

## Influence of water matrix on benzophenone degradation by UV-irradiation

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**Abstract:** This study presents the results from a bench-scale UV irradiation experiment of benzophenone (BP) in different water matrices. Despite the reported resistance of BP to UV-irradiation, it was successfully degraded in solution when intensively irradiated by UV light in a batch reactor for 4 h. In this way, it was possible to remove 56 and 45 % of 1.0 and 10  $\mu\text{g}\cdot\text{L}^{-1}$  of BP in Milli-Q water, respectively. The addition of a mixture of anions suppressed the degradation of BP at the lower concentration level by 20 %. The addition of a dissolved organic carbon (DOC) surrogate mixture (DOC:BP mole ratio of 3000:1) increased the degradation of BP in Milli-Q water (removal 80 %). At 1.0  $\mu\text{g}\cdot\text{L}^{-1}$  of BP and 1.0  $\text{mg}\cdot\text{L}^{-1}$  of DOC, removal was 70 %, while at 10  $\mu\text{g}\cdot\text{L}^{-1}$  of BP and 10  $\text{mg}\cdot\text{L}^{-1}$  of DOC, there was no observable difference in removal compared with the removal in Milli-Q water. The results show that both DOC and anions influence the photodegradation of BP. Furthermore, it was shown that the removal efficiency depends on the concentration of BP. These findings show the importance of a detailed characterisation of the water matrix in studies relating to the removal of micropollutants during UV irradiation.

**Keywords:** micropollutant; fotodegradation; DOC; inorganic ions.

### INTRODUCTION

Benzophenone is a widely used chemical ingredient in insecticides, personal care products and sunscreens, agricultural chemicals, fragrances and as a UV light absorber in plastics and polymers.<sup>1,2</sup> Recent studies, however, have reported its acute ecotoxicity and genotoxicity.<sup>1,3</sup> A comprehensive study on the occurrence of 19 multi-class emerging organic contaminants in three municipal solid waste landfills and three wastewater treatment plants (WWTPs) located in north east Poland was presented by Kapelewska *et al.*<sup>4</sup> Benzophenone was present in all the

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samples analysed, with levels in WWTP effluent and groundwater above  $1 \mu\text{g}\cdot\text{L}^{-1}$ . Wu *et al.*<sup>5</sup> investigated the environmental behaviour of benzophenone-type UV filters and their derivatives in four WWTPs, and their receiving surface waters (SW) in Shanghai, China. Benzophenone and benzophenone-3 were the most abundant and had the highest frequency of detection among the studied benzophenone-type UV-filters. In river water the levels of BP were between 200–713  $\text{ng}\cdot\text{L}^{-1}$  (in two rivers observed mean values were 317 and 407  $\text{ng}\cdot\text{L}^{-1}$ ). Influent water in WWTP had a mean value of 839  $\text{ng}\cdot\text{L}^{-1}$ , while effluent had mean value of 306  $\text{ng}\cdot\text{L}^{-1}$ . Kameda *et al.*<sup>6</sup> investigated the occurrence of eight UV-filters and 10 UV-light stabilizers in SW and sediment (Saitama Prefecture, Japan) during August and September, 2008. Benzophenone was detected in nine out of 18 samples of moderately and heavily polluted river water in the range from 2–68  $\text{ng}\cdot\text{L}^{-1}$ . Kotnik *et al.*<sup>7</sup> published the occurrence of BP in river water (30–88  $\text{ng}\cdot\text{L}^{-1}$ ), lake water (33–120  $\text{ng}\cdot\text{L}^{-1}$ ) and sea water (51–56  $\text{ng}\cdot\text{L}^{-1}$ ) in Slovenia. Loraine and Pettigrove<sup>8</sup> reported the concentrations of BP in non-treated drinking water in the range 0.36–0.79  $\mu\text{g}\cdot\text{L}^{-1}$  (Colorado River, USA). The mean concentration in the treated drinking water was 0.26  $\mu\text{g}\cdot\text{L}^{-1}$ . Similarly, Stackelberg *et al.*<sup>9</sup> reported the highest concentration of BP in a treated drinking water (0.13  $\mu\text{g}\cdot\text{L}^{-1}$ ).

