**Desalination and Water Treatment**
www.deswater.com

doi:10.5004/dwt.2016.0137

61 (2017) 68–81
January

# Degradation and mineralization of Bisphenol A in wastewater by the UV/$H_2O_2$ and UV/persulfate processes

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Received 31 Janaury 2016; Accepted 21 July 2016

## ABSTRACT

A hydroxyl radical based advanced oxidation process, UV/$H_2O_2$, and a sulfate radical based advanced oxidation process, UV/persulfate, were employed to degrade Bisphenol A (BPA) wastewater in this work. The experimental set-up was designed identical to compare two processes. Parameters including oxidant dosage, initial BPA concentration, pH, treatment volume, anions, scavengers and water sources were investigated to demonstrate their effects on degradation and mineralization of BPA. The results presented that BPA wastewater was completely degraded and mineralized by UV/persulfate process. Instead, UV/$H_2O_2$ process can mineralize BPA in moderate level but not thoroughly. However, reaction with UV irradiation alone can achieve 38.7% BPA removal efficiency. For both UV/$H_2O_2$ and UV/persulfate processes, the higher the oxidant dosage applied, the higher the BPA and TOC removal efficiencies can be obtained. The initial pH of 7 was the most effective condition on the BPA degradation for both AOPs. The first-order rate constant is exponentially increased from 0.066 to 2.465 min$^{-1}$ with increasing of volumetric UV dosage, and an empirical equation can be derived to estimate first-order rate constant with known volumetric UV dosage. The anions such as nitrate, sulfate and chloride are not important inhibiting factors affecting the BPA degradation. From scavengers study, UV/persulfate process is dominated by sulfate radicals with high selectivity. The water source study shows that the UV/persulfate process can treat BPA successfully in surface water and groundwater.

*Keywords:* Bisphenol A; Persulfate; Hydrogen peroxide; UV; Hydroxyl radical; Degradation; Mineralization; Endocrine disruption compounds

## 1. Introduction

In consideration of their potential estrogenic effects in humans, endocrine disruption compounds (EDCs) in surface water, drinking water, effluents, and environment occurrence issues have drawn much attention from last decade. Among EDCs, Bisphenol A (BPA) is one of the most frequently detected and discussed chemicals. Related to the industrial production and human life consumption of plastic products, BPA is an important industrial chemical with over six billion pounds of production annually all over the world and is classified as high production volume chemical in USA [1]. The major application of BPA is used as intermediate for polycarbonate plastic and epoxy resin productions. It is no surprise to learn that BPA is released into the environment and has been detected in surface water, effluents from wastewater treatment plants and landfill leachates in relation to the mass production and daily use of polycarbonate plastic and epoxy resin products [2,3]. Furthermore, as a known EDC, BPA presents slight to medium toxicity for aquatic organisms [4]. Moreover, the toxic effects on reproduction, developmental, metabolism and immune systems of BPA have been investigated [5].

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*Presented at the 8th International Conference on Challenges in Environmental Science & Engineering (CESE-2015), 28 September–2 October 2015, Sydney, Australia.*

The occurrence of BPA in surface water investigations were reported by various researchers. By summarizing 182 studies, BPA concentrations were observed from nondetect to 56 µg $l^{-1}$ in surface water worldwide [2]. For example, in Germany, BPA concentration between 0.5–410 ng $l^{-1}$ in 116 surface water samples was measured [6]. Similarly, in Japan, 2–230 ng $l^{-1}$ was reported [7] as well as <1–145 ng $l^{-1}$ in Italy [8]. In Taiwan, the BPA concentration range from < 0.037 to 4.23 µg $l^{-1}$ were measured for 120 samples for Kao-Pin river [9]. Occasionally, higher concentrations up to µg $l^{-1}$ level were reported such as 21 µg $l^{-1}$ in Netherlands surface water [10] and 7–8 µg $l^{-1}$ in USA manufacturing plant effluent [11]. And was measured 1550 ng $l^{-1}$ in Screening effluent and 310 ng $l^{-1}$ in sand filtration effluent in one Portuguese wastewater treatment plant (WWTP) [12]. BPA concentrations in WWTP effluents ranged from nondetect to 370 µg $l^{-1}$, were summarized in a review paper [2,13]. BPA shows a potential for bioaccumulation and adsorption to sludge or sediments. Thus, some studies also reported the presence of BPA in sediments in China, Korea and Japan [14–16] and in WWTPs sludge in 1520 ng $g^{-1}$ dry weight in Korea [17].

From a thoroughly review, it concludes that WWTPs effluents are important point discharges of EDCs to rivers, streams and surface waters. WWTPs Effluents and sludge are major sources of BPA released to the environment [2]. Additionally, the removal of BPA by WWTP was incomplete, ranging from 30% to 90%, related to the treatment processes applied [18]. Therefore, the elimination of BPA within WWTPs is fundamental interest. And it is important to develop effective treatment technologies for the degradation of BPA in water.

