para*-dichloroaminobenzoic acid ($m/z = 331, 219, 202$); (9) unidentified ($m/z = 290, 214, 178$); (10) unidentified ($m/z = 324, 248, 212, 205, 248$).

When the reaction was stopped after 0.5 h, the following compounds were additionally identified: octyl methyl-*para*-aminobenzoic acid ($m/z = 263, 151, 134$), octyl methyl-*para*-chloroaminobenzoic acid ($m/z = 297, 185, 168$), and octyl *para*-chloroaminobenzoic acid ($m/z = 283, 171, 154$). The third reaction system was OD-PABA solution subjected to the action both NaOCl and UV radiation. After 3 h, the same dichlorocompounds were identified among the reaction products as in the reaction without UV radiation (compounds 4, 5, 6, and 8) and additionally, octyl methyl-*para*-chloroaminobenzoic acid (11) ($m/z = 297, 185, 168$) and ethylhexyl alcohol (1) (Fig. 3) were detected.

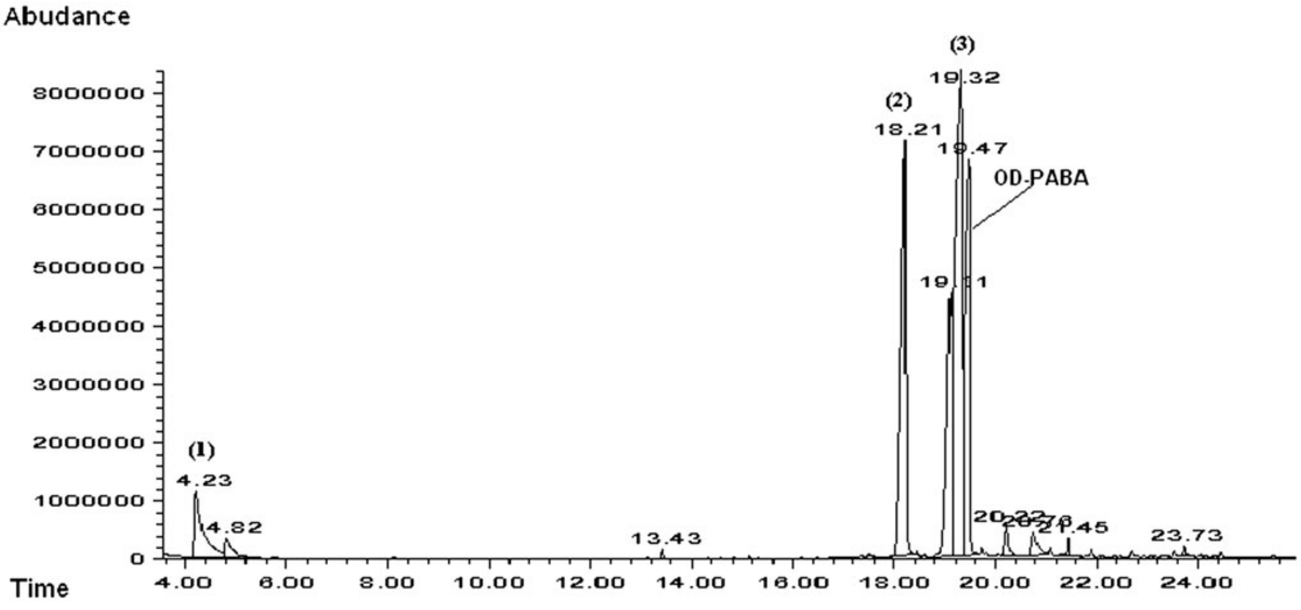

Fig. 1. Total ion chromatogram of OD-PABA in the presence of UV, using GC–MS.

