



# Optimized photodegradation of Bisphenol A in water using ZnO, TiO<sub>2</sub> and SnO<sub>2</sub> photocatalysts under UV radiation as a decontamination procedure

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**Abstract.** Experiments on photodegradation of Bisphenol A (BPA) were carried out in water samples by means photocatalytic and photo-oxidation methods in the presence of ZnO, TiO<sub>2</sub> and SnO<sub>2</sub> catalysts. The objective of this study was to develop an improved technique that can be used as a remediation procedure for a BPA-contaminated surface water and groundwater based on the UV solar radiation. The photodegradation of BPA in water performed under a low-intensity UV source mimics the UVC and UVA spectrum of solar radiation between 254 and 365 nm. The archived results reveal higher degradation rates observed in the presence of ZnO than with TiO<sub>2</sub> and SnO<sub>2</sub> catalysts during 20 h of irradiation. The intervention of the advanced photocatalytic oxidation (PCO) reduces the time of degradation to less than 1 h to reach a degradation rate of 90 % for BPA in water. The study proposes the use of ZnO as a competitor catalyst to the traditional TiO<sub>2</sub>, providing the most effective treatment of contaminated water with phenolic products.

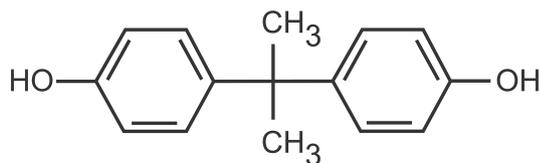
## 1 Introduction

Bisphenol A (BPA; 4,4'-isopropylidenediphenol; Fig. 1) is a common industrial product, manufactured in large quantities worldwide. Almost 99 % of BPA is used as a common intermediate compound in the production of polycarbonate, epoxy resins, unsaturated polyesters and styrene resins (Staples et al., 2000). BPA is used as a coating material for cans, and as an additive in powder paints, thermal paper, dental fillings, antioxidants and polycarbonate plastic as well. Therefore, it is usually found in many plastic products including water pipes, drinking water containers and tableware (Vandenberg et al., 2007).

Recent studies have shown that BPA has potentially toxic effects, inducing estrogenic endocrine disruption and increased risk of tumorigenesis (Keri et al., 2007; Vandenberg et al., 2007). They also indicated that BPA could trigger the disruption of corpuscular function even at very low concentration (0.23 ng L<sup>-1</sup>) leading to disorders of estrogenic hormone secretion (Chiang et al., 2004). BPA is released into water resources not only by discharge from manufacturing

but also from contaminated drainage networks, sewage and landfills (Welshons et al., 2006). In particular in developing countries BPA is produced – but without proper measures in operation regulating and monitoring the discharge of BPA containing fluid and solid waste into the environment, in particular aquatic systems (Arukwe et al., 2012; Baluka and Rumbelha, 2016). Disintegrated BPA derived from various industrial products under different weather conditions could reach surface water and groundwater by leaching processes. Furthermore, BPA can easily enter the human body, producing a broad spectrum of adverse health effects (Zhang et al., 2006). In fact, purification of contaminated surface water and groundwater has become a priority for some countries, a strategy that is in line with the increasing global demand for fresh water. Photodegradation can provide an affordable enhanced natural attenuation solution and add to the arsenal of classic treatment techniques.

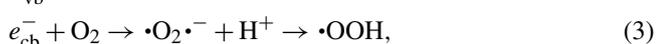
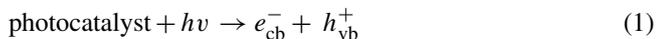
Photodegradation primarily occurs by either photolysis or photo-oxidation. Photolysis is a process in which chemical compounds dissolved in water (e.g., phenols and BPA) absorb sunlight or other illumination sources which directly



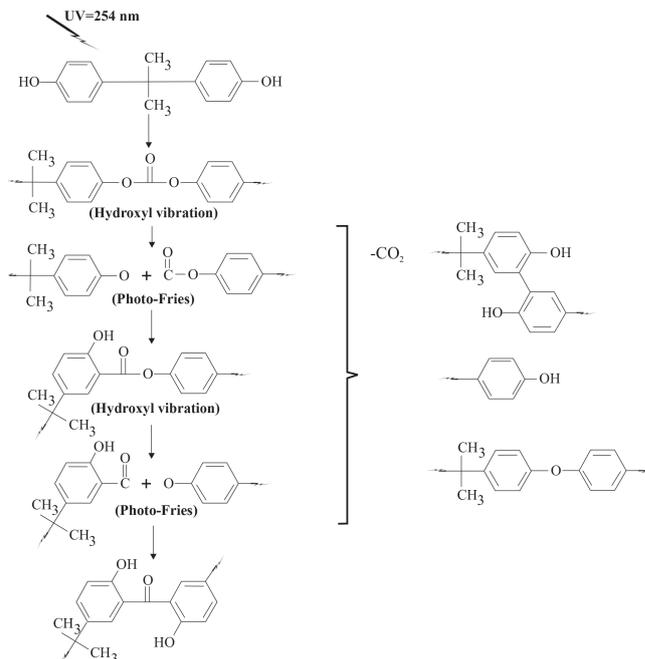
**Figure 1.** Structure of Bisphenol A.

