pH STABILITY AND PHOTODEGRADATION OF SUNSCREEN UV-A FILTER'S (AVOBENZONE) CHLORINATION PRODUCTS

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Introduction

UV filters are a group of chemicals, which are used in sunscreen products to prevent sunburns on human skin. They represent an important group of anthropogenic organic compounds introduced in swimming pools and marine bath waters and are nowadays treated as emerging contaminants [1]. Under chlorination and photolytic conditions, they easily decompose and several degradation products are formed [2, 3, 4]. The degradation products are rarely, or even in most countries never analysed or monitored.

The advantage of chlorination lies in the fact that still nowadays is one of the most efficient pathways of pathogens inactivation. On the other hand, it has some drawbacks. One of them represents the reactions of chlorine with organic matter and other human outputs and the formation of different disinfection by-products (DBPs) [5]. The additional use of advanced oxidation processes (like UV-irradiation, photocatalysis, oxidation) generally lead to the formation of different DBPs as in case of disinfection. Since the toxicity of the transformation products may be higher than that of the parent compound, it is important to take into account not only the initial compounds, but their transformation products as well.

There are several studies dealing with the chlorination of avobenzone - AV, one of the most common UV-A filter [6,7]. The chlorination and UV-irradiation of avobenzone has proved the formation of twenty five compounds, which were identified by GC/MS [3]. The identification of the two primary chlorination products <u>AV-Cl1</u> - (2-chloro-1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)-1,3-propanedione and <u>AV-Cl2</u> - 2,2-dichloro-1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)-1,3-propanedione) led our research in investigation of their pH stability and photostability. Additionally our focus was on the investigation of the possibility of application of TiO_2 photocatalysis as a method for the removal of these persistent chlorinated compounds.

2. Materials and methods

2.1. Materials

The analytical standard of avobenzone (95.0% purity) has been provided by TCI Europe. For stability experiments, avobenzone, chloro-avobenzone and dichloro-avobenzone have been synthesized and characterized according to the literature [3]. Dichloromethane, diethyl ether, petroleum ether, acetonitrile (Chlomasolv gradient grade, for HPLC), acetone, acetic acid have been provided from Sigma Aldrich company, whereas sodium sulfite, sodium sulfate, sodium hydrogen carbonate, from Fluka. The tert-butyl hyprochlorite was prepared in our lab, according to the procedure [8].

Experimental

Stability studies

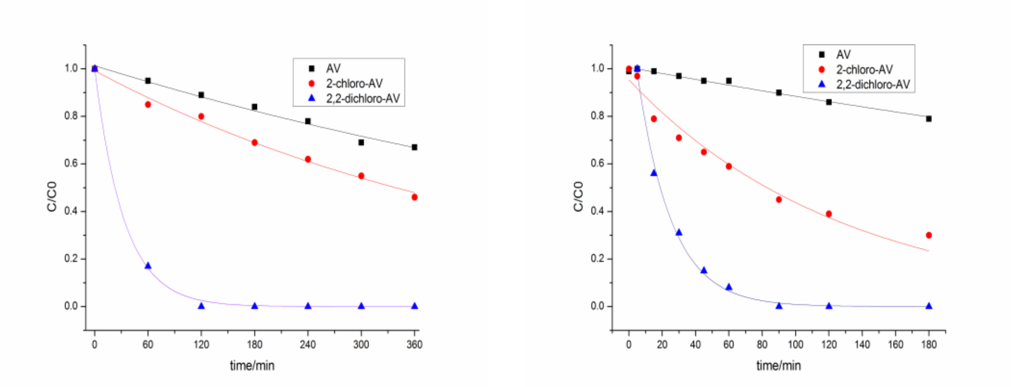
pH stability: 12,5 mL of AV solution in acetone (1000 mg/L) was dilluted with buffers pH 4 and pH 7 up to to 250 mL, and left at room temperature. Everyday up to 10 days 1 mL of solutions have been withdrawed for HPLC analyses. The procedure was same for AV-Cl1 and AV-Cl2.

Photostability: 50 mL of AV solution in acetone (1000 mg/L) was dilluted with deionised water up to 1 L, and the solution was transfer into the UVA reactor, which consisted of a glass tube (280 mm, inner diameter 87 mm) with 1 L of effective volume. The reaction time was set 6 h, and every hour the sample was withdrawed 1 mL for HPLC detection. The procedure was same for AV-Cl1 and AV-Cl2.