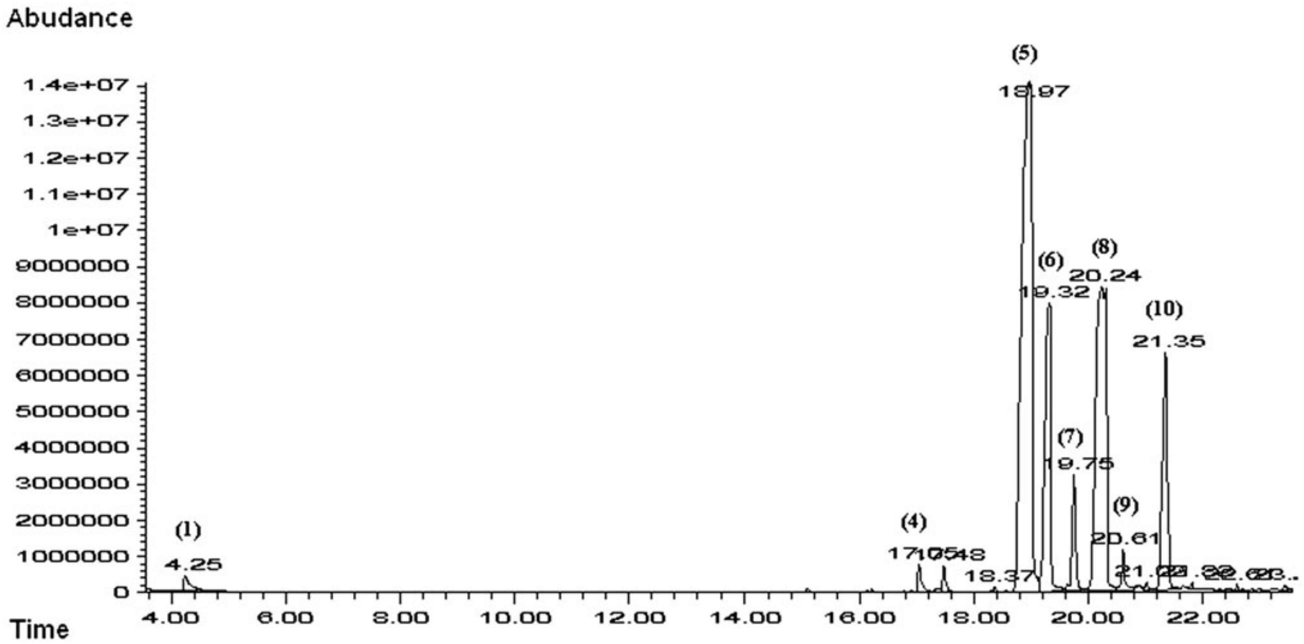

Fig. 2. Total ion chromatogram of OD-PABA in the presence of NaOCl, using GC–MS.

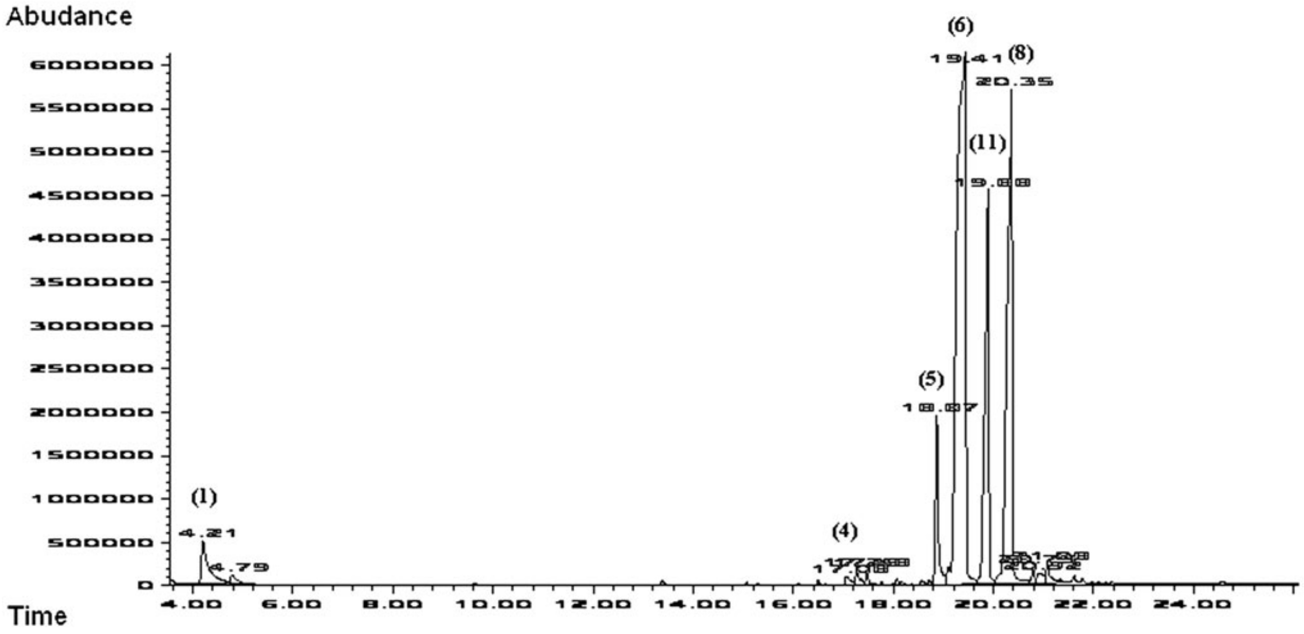

Fig. 3. Total ion chromatogram of OD-PABA in the presence of NaOCl and UV, using GC–MS.