results in their photochemical alternation (Howard, 1991a), while photo-oxidation involves the degradation of compounds through interaction with hydroxyl radicals or other similar oxidants. Both reactions can occur naturally in water and in the atmosphere (Staples et al., 1998). Moreover, disintegration of contaminants by photodegradation also can be explained by the photo-Fries rearrangement of BPA polycarbonate (Rivaton, 1995). The path of degradation is shown in Fig. 2. Photo-Fries is a complex reaction that occurs as a combined or independent process and plays the most important role during the outdoor weathering processes of polycarbonate (Pickett, 2011). The exposure of BPA with short wavelengths leads to substantial rearrangement of the aromatic carbonate into phenylsalicylate and dihydroxybenzophenone derivatives (Diepens and Gijmsan, 2007).

Rivaton et al. (1983) proved that photo-Fries rearrangement reactions are more likely to occur when short UV wavelength are used (< 300 nm). In contrast, advanced degradation (e.g., photo-oxidation) reactions have a high efficiency when wavelengths > 340 nm are used (Rivaton et al., 1983). However, BPA exhibits absorption of UV wavelength exceeding 290 nm in neutral and acidic methanol solutions (Diepens and Gijmsan, 2007; Howard, 1991b). Metal oxides have been widely used as catalysts for photodegradation in recent years and can be used for the successful treatment of water and total oxidation of organic pollutants considering the type and magnitude of contamination (Ferrandon, 2001; Ibadon and Fitzpatrick, 2013; Jackson and Hargreaves, 2009; Patel and Pathan, 2015; Pelizzetti et al., 1993). Generally, the effectiveness of a photocatalyst is characterized by its capacity to simultaneously adsorb reactants and photon energy. This is reflected by the photosensitivity of the catalyst and its large band gap (Du et al., 2009; Sakthivel et al., 2003). Photon energy greater than the semiconductor photocatalyst band gap (wavelength 254 nm) creates electron hole pairs (Horikoshi et al., 1998; Kaneco et al., 2004). The hole pair ( $e^- - h^+$ ) is generated at the surface of photocatalyst as shown in the equations below:



where  $h\nu$  is the photon energy and  $e_{\text{cb}}^-$  is the valence electron which is released to conduct the catalyst band and leaves the hole  $h_{\text{vb}}^+$  in the valence band.



**Figure 2.** Photo-Fries rearrangement of BPA modified after Rivaton (1995).

Currently, sodium hypochlorite (NaOCl) is widely used as a cleaning and disinfection agent that can be easily transported or stored (Rutala and Weber, 1997). The disadvantage of using NaOCl is the strong corrosive material that releases toxic chlorine gas when mixed with acids. Thus, safety precautions must be considered (Fukuzaki, 2006). However, sodium hypochlorite is also used in photo-oxidation of organic contaminants and wastewater treatment. Under UV exposure, the NaOCl produces chlorine and  $\cdot\text{OH}$  radicals, which turn the photolysis process into an advanced oxidation process (El-Kalliny, 2013). The hydroxyl radicals ( $\cdot\text{OH}$ ) are non-selective powerful oxidants that can react rapidly with a wide variety of aromatic ring compounds (Abdollahi et al., 2011; Sakthivel et al., 2003). The decomposition of free chlorine of the NaOCl under UV irradiation can be written as follows (El-Kalliny, 2013):



One of the most popular catalysts,  $\text{TiO}_2$ , is widely used for decontamination of various organic contaminants in water due to its attractive physical properties. Few studies have dealt with other catalysts such as ZnO and  $\text{SnO}_2$ , particularly the ZnO, which has almost the same band gap energy (3.2 eV) as  $\text{TiO}_2$  and exhibits high activity in comparison to other existing catalysts (Hariharan, 2006; Lizama et al., 2002; Poullos and Tsachpinis, 1999; Sakthivel et al., 2003). However, past reports have shown that ZnO is unstable due

to the dissolution in water to form  $\text{Zn}(\text{OH})_2$  (Bahnemann et al., 1987; Hoffman et al., 1994).

The objective of this study was to optimize the treatment procedure accelerating the photodegradation process of BPA and other phenolic compounds in natural water by using various photodegradation approaches: photodegradation, photo-oxidation/photocatalytic degradation and advanced photocatalytic oxidation degradation.