Based on its environmental occurrence, BP is likely to occur in water sources used for drinking water supply from either river water or bank filtered water, even though studies show that it is biodegradable in natural waters. In their study on the natural degradation of BP ( $10 \mu\text{g}\cdot\text{L}^{-1}$ ) in environmental waters by photo- and microbial degradation, Chen *et al.*<sup>10</sup> found that the photodegradation rates were faster under solar irradiation in natural water than in pure waters. The half-life of BP in pure water was 16.23 h, while for lake and river water it was 10.62 and 8.67 h, respectively. Natural water contains various common constituents including  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Fe}^{3+}$ ,  $\text{NO}_3^-$  and dissolved organic compounds such as humic and fulvic acids, which explains the observed differences in the photodegradable potential between pure and natural water. In pure water, the photodegradation rate is known to decrease with the increasing amounts of BP ( $10\text{--}500 \mu\text{g}\cdot\text{L}^{-1}$ ). Microbial degradation of BP also occurs in real water samples. Bogunović *et al.*<sup>11</sup> reported a half-life of 1.4 h for BP when testing the biodegradability of a mixture of compounds (BP, benzophenone-3, carbamazepine and caffeine) in a laboratory test filter filled with an inert support.

When river water is used as a drinking water source, it is usually disinfected first, and one of the techniques that can be used for this is UV irradiation. Typically, this uses low-pressure UV lamps (UV-LP), which irradiate the water at absorption maximum of DNA, which is in the range 240–260 nm. UV-irradiation can also degrade sensitive micro-pollutants. However, any natural organic matter (NOM) present can influence the overall removal process. Photodegradation can proceed *via* direct photodecomposition due to the absorption of photons or *via*

indirect photodecomposition induced by the reactions with excited states of other components or oxide radicals, *e.g.*,  $\cdot\text{OH}$  and  $\text{CO}_3^{\cdot-}$ ), present in a certain water body.<sup>12</sup> For instance,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$  can either inhibit or enhance photo-alteration of organic compounds, by scavenging or generating photo-oxidants.<sup>13,14</sup> Giokas and Vlessidis<sup>15</sup> showed that the formation of photo sensitizers by photolysis of humic acids, sodium chloride and nitrate, can induce the photodegradation of UV filters. During the treatment, the photo sensitizers in natural waters can also compete with the target compounds for photons, and act as a filter hindering the transmission of light resulting in lower photolysis rates.<sup>1</sup> Several studies have also found that the matrix affects the removal of selected pharmaceuticals by UV-C induced direct phototransformation. For example, Canonica *et al.*<sup>16</sup> observed an accelerated depletion of  $17\alpha$ -ethinylestradiol in natural waters containing DOC ( $1.7\text{--}2.1\text{ mg}\cdot\text{L}^{-1}$ ) and nitrate ( $37\text{ mg}\cdot\text{L}^{-1}$ ), while for diclofenac, sulphamethoxazole and iopromide no significant changes were observed. This is because of the presence of different photo-oxidants resulting in indirect phototransformation that is important only for this particular compound in natural water. Contrary to that, other compounds are affected by the direct phototransformation. The authors also showed that phototransformation must be taken into account when evaluating the formation of UV disinfection by-products of pharmaceutical residues in water, and that water quality influences photodegradation induced by natural water constituents. It is not only a reduction in rate that is possible due to the presence of UV light absorbing compounds, *e.g.*, DOC, but also enhanced degradation *via* indirect transformations must be taken into account. It was concluded that this is important for compounds less sensitive to direct phototransformation and those that have a high propensity to be oxidized. Yuan *et al.*<sup>17</sup> observed that in the presence of humic acid ( $2\text{ mg}\cdot\text{L}^{-1}$  DOC), bicarbonates ( $2\text{ mmol}\cdot\text{L}^{-1}$ ) and nitrates ( $1.4\text{ mg}\cdot\text{L}^{-1}$ ), degradation of ibuprofen, diphenhydramine and phenytoine decreased due to competition from humic acid for photons. In opposition to that, the degradation of phenazone slightly increased, due to indirect production of  $\cdot\text{OH}$  from the reaction of UV light, humic acid and nitrate. This is an important source of  $\cdot\text{OH}$  and nitrogen dioxide.