TiO_2 photocatalytical study: Photocatalytic experiments with AV, AV-Cl1 and AV-Cl2 were done in UVA photoreactor, which consisted of a glass tube (280 mm, inner diameter 87 mm) with 1 L of effective volume. Twelve glass slides with immobilised TiO_2 catalyst were fastened around the axis of a spinning basket and immersed into the photocatalytic glass tube [9]. The reaction time was set to 3 h. At different time intervals (5, 15, 30, 45, 60, 90, 120, and 180), samples of 1 mL were taken for HPLC analyses.

	pH=4			**pH=7**		
	AV	**AV-Cl1**	**AV-Cl2**	**AV**	**AV-Cl1**	**AV-Cl2**
Rate constant (day^{-1})	0.71±0.04	1.19±0.05	1.63±0.04	0.20±0.01	0.85±0.09	5.67±0.47
$t_{1/2}$ (day)	1.44±0.14	0.85±0.06	0.60±0.02	3.54±0.31	1.22±0.15	0.20±0.01

Table 1: Stability of avobenzone, chloro and dichloro-avobenzone at different pHs



(a)photolytic stability (b) photocatalytic curve

Figure 1: Disappearance curves of avobenzone, chloro-avobenzone and dichloro-avobenzone aqueous solutions via (a): UV A photolysis and (b) UV A photocatalysis with TiO_2

Analytical methods: Aqueous solutions of AV, AV-Cl1 and AV-Cl2 were analysed by Agilent 1000 HPLC - UV-Vis chromatograph. The separation was done using C18 column (150 mm × 4.6 mm), the mobile phase consisted of 70% acetonitrile and 30% distilled water with the flow rate of 1.0 mL/min and the wavelength was set at 330 nm. The retention time for avobenzone was 16.0 min, for chloro-avobenzone 5.34 min, and for the dichloro-avobenzone 10.48 min. For the quantification purposes, the calibration curve was ranged from 1.0 mg/L to 200 mg/L with 9 different concentrations; all the coefficient of determination (r^2) was above 0.99. To decrease the error, all the experiments were repeated twice.

Results and discussion

pH stability: The differences in stability of all three studied compounds in relation of the pH value are presented in Table1. At acidic conditions, all three compounds degraded fast with half-lives from 0.60±0.02 day (AV-Cl2) and 0.85±0.06 day (AV-Cl1) for chlorinated products, to 1.44±0.14 day in the case of parent one. At neutral conditions, only AV-Cl2 degraded fast (half-life 0.20±0.01 day), while AV and AV-Cl1 expressed higher stability (up to 3.54±0.31day in the case of AV).

Photolysis and photocatalysis: The differences in stability of all three studied compounds under photolytic and photocatalytic conditions are presented in Figure 1. In the case of photolysis under UV-A light, AV-Cl2 expressed the lowest UV-A stability (half-life 33.5 ± 1.6min), followed by AV-Cl1 and AV. In case of photocatalysis the expressed tendency of faster degradation was again achieved in case of AV-Cl2 (half-life 20.3 ±1.3 min), while AV-Cl1 had an average half-live of 68.6 ± 10.7 min.

Conclusions

The study of avobenzone, one of the most used UV-A filter in sunscreen products and its two most common DBPs, AV-Cl1 and AV-Cl2, indicates, that contrarily to avobenzone, which is a relatively stable compound, AV-Cl1 and AV-Cl2 are more polar and they both degrade faster under photolytic and under photocatalytic experiments. Besides, AV-Cl1 and AV-Cl2 are both more susceptible to acidic hydrolysis. Our findings are positive in relation with the fact that avobenzone is widely used, non-polar and environmently stable compound, its two DBS are less stable and degrades more easily then the parent compound.

References

[1] Lebedev, A.T., 2013. Environmental mass spectrometry. Annu. Rev. Anal. Chem. 6, 163-189

[2] Santos, A.J.M., Crista, D.M.A., Miranda, M.S., Almeida, I.F., de Silva, J.P.S., Costa, P.C., Amaral, M.H., Lobao, P.A.L., Lobo, J.M.S., da Silva, J.C.G.E., 2013. Environ. Chem. 10 (2), 127-134

[3] Trebse, P., Polyakova, O.V., Baranova, M., Bavcon Kralj, M., Dolenc, D., Sarakha, M., Kutin, A., Lebedev, A.T. Water Research 101 (2016) 95-102

[4] Shujuan Zhang, Xiaomao Wang, Hongwei Yang, Yuefeng F. Xie, Chemosphere 154 (2016) 521-527

[5] Chowdhury, S., Alhooshani, K., Karanfil, T., 2014. Water Res. 53, 68-109

[6] A. J. M. Santos, D. M. A. Crista, M. S. Miranda, I. F. Almeida, J. P. S. de Silva, P. C. Costa, M. H. Amaral, P. A. L. Lobão, J. M. S. Lobo, J. C. G. E. da Silva. Environ. Chem. 2013,10 (2), 127-134;

[7] D. M. A. Crista, M. S. Miranda, J. C. G. Esteves da Silva. Environmental Technology 2015, 36 (10), 1319-1326

[8] A. Vogel, Vogel's Textbook of Practical Organic Chemistry, 4th ed. Longman: London, 1978, P. 405.

[9] M. Kete, E. Pavlica, F. Fresno, G. Bratina, U. Lavrenčič Štangar. Environmental Science and Pollution Research 2014, 21 (19), 11238-11249.