## 2 Materials and methods

The treatment approach was optimized through different stages considering various factors affecting photodegradation. High-purity Bisphenol A (99.99%), acetonitrile (HPLC grade > 99.99%) and sodium hypochlorite NaOCl (14–16%) were purchased from Merck (Darmstadt, Germany). The concentration of NaOCl is determined by titration with sodium thiosulfate. Ultra-pure water was provided using TKA MicroLab UV system (Niederelbert, Germany). High-purity ZnO and SnO<sub>2</sub> powder-grade catalysts (> 99.999%; powder < 5 μm) were purchased from Alfa Aesar (Karlruhe, Germany) and TiO<sub>2</sub> rutile grade (> 99.999%; powder < 5 μm) from Sigma Aldrich (Hamburg, Germany). Water sample filtration was performed using 0.45 μm polytetrafluoroethylene filter (Restek). BPA was analyzed by HPLC equipped with an L-4250 UV-VIS detector (Merck-Hitachi D6200A, Tokyo, Japan) at a wavelength of 254 nm using a Nucleosil C18-EC 125/4 column (Macherey-Nagel GmbH; Düren, Germany). Analyses were performed isocratically at a flow rate of 1 mL min<sup>-1</sup> and a 20 μL sample loop. As a mobile phase, a mixture of acetonitrile and water (70 : 30) was used. The quantification was carried out by external calibration (linear regression) with seven standard solutions in the range 5 to 60 ppm prepared using a 100 ppm BPA stock solution in acetonitrile solvent. Each of the BPA standards were prepared in 25 mL distilled water. Since the UV absorbance range is one of the most important factors affecting photodegradation, the maximum absorption value of BPA in aqueous samples was investigated using an Ocean Optics USB2000+ spectrometer (Dunedin, USA) equipped with a deuterium tungsten halogen light source (DH-2000); 1.5 mL of 25 ppm BPA solution prepared in water was filled in a 2 mL optical cell and analyzed in the wavelength range of 220–400 nm.

### 2.1 Photodegradation under UV

Photodegradation of 25 and 50 ppm BPA in 100 mL aqueous samples was achieved using low-pressure UV illumination provided by Köhler NU-6KL (Neulußheim, Germany) equipped with two UV lamps. The wide solar UV exposure (200–400 nm) is difficult to mimic in the laboratory. Therefore, the study evaluates the degradation process under the spectrum between 254 and 365 nm and an intensity range from 600 to 800 μW cm<sup>-2</sup>. The BPA samples in 250 mL rect-

angular glass beakers were exposed to direct UV irradiation (254 nm wavelength) with a distance of about 5 cm between the aqueous phase and the UV source. During the experiment, 5 mL of water samples was taken every 60 min; 100 μL of the filtered samples containing BPA was injected into the HPLC device by using a 250 μL glass syringe in order to observe the changes in concentration of BPA over time and the effect of the initial concentration on photodegradation. The above-mentioned HPLC procedure was used in the experiment.

### 2.2 Photocatalytic photodegradation

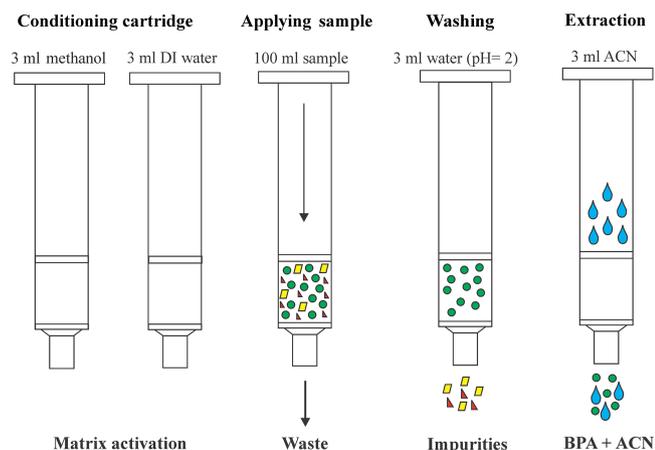
Photocatalytic degradation was used as a more advanced decontamination technique to remove BPA from water sample. Suspensions of the catalysts ZnO, TiO<sub>2</sub> and SnO<sub>2</sub> (each with 0.1% (w/w)) and 25 ppm BPA in 100 mL ultra-pure water was prepared and mixed for 15 min using a magnetic stirrer at 400 rpm rotation speed in order to allow maximal sorption of BPA on the catalysts' surface. Then the suspensions of the catalysts were directly irradiated at 250 rpm stirring speed for 5 h using both wavelengths (254 and 365 nm). Changes in BPA concentration were measured every 60 min using HPLC. Since the catalysts' amount is an important factor for photodegradation, the influence of catalysts' concentration on the photodegradation efficiency was investigated using two different concentrations of 0.1 and 0.2% (w/w).

### 2.3 Advanced photocatalytic oxidation

Advanced photocatalytic oxidation (PCO) experiments were carried out using a relatively low concentration of sodium hypochlorite (NaOCl) as an oxidizing agent in the presence of photocatalysts. Photodegradation was studied using suspensions of 25 ppm BPA in 100 mL ultra-pure water, 0.1% (w/w) of ZnO, TiO<sub>2</sub> and SnO<sub>2</sub> catalysts and 0.3 mM NaOCl. The samples were mixed for 15 min and placed under direct UV irradiation using both wavelengths 254 and 365 nm. Changes in BPA concentration were measured every 15 min during the total irradiation time of 1 h. Furthermore, the influence of different amounts of NaOCl on the photodegradation of BPA was investigated using ZnO as a photocatalyst and 0.1, 0.3 and 0.5 mM of NaOCl, respectively. A total of 100 μL of the filtered aqueous samples was analyzed by HPLC at each time interval.