The prolonged irradiation causes the degradation of BP even though BP itself is not prone to photodegradation.<sup>1</sup> The photodegradation of benzophenones is accelerated in lake water (DOC  $1.61\text{ mg}\cdot\text{L}^{-1}$ , nitrates  $5.62\text{ mg}\cdot\text{L}^{-1}$ ) in comparison to distilled water.<sup>1</sup> However, in seawater (DOC  $1.18\text{ mg}\cdot\text{L}^{-1}$ , nitrates  $0.13\text{ mg}\cdot\text{L}^{-1}$ ), the half-lives of the majority of the studied benzophenones were longer. Photosensitizers (*e.g.*, nitrates) that can produce various reactive species were noticed as important for the observed differences in various water matrices. Li *et al.*<sup>18</sup> investigated the photolytic degradation of benzophenone-3 and its metabolite 4-hydroxybenzophenone. Here, the photolytic rate was faster in natural waters. It was shown that only anionic forms can undergo direct photodegrad-

ation, while in seawater and freshwater an indirect mechanism involves the triplet-excited dissolved organic matter. In addition, in fresh water, the hydroxyl radical mechanism is also involved. Semones *et al.*<sup>19</sup> showed that the degradation by simulated solar irradiation of benzophenone-3 and sulisobenzene was enhanced in the presence of fulvic acid, a natural organic matter, and in filtered wastewater effluent and river water. The main pathway for degradation is the reaction with  $\bullet\text{OH}$ . Common to all these studies is that the DOC was either commercially obtained or isolated from natural water without any knowledge of its chemical composition. The use of DOC surrogates with defined structure and content is known from the literature and the application of it allows experimental results to be compared. This approach was used by Bond *et al.*<sup>20</sup> who studied the formation of disinfection by-products from different types of DOC by oxidation. In another study, Autin *et al.*<sup>21</sup> compared two advanced oxidation processes (UV/H<sub>2</sub>O<sub>2</sub> and UV/TiO<sub>2</sub>) for removing metaldehyde. In this study, metaldehyde: a NOM surrogate with a mole ratio of 1:1000 with equimolar concentrations of serine, leucine and resorcinol was applied. The mixture of two hydrophilic amino acids (serine and leucine) and a hydrophobic neutral compound, resorcinol, is representative of the low molecular dissolved organic carbon that is anticipated as a post-coagulation residual in water treatment. Since amino acids represent components in algae-rich waters,<sup>20</sup> this approach was adopted in this study with the aim to test the influence of DOC with the defined composition on the removal of poorly photodegradable BP by UV irradiation. The photodegradation was performed using an UV-LP lamp in the presence and in the absence of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>, which are common anions in drinking water. It needs to be mentioned that nitrates, which can also contribute towards degradation, were not added to the matrix. Although this does not reflect the “real” situation, the results will contribute to the better understanding of the effect that water matrix constituents have on the UV degradation of BP.

## EXPERIMENTAL

### *Water matrices*

Benzophenone irradiation experiments were performed in: a) Milli-Q water (18.2 M $\Omega$ ·cm, 25 °C; Milipore) and b) synthetic water prepared from Milli-Q water with the addition of sodium bicarbonate (99.5 % purity; Acros Organics, USA), CaCl<sub>2</sub>·2H<sub>2</sub>O (*p.a.* Zorka Šabac, Serbia) and MgSO<sub>4</sub>·7H<sub>2</sub>O (*p.a.* Merck, Germany). Its composition was in accordance with the DIN 12902 standard with the following final concentrations of ions: 0.6 mmol Cl<sup>-</sup>·L<sup>-1</sup>, 0.5 mmol HCO<sub>3</sub><sup>-</sup>·L<sup>-1</sup> and 0.2 mmol SO<sub>4</sub><sup>2-</sup>·L<sup>-1</sup>. Both matrices were tested with and without the addition of a DOC surrogate at concentrations of 1.0 and 10 mg·L<sup>-1</sup>. The equimolar ratios of surrogates were used to obtain solutions of DOC. The DOC surrogate solution was prepared using 500 mg·L<sup>-1</sup> solutions of L-leucine, L-serine and resorcinol (all from Reagent Plus; 99 %; Sigma Aldrich) in MilliQ water.

### *Benzophenone standard solutions*

Experimentally, two concentrations of benzophenone (Reagent Plus 99 %; Sigma Aldrich) were used: 1.0 and 10  $\mu\text{g}\cdot\text{L}^{-1}$ . The lower concentration represents the environmentally relevant level. Radical scavenging in the photolytic reactor was avoided by using an acetonitrile spiking solution. A DOC surrogate solution was spiked into Milli-Q and synthetic water to simulate realistic mole ratio of BP:DOC (1:3000) in all experiments. In the experiments including 1.0 and 10  $\mu\text{g}\cdot\text{L}^{-1}$  of BP, the total DOC content was 1.0 and 10  $\text{mg}\cdot\text{L}^{-1}$ , respectively.