The obtained results indicate that in the presence of UV radiation, the demethylation reactions of amino group occur (Fig. 4). Besides octyl methyl-*para*-aminobenzoic acid and octyl *para*-aminobenzoic acid also ethylhexyl alcohol was identified in the reaction products. The presence of alcohol suggests that it is formed as a result of alkyl group detachment. Therefore, another product of OD-PABA degradation can be *para*-aminobenzoic acid. However, the authors have not found unequivocally the presence of acid in the reaction products. Chromatographic analysis of *para*-aminobenzoic acid standard showed that the retention time of

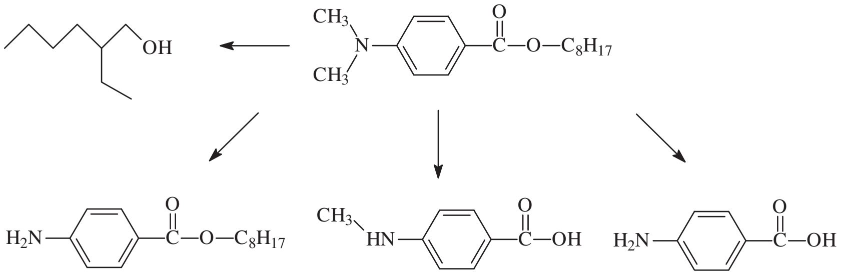

Fig. 4. Products of OD-PABA conversions under the influence of UV radiation.

standard coincided with retention time of another product which was octyl methyl-*para*-aminobenzoic acid. On the other hand, León et al. [8] identified methyl-*para*-aminobenzoic acid and dimethyl-*para*-aminobenzoic acid as metabolites of OD-PABA conversions in human urine. However, Suhag et al. [18] showed that one of the OD-PABA degradation products is *para*-aminobenzoic acid formed as a result of direct photolysis.

In the case of OD-PABA reaction with NaOCl, it was shown that chloroderivatives of OD-PABA were present among the reaction products, and both mono and dichloroderivatives were formed (Fig. 5). Moreover, demethylation of amine group occurred. Similar products of OD-PABA chlorination were proposed by Sakkas et al. [19] and Nikajima et al. [20]. Furthermore, Nikajima et al. [20] explain that the dimethylamino group, being stronger π-donor group, activates the benzoic ring for additional chlorine attack, more extensively than the methyl group. Thus, in the first step, chlorination occurs and then demethylation of amine group. It should be noted that octyl *para*-chorohydroxybenzoic acid, which can be an oxidation product of OD-PABA, was not identified by the mentioned above authors. Zhou et al. [11] showed that *para*-aminobenzoic acid in the presence of dissolved organic matter and sunlight underwent hydroxylation among others. As a result of this reaction, *para*-hydroxybenzoic acid is formed. It can be assumed that in the case of OD-PABA in the presence of NaOCl, a similar conversion occurs. In the first stage, the addition of chlorine to benzenic ring occurs and then deamination and hydroxylation takes place.

