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Review

The degradation products of UV filters in aqueous and chlorinated aqueous solutions

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ABSTRACT

Ultraviolet (UV) filters are vital constituents of sunscreens and other personal care products since they absorb, reflect and/or scatter UV radiation, therefore protecting us from the sun's deleterious UV radiation and its effects. However, they suffer degradation, mainly through exposure towards sunlight and from reactions with disinfectant products such as chlorine. On the basis of their increasing production and use, UV filters and their degradation products have already been detected in the aquatic environment, especially in bathing waters. This paper presents a comprehensive review on the work done so far as to identify and determine the by-products of UV filter photodegradation in aqueous solutions and those subsequent to disinfection-induced degradation in chlorinated aqueous solutions, namely swimming pools.

Contents

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1. Introduction

The increasing concern about the effects of ultraviolet (UV) radiation resulted in an increased production and use of UV filters throughout the last decades. UV filters are vital ingredients of sunscreens and other personal care products as they absorb, reflect and/or scatter UV radiation (320–400 nm for UVA and 290–320 for UVB), therefore protecting us from its harmful effects on human skin and health. UV filters can be inorganic compounds (also regarded as physical UV filters) which reflect and scatter UV radiation or organic compounds (also regarded as chemical UV filters) which absorb the UV radiation. Despite this distinction, there are only two inorganic UV filters known to exist, titanium dioxide (TiO_2) and zinc oxide (ZnO). Organic UV filters comprise various classes of compounds, with the most common being the *para*-aminobenzoates, cinnamates, benzophenones, dibenzoylmethanes, camphor derivatives and benzimidazoles (Shaath, 2010; Giokas et al., 2007). In general these compounds possess one benzenic moiety (or several), conjugated with electron releasing and electron accepting groups in either *ortho* or *para* positions, therefore allowing an efficient electronic delocalization and rendering them a specific maximum absorbance wavelength.

In our days, many commercial products are marketed, with varying compositions which afford protection against UVA and UVB radiations. However, many UV filters have shown to present toxic effects, thus maximum concentrations have been established with a compromise between adequate protection and minimum side effects for users. Several papers have reported reviews on the toxicological effects of organic UV filters (Díaz-Cruz and Barceló, 2009; Fent et al., 2010; Kunz et al., 2006; Zucchi et al., 2011). A wide number of UV filters have been found to exhibit oestrogenic, antiestrogenic, androgenic and antiandrogenic activities.

There are about 55 UV filters approved for use in sunscreen products worldwide (EU, USA, Australia/New Zealand, Canada, Japan, S. Africa) (Shaath, 2010) with only 10 uniformly approved: benzophenone-3 (BP3), butyl methoxydibenzoylmethane (BMDM), ethylhexyl dimethyl PABA (EHDPABA), ethylhexyl methoxycinnamate (EHMC), ethylhexyl salicylate (EHS), homosalate (HS), octocrylene (OCR), PABA, phenyl benzimidazole sulfonic acid (PBSA) and titanium dioxide (TiO_2). Relevant information on all the UV filters approved worldwide is presented in Table 1. Table 2 presents the physicochemical properties for all the UV filters approved in the EU, which includes all the most important and popular filters approved worldwide. Depending on the intended degree of protection and UV protection zone, several organic UV filters are typically combined and used in sunscreens and personal care products in concentrations that in general do not exceed 10% in combination with also an inorganic UV filter.

The main concern used to focus merely on the UV filters utility and efficiency in protecting human skin and health from the harmful effects of UV radiation. Only very recently, concern has been raised regarding their path and their fate in the environment.

UV filters may enter the environment through direct and indirect sources (Giokas et al., 2007). The direct sources regard the washing off effect during bathing activities in the ocean, lakes, rivers and swimming pools as well as industrial waste water discharges. Indirect inputs are related to domestic waste water discharges (during showering, clothes washing and urine excretion) and via waste water treatment plants. The main environmental concerns regarding these compounds are related to their considerable octanol–water coefficients, bioconcentration factors and organic carbon coefficients, as is visible in Table 2, which means that these compounds are significantly lipophilic and have a particular tendency to concentrate and/or accumulate in the aquatic environment's soils and sediments as well as in the food chain (Díaz-Cruz et al., 2008; Díaz-Cruz and Barceló, 2009; Giokas et al., 2007).

The increased release of UV filters into the environment has prompted them to be considered a new class of pollutants. Díaz-Cruz (Díaz-Cruz et al., 2008) compiled data regarding UV filters levels in the aquatic environment. According to this review the reported concentrations varied depending on the sampling location and the intensity of the recreational activities. UV filters have been primarily detected in bathing waters (rivers, lakes, sea water) with concentrations up to 10 μg/L. The maximum concentrations have been measured during the warmest summer days, especially in noon hours when sunscreen application is also maximum, as a consequence of the increased sunlight irradiation intensity and exposure. UV filters have also been detected in sewage water (untreated and treated sewage effluents), sludge, sediments and soils with levels that reach mg/L values, and in fish from rivers and lakes used for bathing, with levels that reach several g/kg.

More recently UV filters have also been detected in human breast milk (Schlumpf et al., 2010) and human urine (León et al., 2010).

Data regarding the presence of UV filters in swimming-pool water are rather scarce. Lambropoulou (Lambropoulou et al., 2002) reported the determination of two UV filters, BP3 and EHDPABA, in swimming-pool waters and in showers waste waters near swimming pools, in concentrations from 2 to 10 μg/L. Giokas (Giokas et al., 2004) reported the determination of three UV filters [BP3, EHMC and 4-methylbenzylidene camphor (4MBC)] in swimming-pool waters and in shower waste waters near swimming pools. The study showed that UV filters were present in concentrations up to 10 ng/L. Vidal (Vidal et al., 2010) reported the determination of UV filters [BP3, isoamyl *p*-methoxycinnamate (IMC), 4MBC, OCR, EHDPABA and EHMC] on two swimming pools, one public and