### *Photodegradation*

Photodegradation was achieved with a low-pressure (LP) mercury UV lamp emitting 90 % of its radiation at 254 nm.<sup>1</sup> Experiments were performed in a cylindrical glass reactor vessel with the lamp placed in a water-cooled quartz immersion well. The UV irradiation had an intensity of  $8.91\times 10^{-7}$  Einstein $\cdot\text{s}^{-1}$ . Sample solutions (760 mL) were exposed for 4 h in a series of batch experiments with constant stirring (magnetic stirrer: 400 rpm). A long irradiation time was necessary to achieve the measurable changes in BP concentrations, since BP is resistant to photodegradation. Accordingly, experimental conditions are not directly related to drinking water disinfection fluence (dose) of 400  $\text{J}\cdot\text{m}^{-2}$ .

### *Sample preparation and chemical analysis*

Samples were first pre-concentrated using solid-phase (SPE) extraction (Oasis HLB: 3cc, 60 mg, Waters Corporation, MA, USA), derivatized with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA, Sigma Aldrich) in methanol and analysed using gas chromatography–mass spectrometry (GC–MS). Full details are given in Kotnik *et al.*<sup>1</sup>

The removal of BP was calculated as the ratio between  $A_{\text{IRR}}/A_{\text{IS}}$  and  $A_0/A_{\text{IS}}$ , where  $A_0$  is the area under the curve (AUC) of the targeted ion peak for BP ( $m/z$  377) in the initial solution,  $A_{\text{IS}}$  is the AUC of the targeted ion peak of the internal standard (benzophenone d-5,  $m/z$  382), and  $A_{\text{IRR}}$  is the AUC of the targeted ion peak of BP ( $m/z$  377) after 4 h irradiation. Separate QC checks were performed to assess the relative standard deviation of the analytical measurements and of the whole experimental procedure repeatability. The relative standard deviation of removal ( $n = 2$ , analytical procedure only) was 8 % and < 0.1 % at 10 and 1.0  $\mu\text{g}\cdot\text{L}^{-1}$  BP, respectively. To test method repeatability, two experiments were performed in duplicate: irradiation in MilliQ water at low BP and DOC concentrations and irradiation in synthetic water with a high concentration of BP but without the DOC surrogate. Differences in removal between the repeated experiments in comparison to the first test were –16 and –12 %.

## RESULTS AND DISCUSSION

The results of irradiation experiments involving Milli-Q and synthetic water matrices with and without the addition of surrogate DOC are presented in Fig. 1.

The results revealed 56 and 45 % removal of BP in Milli-Q water after 4 h at an initial concentration of 1.0 and 10  $\mu\text{g}\cdot\text{L}^{-1}$ , respectively (Fig. 1). In the case of synthetic water BP removal was 35 and 49 %. These results agree with those obtained by Kotnik *et al.*<sup>1</sup> who report of a  $t_{1/2}$  of 4.44 h in distilled water.

### *Influence of DOC*

With the exception of synthetic water, at a BP concentration of 10  $\mu\text{g}\cdot\text{L}^{-1}$  removal was between 21-36 % higher in the presence of DOC (Fig. 1). All changes in BP concentration above 16 % were assumed relevant for discussion

based on the experimental repeatability, *i.e.*, irradiation in MilliQ water at low levels of BP and DOC and irradiation in synthetic water at higher BP levels, without the addition of the DOC surrogate. Differences between the duplicates for these experiments were  $-16$  and  $-12$  % in overall BP removal. Clearly, low molecular weight DOC contributes to the degradation of low levels of BP ( $1.0 \mu\text{g}\cdot\text{L}^{-1}$ ). This agrees with literature findings for compounds that are prone to indirect photodegradation.<sup>16–19</sup>