Technologies dealing with treatment of BPA in WWTPs effluents have been developed recently. Al-Rifai et al. [19] developed advanced water treatment plant utilized microfiltration (MF) and reverse osmosis (RO) for remove pharmaceuticals and EDCs in wastewater treatment effluent for recycling purpose. Moreover, a pilot study on removal of emerging contaminants including BPA from WWTP secondary effluent by solar photocatalytic ozonation was reported [20]. The results showed effective removal of BPA, but difficult to mineralize total organic carbons (TOC). Mailler et al. [21] implemented a tertiary treatment, powdered activated carbon (PAC) pilot, in actual WWTP and achieved BPA removal from influent concentration of 259 ng $l^{-1}$ to effluent concentration of 78 ng $l^{-1}$ and presented 70% removal efficiency [21]. A photo-Fenton like process utilizing waste iron oxide catalyst in a 1.5 L fluidized bed reactor was developed to effectively treat BPA (as TOC) in wastewater [22].

A very powerful environmental technologies family named advanced oxidation processes (AOPs) with various arrangements including UV irradiation, oxidants (ozone and hydrogen peroxide), Fenton reagents, and photo-catalysts ($TiO_2$ and ZnO) has been conducted to destruct all different kind of pollutants into simplest final products i.e., carbon dioxide and water. Above mentioned AOPs are based on the production of hydroxyl radical which is a very strong oxidant and can react with wide range of pollutants non-selectively [23].

The hydroxyl radical based advanced oxidation processes (HR-AOPs) utilizing hydroxyl radicals have the capability to completely degrade wide range of refractory environmental pollutants. Among HR-AOPs, UV/$H_2O_2$ process is extensively applied for a variety of pollutants including chlorophenols [24,25], pesticides [26,27], explosive [28,29], landfill leachates [30], pulp industrial wastewater [31,32], and dye wastewater [33,34].

On the other hand, new applications of AOPs employing sulfate radicals, $SO_4^{-}\cdot$, (SR–AOPs) as alternative AOPs to the HR–AOPs have developed a new choice for wastewater treatment. Generally, SR-AOPs employ either persulfate (PS) or peroxymonosulfate (PMS) as oxidant to be further activated to form sulfate radicals. With activation of heat [35,36], UV irradiation [37,38], and transition metal ions [39–41], sulfate radicals can be produced by transforming PS or PMS in a SR–AOP. Sulfate radical is a powerful oxidant with high oxidation-reduction potential (ORP) of +2.5 – +3.1 V [42] to destruct pollutants in wastewater as well as hydroxyl radical.

In a UV/persulfate process, persulfate anion can be activated by UV irradiation to form sulfate radical ($SO_4^{-}\cdot$) which supports the fundamentals of UV/persulfate SR–AOP. Recently, UV/persulfate process has been broadly applied to degrade environmental pollutants such as dye wastewater [43], chlorophenols [37,44], landfill leachate [45], personal care pharmaceuticals [46] and pesticides [47]. Some investigations aimed to compare the capability of UV/persulfate and UV/$H_2O_2$ processes for their treatment of polyvinyl alcohol, atrazine, cylindrospermopsin and bisphenol A. In most of the cases, UV/persulfate presented more effective to degrade pollutants than UV/$H_2O_2$ process [48–51]. On the other hand, a case of degrading antipyrine was reported by Tan et al. [52], in which study, UV/$H_2O_2$ demonstrated better degradation performance than UV/persulfate process.

The objectives of this work are to compare UV/$H_2O_2$ and UV/persulfate processes on the treatment capabilities of BPA in wastewater and develop a scale up setup for treating larger amount of BPA wastewater through changing treatment volume. An identical recirculated thin gap annular photochemical reactor with formation of free radicals was conducted in both AOPs. Operating parameters such as oxidant dosage, initial BPA concentration, initial pH, and treatment volume were investigated to evaluate the performance of BPA degradation and mineralization in both AOPs. Sampling and measurement of BPA concentration, total organic carbon (TOC), pH, oxidation reduction potential (ORP) were used to assess the performance of these two AOPs.

## 2. Materials and methods

### 2.1. Materials and apparatus

Reagent grade Bisphenol A ($C_{15}H_{16}O_2$) with molecular weight of 228.29 and 99% purity was obtained from Jin-Ming Chemicals, Taiwan. Hydrogen peroxide ($H_2O_2$) 34.5–36.5% solution, ethanol, and tert-butyl alcohol (TBA) were purchased from Sigma–Aldrich Inc. Sodium Persulfate ($Na_2S_2O_8$) with 550 g $l^{-1}$ solubility and Acetonitrile as liquid chromatograph mobile phase were purchased from Merck, Inc.