### 2.4 Degradation products

Photodegradation products of the advanced photocatalytic oxidation experiments were investigated using Thermo Scientific Trace GC-MS (Bonn, Germany) equipped with a TG-1MT capillary column (30 m × 0.25 mm × 0.25 μm). For the experiments, suspension of 25 ppm BPA, 0.1% (w/w) ZnO catalyst and 0.1 mM NaOCl in 500 mL ultra-pure water were prepared in rectangular glass beakers; 50 mL of the



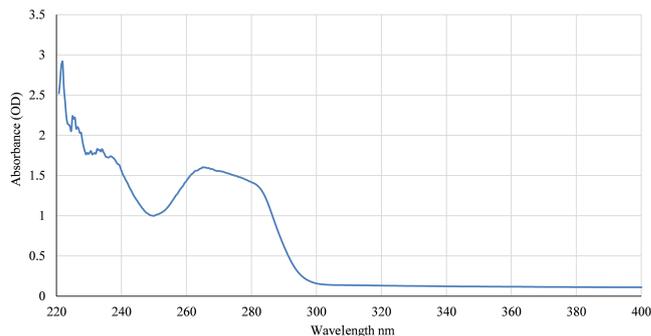
**Figure 3.** The steps of solid-phase extraction.

suspension were taken during the photodegradation experiment every 15 min. They were pre-concentrated using solid-phase extraction (SPE; Fig. 3). This was performed using 3 mL Chromabond HR-P glass cartridges purchased from Macherey-Nagel (Düren, Germany) filled with 200 mg of a highly porous polystyrene-divinylbenzene copolymer with high binding capacity up to 30 % of the adsorbent weight. The extraction of aqueous samples was carried out using the following procedure: SPE cartridges were conditioned using 3 mL of methanol followed by 3 mL of water; 50 mL water samples were applied into the cartridges at a flow rate of  $15 \text{ mL min}^{-1}$ ; 3 mL of water adjusted to pH 2.0 using 0.1 M HCl was used in the washing stage. Then organic compounds were extracted using 3 mL of high-purity acetonitrile as a final step; 1  $\mu\text{L}$  of the finally extracted samples was then injected into the GC-MS device in splitless mode. The injection temperature was  $260^\circ\text{C}$ . The oven temperature was adjusted as follows: initial oven temperature was  $120^\circ\text{C}$  for 4 min. Then, it was increased to  $250^\circ\text{C}$  with  $30^\circ\text{C min}^{-1}$  followed by a hold time of 1 min, after which the temperature was increased to  $270^\circ\text{C}$  at  $20^\circ\text{C min}^{-1}$  and held for 3 min. The transfer line temperature was adjusted to  $300^\circ\text{C}$ . Helium was used as a carrier gas with a flow rate of  $1.2 \text{ mL min}^{-1}$ . The temperature of the ionization source was adjusted to  $300^\circ\text{C}$ . Qualitative analysis was achieved using electron ionization at 70 eV and scan mode range from 45 to  $400 m/z$ .

### 3 Results and discussion

#### 3.1 UV–VIS absorbance spectrum

The UV spectrum of BPA in aqueous solution was measured as illustrated in Fig. 4. The results showed significant UV absorption at wavelengths greater than 250 nm. The spectrum showed a high optical density (OD) in the range of 250–290 nm with  $\lambda_{\text{max}}$  at 265 nm, confirming previously published findings (Diepens and Gijssman, 2008). Therefore, two



**Figure 4.** Bisphenol A UV–VIS absorbance spectrum in water (OD: optical density).

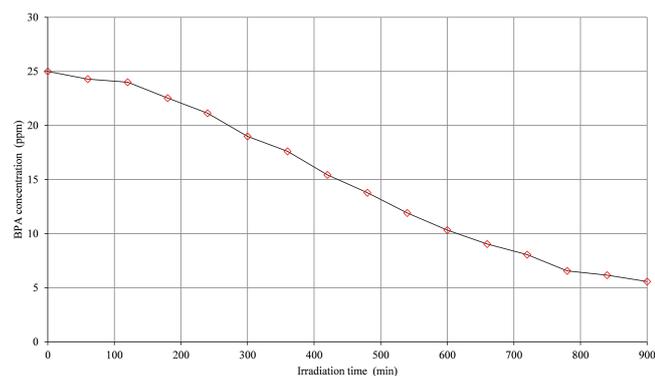
ranges of UV irradiation were used to insure maximum absorption to accelerate the disintegration reactions.