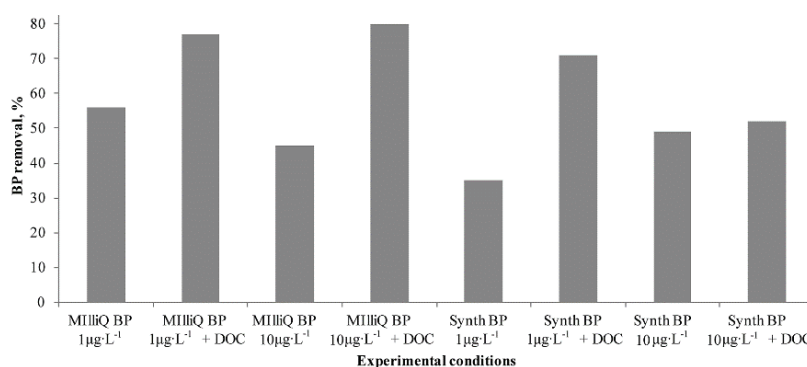


Fig. 1. Benzophenone removal by UV irradiation (4 h) in different water matrices. Concentration of BP:  $1.0$  and  $10 \mu\text{g}\cdot\text{L}^{-1}$ .

Interestingly, when DOC was increased, the increase in the removal of BP was similar regardless of the presence of  $\text{HCO}_3^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ . Additionally, the salt mixture did not contain  $\text{NO}_3^-$ , which is usually thought of as being responsible for enhancing degradation.<sup>1,12</sup> The competitive effects of DOC for UV light were not observed in Milli-Q water at both concentrations of BP, although it is known that resorcinol, L-serine and L-leucine can be degraded to different extents by UV light.<sup>20</sup> This was not observed at the lower level of BP and DOC in the synthetic water matrix, too. However, in the case of the higher level of BP and DOC, the results indicate that DOC competition for UV light is enhanced by the presence of salts, and/or simply that the higher amount of DOC acts as a self-quenching agent.

#### *Salts influence*

The influence of adding salts (mixture of  $\text{HCO}_3^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) is shown in Fig. 2. The difference in BP removal was calculated by the subtraction of the removal obtained in samples without salts from the removal observed in samples with salts addition. Salt addition did not influence the removal of BP by irradiation at a BP concentration of  $10 \mu\text{g}\cdot\text{L}^{-1}$  in MilliQ water and  $1.0 \mu\text{g}\cdot\text{L}^{-1}$  in the presence of surrogate DOC. However, a reduction in removal is observed at  $1.0 \mu\text{g}\cdot\text{L}^{-1}$  of BP, in MilliQ water (21 %) and at a higher concentration of BP and DOC (28 %).



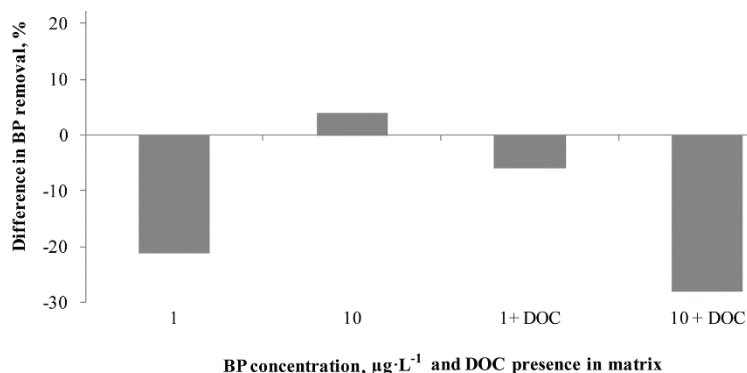


Fig. 2. Differences in BP removal due to salt addition in MilliQ and MilliQ enriched with DOC surrogates.

This is probably due to the scavenging effect of anions (observable in the experiment at a low BP concentration without DOC) and to the competition from DOC for photons, and/or reactive photo oxidants in solution (present only in the case of a higher level of DOC). When DOC was not present and the initial BP concentration was  $10 \mu\text{g}\cdot\text{L}^{-1}$ , the anion scavenging was not important. This can be explained by the higher initial concentration of BP that competes for photons, while the concentration of the scavenging anions is the same in both cases. At the low amounts of DOC and BP, no significant degradation suppression with salt addition was observed. From the literature<sup>20</sup> it is known that the DOC surrogates used in the present study are degraded by UV-C *via* photon absorption, rather than by reacting with hydroxyl radicals, allowing them to compete for photons. In contrast, anions can act both as scavengers and generators of photo-oxidants. The overall result is that degradation of BP was not suppressed. A possible explanation is that bicarbonate generates carbonate radicals, if other organic radicals are present in solution due to the photolysis of organic molecules. The carbonate radical has been shown to be selective to certain micro-pollutants by acting as an electrophilic agent.<sup>22,12</sup> Such an accelerating effect is diminished at the higher concentrations of DOC and BP due to the aforementioned reasons, *e.g.*, the absorption of photons by DOC, and/or competition for reactive species by self-quenching. Peng *et al.*<sup>12</sup> reported that an increasing amount of bicarbonate (from  $2.0$  to  $16 \text{ mmol}\cdot\text{L}^{-1}$ ) causes slowing down the osmosis of photons and the solution becomes impermeable to UV radiation. The authors also showed that the rate of nonyl-phenol photodegradation was the highest at the lowest bicarbonate concentration ( $2.0 \text{ mmol}\cdot\text{L}^{-1}$ ). The lower permeability towards photons, due to an increase in the amount of bicarbonate by a factor of 5–8, causes a lower concentration of the excited states of organic molecules or radicals that would otherwise contribute to the formation of carbonate radicals (responsible for degradation). Results obtained in this work, where on the one side salts do not have a negative