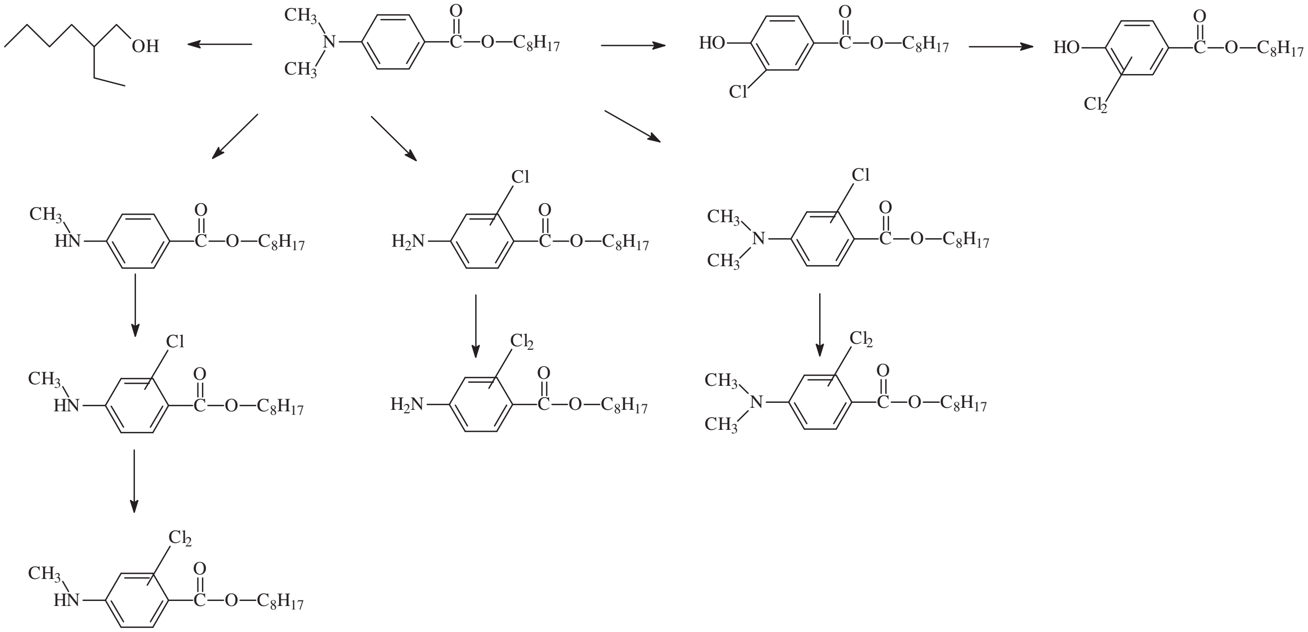

Fig. 5. Products of OD-PABA conversion under the influence of NaOCl.

In the case of OD-PABA reaction with NaOCl in the presence of UV, no significant differences were observed. Among the reaction products, the chloro compounds, formed also in the reaction without UV participation, were identified.

Application of disinfecting agents in swimming pool water, on one hand destroys pathogens and, on the other hand, can contribute to formation of chloroorganic products of OD-PABA conversions. The results obtained by different authors confirm formation of mono and dichloroderivatives of OD-PABA. However, our studies allowed one to identify additionally the products of hydroxylation. In turn, in the presence of UV radiation, demethylation of OD-PABA and oxidation to *para*-aminobenzoic acid and ethylhexyl alcohol occurred.

4. Conclusion

New environmental pollutions pose a potential threat to living organisms. Understanding the behavior of these pollutants in the presence of various factors allows for proper monitoring of the environment. Recently, the number of publications concerning identification and determination of chemical UV filters in water samples and sewage permanently increases. At the same time, the studies are carried out in order to understand the pathway of conversions of these pollutants. Studies on OD-PABA behavior in the presence of disinfectant, which is NaOCl, indicated formation of mono and dichloroderivatives besides the oxidation products. It was found that products of OD-PABA oxidation also undergo chlorination. Moreover, it was shown that OD-PABA is unstable in the presence of UV radiation. The results obtained for model samples provide some information regarding which conversion products can be expected in water of swimming pools and sewage subjected to the action of NaOCl and UV.

References

[1] A. Wawrzyńczak, I. Nowak, Spectrophotometric determination of UV protection provided by cosmetic products with sunscreen properties, Chemik 65 (2011) 655–660.

[2] P. Gago-Ferrero, M.S. Díaz-Cruz, D. Barceló, Fast pressurized liquid extraction with in-cell purification and analysis by liquid chromatography tandem mass spectrometry for the determination of UV filters and their degradation products in sediments, Anal. Bioanal.Chem. 400 (2011) 2195–2204.

[3] H.-R. Buser, M.E. Balmer, P. Schmid, M. Kohler, Occurrence of UV Filters 4-methylbenzylidene camphor and octocrylene in fish from various swiss rivers with inputs from wastewater treatment plants, Environ. Sci. Technol. 40 (2006) 1427–1431.

[4] W. Li, Y. Ma, C. Guo, W. Hu, K. Liu, Y. Wang, T. Zhu, Occurrence and behavior of four of the most used sunscreen UV filters in a wastewater reclamation plant, Water Res. 41 (2007) 3506–3512.