#### 3.2 BPA photodegradation under UV

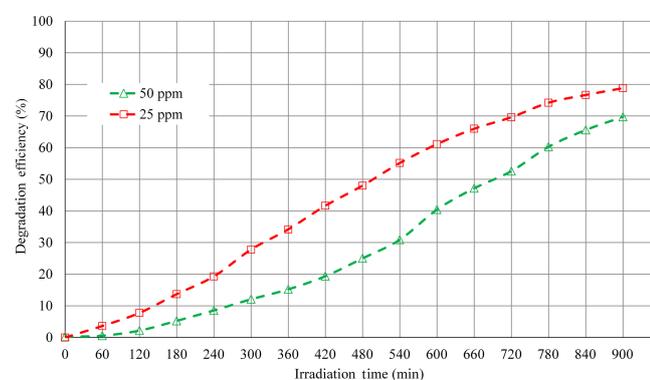
The results show a significant decrease in BPA concentration in the aqueous samples (Fig. 5). This accompanied color changes of the solution to yellow and light greenish-yellow as a result of the disintegration of BPA into other derivative products, which could be an indicator of the degradative progress. The change in pH was investigated during the experiment, and it showed a decrease during the experimental time ranging from 0.3 to 0.5 units below the initial value ( $\text{pH} = 5.8$ ). This can be explained by the increase in carbonic acid ( $\text{H}_2\text{CO}_3$ ) concentration resulting from dissolved  $\text{CO}_2$  in water (Donald, 1997). The photodegradation was relatively slow within the first 4 h of the experiment but thereafter occurred rapidly. This could be explained by the higher concentration of dihydroxybenzophenone near the surface, which decelerates the degradation process by efficient adsorption of UV irradiation, retarding the degradation of BPA (Pickett, 2011). However, the accelerated breakdown after 240 min of irradiation might be explained by more effective photo-Fries rearrangement coinciding with the disintegration of dihydroxybenzophenone compound that led to an increase in the photo-oxidation rate (radical formation; Diepens and Gijssman, 2007; Pickett, 2011). This process breaks the bonds between the atoms of BPA at specific moments and produces simpler organic compounds that can be easily disintegrated.

#### 3.3 Influence of BPA initial concentration

The results also revealed a linear relationship between the initial concentration of BPA and degradation rate (Fig. 6). It can be seen that the photodegradation efficiency of BPA decreased with the increase of the initial concentration. After 10 h of irradiation, about 46 (23 ppm) to 60 % (15 ppm) of the total amounts of BPA were disintegrated for the 50 and 25 ppm contaminated samples, respectively. The average degradation efficiency was 20 % higher than that of 50 ppm



**Figure 5.** Photodegradation of BPA in pure water samples under low-intensity UV irradiation.

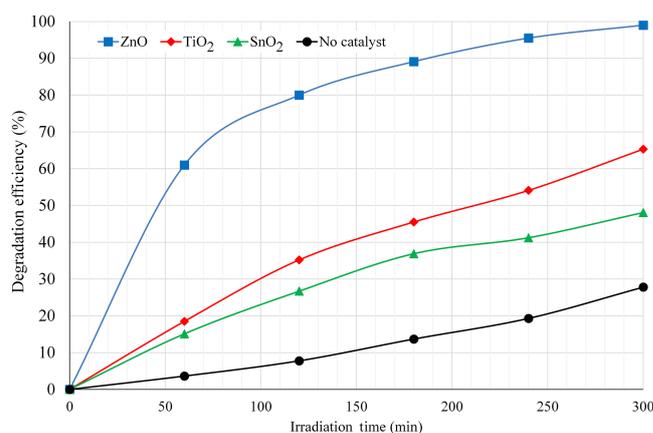


**Figure 6.** The effect of the BPA initial concentration on the progress of photodegradation.

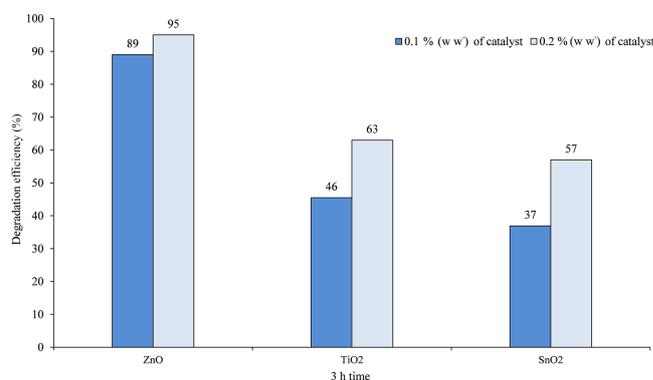
solution, resulting in efficient photoionization process and relatively more generated  $\bullet\text{OH}$  under the same amount of water and lower BPA concentration.

### 3.4 Photocatalytic degradation of BPA

Higher degradation rate was achieved when ZnO suspension was used rather than one of the other catalysts (Fig. 7) so that 98 % of BPA was degraded after 5 h. The results showed also that ZnO seems to be a suitable alternative to  $\text{TiO}_2$  that is commonly used. ZnO shows high efficiency during degradation due to the wider band gap ( $\Delta_{\text{ZnO}} = 3.4 \text{ eV}$ ), higher photosensitivity, electron mobility, lifetime and photocatalytic capacity compared to other semiconductors ( $\Delta_{\text{TiO}_2} = 3.2$ ,  $\Delta_{\text{SnO}_2} = 3.3 \text{ eV}$ ) (Hernandez et al., 2015; Thomazi et al., 2009; Yang et al., 2006). Furthermore, many reports showed that ZnO has similar photodegradation mechanism as  $\text{TiO}_2$  so that under UV light superoxide radicals ( $\bullet\text{O}_2^-$ ) and hydroxyl radicals ( $\bullet\text{OH}$ ) are generated in water, accelerating the oxidation of organic contaminants (Mills and Le Hunte, 1997; Rusmidah et al., 2010; Yamaguchi et al., 1998). These properties make the ZnO catalyst more susceptible to absorbing UV light below 380 nm as well as a visible spec-



**Figure 7.** Degradation efficiency of BPA in aqueous suspensions of ZnO,  $\text{TiO}_2$  and  $\text{SnO}_2$  under UV irradiation.