effect on degradation (low BP and DOC concentration), while on the other they suppress degradation (higher DOC and BP concentration), agree with the literature findings.

#### CONCLUSION

This study shows the effect that inorganic and organic water constituents have on the degradation of BP by UV irradiation. This effect is dependant on BP and DOC concentrations. Surrogate DOC ( $1.0 \text{ mg}\cdot\text{L}^{-1}$ ) increased the efficiency of BP degradation in Milli-Q water at BP concentrations of  $1.0$  and  $10 \text{ }\mu\text{g}\cdot\text{L}^{-1}$  by 21 and 31 %, respectively. The same effect was observed in water containing inorganic ions and  $1.0 \text{ }\mu\text{g}\cdot\text{L}^{-1}$  of BP. However, at  $10 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ , BP removal was 49 %, and did not increase in the presence of anions and at the higher DOC content. It was shown that the addition of ions suppressed the degradation at the lower level of BP in Milli-Q water, due to the scavenging effects of the anions. Such degradation suppression happens at the high BP concentration and in the presence of DOC. This is because of the competitive behaviour of DOC, either for UV light, and/or for photoinduced reactants. The other factor affecting the results is the lower permeability of the solution towards UV radiation.

The main conclusion is that, in addition to direct or indirect photodegradability of micropollutants, it is important to evaluate in detail the quality of the environmentally relevant water matrices exposed to UV irradiation. Besides the anion characterisation, the future research work should consider possible variations in DOC (*e.g.*, fluctuations related not only to DOC quantity, but also qualitative characteristics of its constituents). Further investigations should also include exploring the possible contribution of the UV disinfection process to micropollutants removal, within practically relevant water treatments (*e.g.*, related to irradiation positioning within treatment line and its fluence).

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#### ИЗВОД

#### УТИЦАЈ ВОДЕНЕ МАТРИЦЕ НА РАЗГРАДЊУ БЕНЗОФЕНОНА UV ЗРАЧЕЊЕМ

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У раду су представљени резултати лабораторијског експеримента излагања бензофенона (BP) UV зрачењу у различитим воденим матрицама. Упркос познатој отпорности BP на UV зрачење, он је успешно разграђен у раствору који је интензивно зрачен током 4 h у шаржном реактору. На овај начин било је могуће уклонити 56 и 45 % BP у растворима



концентрације 1,0 и 10  $\mu\text{g}\cdot\text{L}^{-1}$  у Milli-Q води, редом. Додатак смеше анјона изазвао је смањење деградације ВР на концентрационом нивоу нижем за 20 %. Додатак сурогат смеше раствореног органског угљеника (DOC, молски однос DOC:ВР = 3000:1) стимулисао је разградњу бензофенона у Milli-Q води (уклањање 80 %). Код концентрације 1,0  $\mu\text{g}\cdot\text{L}^{-1}$  ВР и 1,0  $\mu\text{g}\cdot\text{L}^{-1}$  DOC, ефикасност уклањања је била 70 %, док код концентрације од 10  $\mu\text{g}\cdot\text{L}^{-1}$  ВР и 10  $\mu\text{g}\cdot\text{L}^{-1}$  DOC није било приметне разлике у ефикасности уклањања, у поређењу са уклањањем постигнутим у Milli-Q води. Резултати показују да и DOC и анјони и утичу на фотодеградацију ВР. Додатно је утврђено да ефикасност уклањања зависи од концентрације ВР. Резултати указују на значај детаљне карактеризације воденог матрица у студијама који се баве уклањањем микрополутаната при излагању UV зрачењу.

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