[5] A.J.M. Santos, M.S. Miranda Esteves, J.C.G. da Silva, The degradation products of UV filters in aqueous and chlorinated aqueous solutions. Water Res. 46 (2012) 3167–3176.

[6] O. Zuloaga, P. Navarro, E. Bizkarguenaga, A. Iparraguirre, A. Vallejo, M. Olivares, A. Prieto, Overview of extraction, clean-up and detection techniques for the determination of organic pollutants in sewage sludge: A review, Anal. Chim. Acta 736 (2012) 7–29.

[7] D.L. Giokas, A. Salvador, A. Chisvert, UV filters: From sunscreens to human body and the environment, TrAC, Trends Anal. Chem. 26 (2007) 360–374.

[8] Z. León, J. Vlieger, A. Chisvert, A. Salvador, H. Lingeman, H. Irth, M. Giera, Identification of the biotransformation products of 2-ethylhexyl 4-(N,N-dimethylamino)benzoate, Chromatographia 71 (2010) 55–63.

[9] M.S. Díaz-Cruz, D. Barceló, Chemical analysis and ecotoxicological effects of organic UV-absorbing compounds in aquatic ecosystems, TrAC, Trends Anal. Chem. 28 (2009) 708–717.

[10] J.F. Nash, P.R. Tanner, Relevance of UV filter/sunscreen product photostability to human safety, Photodermatol. Photoimmunol. Photomed. 30 (2014) 88–95.

[11] L. Zhou, Y. Ji, Ch Zeng, Y. Zhang, Z. Wang, X. Yang, Aquatic photodegradation of sunscreen agent *p*-aminobenzoic acid in the presence of dissolved organic matter, Water Res. 47 (2013) 153–162.

[12] Y. Ji, L. Zhou, Y. Zhang, C. Ferronato, M. Brigante, G. Mailhot, X. Yang, J.M. Chovelon, Photochemical degradation of sunscreen agent 2-phenylbenzimidazole-5-sulfonic acid in different water matrices, Water Res. 47 (2013) 5865–5875.

[13] Y.-P. Chin, P.L. Miller, K. Cawley, L.K. Weavers, Photosensitized degradation of bisphenol A by dissolved organic matter, Environ. Sci. Technol. 38 (2004) 5888–5894.

[14] J. van Leeuwen, R. Daly, M. Holmes, Modeling the treatment of drinking water to maximize dissolved organic matter removal and minimize disinfection by-product formation, Desalination 176 (2005) 81–89.

[15] D. Ghernaout, B. Ghernaout, From chemical disinfection to electrodisinfection: The obligatory itinerary? Desalin. Water Treat. 16 (2010) 156–175.

[16] A. Gackowska, M. Przybyłek, W. Studziński, J. Gaca, Experimental and theoretical studies on the photodegradation of 2-ethylhexyl 4-methoxycinnamate in the presence of reactive oxygen and chlorine species, Cent. Eur. J. Chem. 12 (2014) 612–623.

[17] N. Negreira, P. Canosa, I. Rodriguez, R. Rubi, R. Cele, Study of some UV filters stability in chlorinated water and identification of halogenated by-products by gas chromatography-mass spectrometry, J. Chromatogr. A 1178 (2008) 208–214.

[18] S. Suhag, S.K. Bercovici, M.G. Paulick, L.A. MacManus-Spencer, Investigating the toxicity of the ultraviolet filter chemical octyl dimethyl para-aminobenzoic acid and its photochemical degradation products, Abstracts of Papers American Chemical Society, San Diego, CA, 243: 362-ENVR MAR 25 2012.

[19] V.A. Sakkas, D.A. Giokas, D.A. Lambropoulou, T.A. Albanis, Aqueous photolysis of the sunscreen agent octyl-dimethyl-*p*-aminobenzoic acid formation of disinfection byproducts in chlorinated swimming pool water, J. Chromatogr. A 1016 (2003) 211–222.

[20] M. Nakajima, T. Kawakami, T. Niino, Y. Takahashi, S. Onodera, Aquatic fate of sunscreen agents octyl-4-methoxycinnamate and octyl-4-dimethylaminobenzoate in model swimming pools and the mutagenic assays of their chlorination byproducts, J. Health Sci. 55 (2009) 363–372.