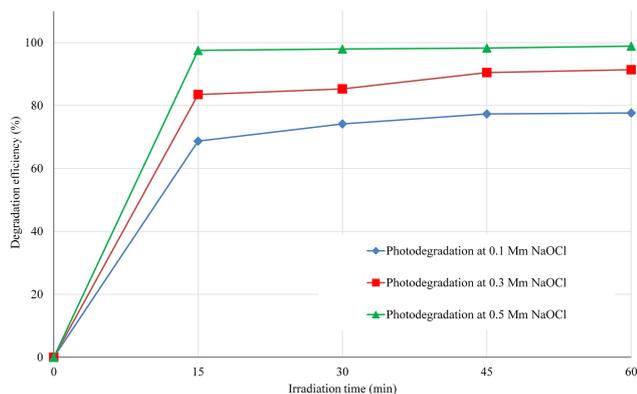


**Figure 8.** The impact of catalyst concentration on the efficiency of photodegradation.

trum range when it mixed with different materials (Guo et al., 2011). The GC-MS results for already degraded samples showed concentrations of both butylated hydroxytoluene and chlorohydroquinone as the major degradation byproducts at 88 % confidence. The butylated hydroxytoluene (BHT) is characterized chemically as a derivative of phenol and used primarily as an additive for food and cosmetics due to its antioxidant properties. It is non-toxic at intake rates above  $50 \text{ mg kg}^{-1} \text{ day}^{-1}$  (Branen, 1975). Chlorohydroquinone exposure has been listed in the classification of the National Fire Protection Association (NFPA) standard system for the identification of the hazards of materials for emergency response at the level 1 on a scale from 0 (no hazard) to 4 (severe risk) (NFPA, 2011).

### 3.5 Effect of the catalyst amount

The efficiency of photodegradation was found to increase rapidly with an increase in the amount of catalyst in all six prepared samples under the same experimental conditions and initial concentration of BPA of 25 ppm. The sam-

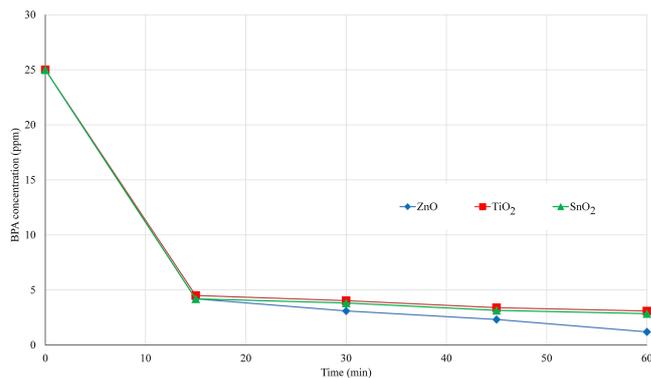


**Figure 9.** The efficiency of the BPA degradation by different doses of NaOCl in suspensions of ZnO.

**Table 1.** The effect of different oxidant concentration on the photodegradation of BPA within 1 h of irradiation.

Sample vol. (mL)/ conc. (ppm)	Catalyst 0.1 % (w/w)	Sodium hypochlorite mM	Degradation %
100/25	ZnO	0.1	77.6
		0.3	94.7
		0.5	99.9
100/25	TiO <sub>2</sub>	0.1	56.1
		0.3	87.7
		0.5	98.1
100/25	SnO <sub>2</sub>	0.1	56.7
		0.3	88.5
		0.5	94.3

ples were exposed to UV irradiation for 3 h. An increase in the catalyst concentration by 0.1 % (w/w) accelerated the photodegradation efficiency of BPA by 54 % for SnO<sub>2</sub> and 37 % for TiO<sub>2</sub>, whereas there were less significant changes achieved for ZnO with a relative increase of 6.7 % (Fig. 8). In fact, ZnO exhibits higher UV absorption and thus more capability to break the BPA than TiO<sub>2</sub> and SnO<sub>2</sub> at even low concentration of the catalyst (Lizama et al., 2002; Poulis and Tsachpinis, 1999; Sakthivel et al., 2003). Furthermore, ZnO shows a higher capacity to degrade BPA by releasing more free oxidative radicals (e.g., hydroxyl radicals •OH) into the aqueous suspension so that about 95 % of degradation could be achieved using 0.2 % (w/w) ZnO after 3 h of degradation, whereas only 63 and 57 % were achieved for the other catalysts TiO<sub>2</sub> and SnO<sub>2</sub>, respectively. Based on what was mentioned above, the subsequent decontamination approach was implemented using the lowest possible amount of the catalysts considering the preservation of physical and chemical condition of water; hence only 0.1 % (w/w) of the catalysts were used.

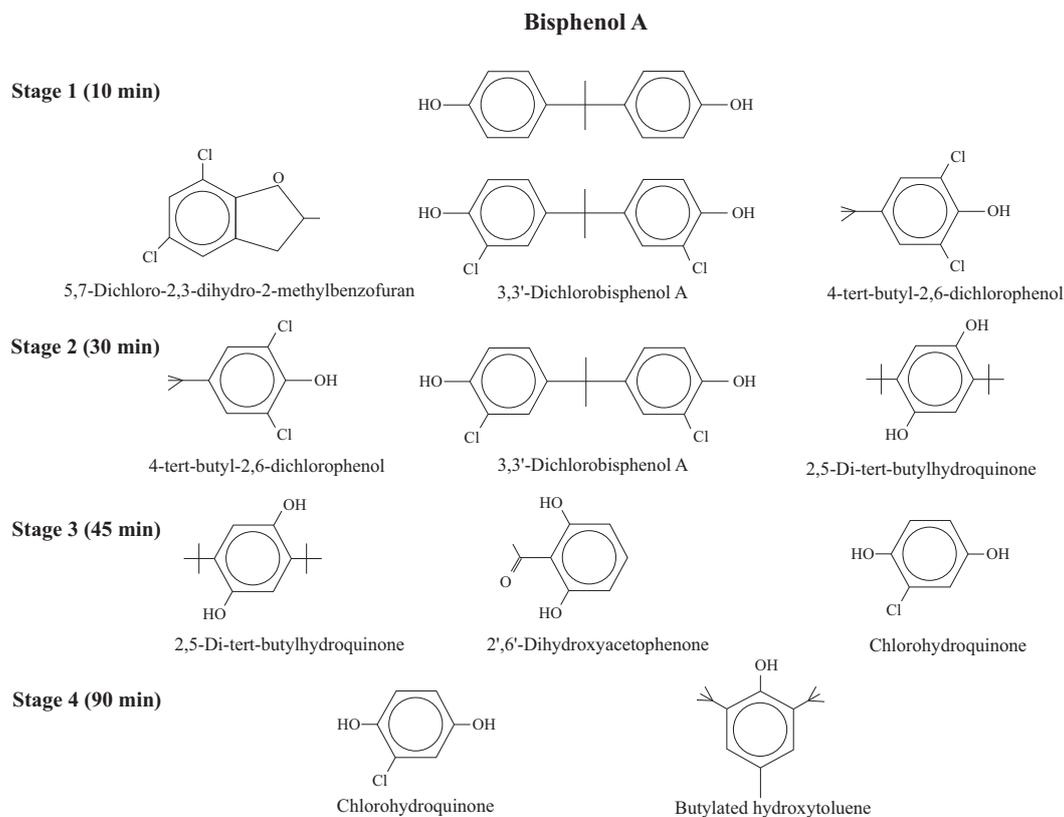


**Figure 10.** The concentration decrease of BPA using ZnO, TiO<sub>2</sub> and SnO<sub>2</sub> suspensions and advanced photooxidation (0.3 mM NaOCl).

### 3.6 Advanced photocatalytic oxidation

The experiments show high dependency of photodegradation on the initial oxidant concentration. The efficiency of photodegradation increases proportionally with the NaOCl concentration in aqueous samples as shown the Table 1. Therefore, a slight increase in the oxidant concentration had a significant effect on the degradation of BPA. The results show that 93 % of degradation was achieved within less than 1 h using ZnO as a catalyst at 0.3 mM NaOCl (Fig. 9). It is clear that the initial concentration of NaOCl influenced the degradation process and significantly accelerated the disintegration reactions of BPA. For instance, with an increase of the NaOCl concentration by 0.2 mM a higher degradation can be achieved (about 15–20 %). However, the applied amounts of NaOCl are relatively high in terms of drinking water quality, and thus minimal doses of sodium hypochlorite are recommended (<0.1 mM) to neutralize the chlorination effects and emerging disinfection byproducts (DBPs).

In this study, two reaction phases were distinguished under PCO treatment method. The first is characterized by a steep decrease in BPA concentration (in the first 15 min of the experiment, oxidation effect of HOCl). In the second stage, the efficiency of degradation stabilized over time and the reaction reached a steady state (less significant change in concentration). This can be explained either by less generation of  $e^-/h^+$  (valence electron/hole in the valence band), which reduced the photodegradation efficiency (Konstantinou and Albanis, 2004), or less formed •OH and O<sub>2</sub><sup>2-</sup> on the surface of the catalyst resulting in low relative ratios of •OH and O<sub>2</sub><sup>2-</sup> present for attacking BPA and thus retarding the photodegradation (Lathasree et al., 2004). The degradation progresses until complete oxidation is achieved. Figure 10 shows that the ZnO suspension exhibits high performance to remove BPA from water samples (second part of the reaction curve). This is explained by its ability to absorb larger fractions of photon energy than the other photocatalysts (Pardeshi and Patil, 2008).



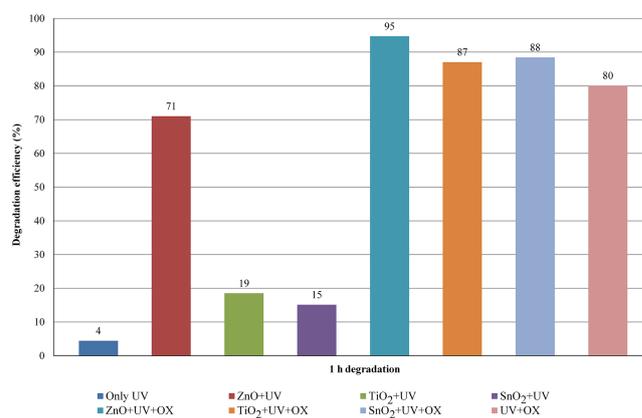
**Figure 11.** Advanced photocatalytic oxidation of BPA and predicted degradation compounds in GC-MS of the BPA aqueous samples.

**Table 2.** The final degradation products indicated by GC-MS.

Peak no.	Retention time (min)	$m/z$ (abundance %)	Molecular weight $m/z$	Formula
1	3.49	144, (47)	144.56	$C_6H_3(OH)_2Cl$
2	4.28	220, (98)	220.34	$C_{15}H_{24}O$

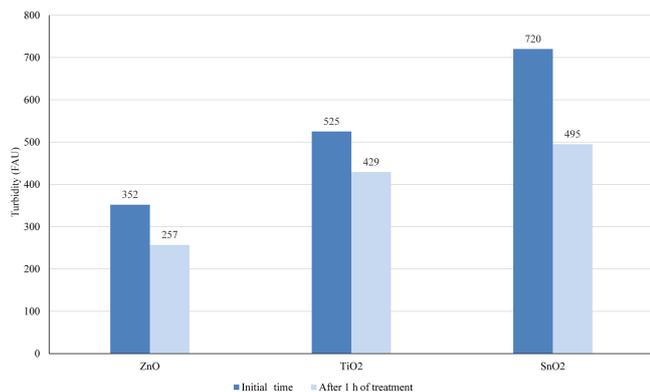
### 3.7 Byproducts of photocatalytic oxidation

Degradation byproducts were investigated using GC-MS. The analyses indicated the presence of phenol-derivative products, butylated hydroxytoluene and chlorohydroquinone based on the library database of the National Institute of Standard and Technology (NIST). Table 2 lists fragments ( $m/z$ ) and their relative abundances (%) for the main two disintegration products. The disintegration process of BPA into different relevant phenolic products has been divided into four stages over time, as shown in Fig. 11. The results show that BPA reacts rapidly with hypochlorous acid. It is likely that a chlorination dominates the degradation process by the electrophilic attack of HOCl on the phenoxide ions. As a result, various chlorinated derivatives can be observed after 10 min of degradation. Oxidation reaction of BPA progresses obviously after 30 min by the formation of three phenolate species of 4-tert-butyl-2,6-dichlorophenol, 3,3'-



**Figure 12.** Degradation performance of different methods for removing BPA from water.

dichlorobisphenol A, and 2,5-di-tert-butylhydroquinone. After 45 min, BPA disappeared and the photocatalytic oxidation is completed by formation of more simple phenolic compounds. The results were verified and compared with the NIST database for each stage. However, the kinetic of degradation for endocrine compounds such as BPA is rather complex and requires further investigation.



**Figure 13.** The change in turbidity of aqueous suspensions of ZnO, TiO<sub>2</sub> and SnO<sub>2</sub> in the beginning and after 1h of treatment using the advanced oxidation method with NaOCl. (The turbidity index is given in formazin attenuation units, FAUs.)

### 3.8 Assessment of degradation approaches

The performance of decontamination approaches was evaluated through two key factors: (i) treatment time at the lowest amount of catalysts as well as NaOCl (ii) and the achieved purification success. Figure 12 compares different methods used to remove BPA from water at fixed illumination time of 1 h and shows that photodegradation using ZnO and NaOCl as an oxidizing agent is the best option to remove BPA from water. As previously noted, ZnO exhibited a higher capacity to disintegrate organic contaminants from water in the presence of UV irradiation and it offers additional advantage of lower turbidity (easy removal of ZnO particles from treated water) which was not the case for the other catalysts (Fig. 13).

## 4 Conclusions

Photodegradation of BPA using PCO with ZnO as a catalyst is highly sensitive to UV intensity and the initial concentration of oxidant. ZnO showed distinctive properties and was very stable during the degradation process. However, future research should investigate the stability of ZnO and its suitability in degrading real contaminated surface water and groundwater. The removal of BPA from water was significantly enhanced by low doses of oxidant (NaOCl). The proposed remediation approach can be adopted for removal of BPA and phenolic products in natural water. More investigation is required to study the disintegration of BPA by photodegradation under various natural conditions at different temperatures and pH levels and in the presence of different cations and anions. Also the effect of the treatment on the mineralization of natural aqueous system should be studied in order to achieve the best ecological way to remove BPA and phenolic contaminants from natural water resources. A last point for further investigation is the utilization of the cat-

alysts in a real-world scenario and whether NaOCl can be replaced, for example, by ozone which could be produced by means of a solar-driven ozone generator.

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