UV/$H_2O_2$ and UV/persulfate processes experiments were conducted in an identical experimental setup scheme as shown in Fig. 1 to compare the BPA degradation and mineralization capabilities. The major part of the photochemical reactor is constricted with a stainless steel outer shell (ID = 2.8 cm, L = 36.5 cm). An input tubing position

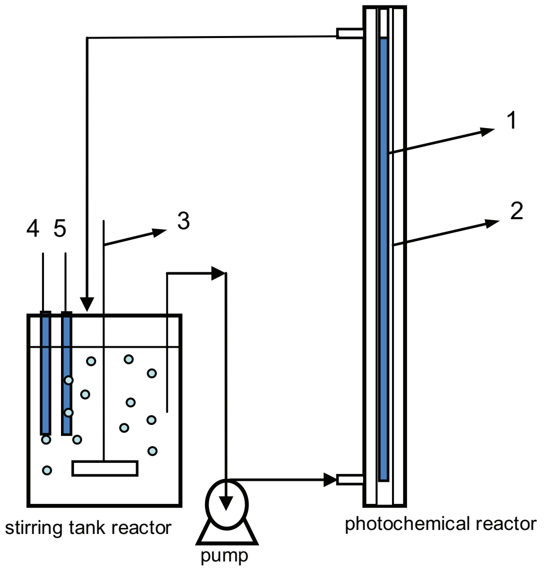

Fig. 1. The schematic drawing of the thin gap annular photochemical reactor employed. (1-UV lamp, 2-quartz pipe, 3-agitator, 4-pH probe, 5-ORP probe)

is located at bottom of the stainless shell and an output tubing position is located at the top as well. A quartz pipe with outer diameter of 2.0 cm and length of 36.5 cm is fixed to protect the UV lamp at the center of reactor. Moreover, inside the quartz pipe, an R-Can made (Model S287RL) low pressure mercury UV lamp with irradiation wavelength 253.7 nm and input power of 15 watts is employed. For batch recirculation purpose, a one liter stirring tank reactor was pumping connected with photochemical reactor to recirculate and photochemical treatment of BPA wastewater. The pH and ORP monitoring probe and agitator were all equipped in this stirring tank reactor. For scale up and investigation of treatment volume, another photochemical reactor is equipped with same diameter of stainless steel shell and quartz pipe of 85 cm length. Inside the quartz pipe, a Phillip made 30 watts low pressure mercury UV lamp was employed. And the stirring tank reactor was enlarged to a 10 liter volume. The UV light intensity of both UV lamps yielded a surface light energy of 5.0 mW cm$^{-2}$ measured at the outer surface of quartz tube. The difference between two UV lamps is only on their lengths.

Before the experiment, wastewater with designated BPA concentration and oxidant dosage was prepared with 1 L volume and poured into the stirring tank reactor and mixed, continuously monitored with pH and ORP. To star the reaction, wastewater was pumped through the input port of photochemical reactor and discharged through the output port, then flowed back to the stirring tank reactor for recirculation purpose. Once turn on the UV lamp, the timer started to keep right sampling time intervals.

### *2.2. Experimental procedure and analysis*

The operating parameters studied included reaction time, oxidant (hydrogen peroxide or persulfate) dosage, initial BPA concentration, initial pH value, and treatment volume. The volumetric UV dosage effect on BPA degradation was also investigated. Wastewater with various BPA concentrations (1–10 mg l$^{-1}$) and oxidant dosages (1.2–23.3 mM for $H_2O_2$ and 0.79–6.3 mM for persulfate) were prepared with de-ionized water and various amounts of BPA and oxidant. In the case of pH effect study, the experiments were conducted by adjusting the initial pH value of 7 to the range of 3 to 11 using HCl and/or NaOH with initial BPA concentration of 10 mg l$^{-1}$ and $H_2O_2$ dosage of 23.3 mM (or persulfate dosage 6.3 mM). The designated experiments are summarized in Table 1(a) for UV/$H_2O_2$ process and Table 1(b) for UV/persulfate process.

At a predetermined reaction time, an aliquot of the solution was withdrawn and analyzed for residual BPA concentration and TOC. BPA concentration was determined by measuring the peak areas at certain retention time using Hitachi high pressure liquid chromatograph (HPLC). An Agilent HP 5973 GC/MS was used for reaction intermediates identification. The pH and redox potential (ORP) were monitored by a Eutech PH5500 dual channel pH/ion meter with specific probes. TOC was obtained with a Total Organic Carbon Analyzer from O.I. Analytical Aurora, model 1030. The BPA concentration was quantified with a Hitachi ID2000 HPLC equipped with a fluorescence detector and the excitation wavelength set at 281 nm, scattered light wavelength set at 306 nm. A $C_{18}$ Mightysil RP–18 column (3.9 mm x 250 mm; 5 µm particle size) was employed as stationary phase. The mobile phase was a mixture of acetonitrile/water in 60/40 ratio (v/v). The flow rate was set as 0.8 ml min$^{-1}$ under operating pressure of 7.5–8.5 MPa, and the temperature was ambient.

Table 1(a)
UV/$H_2O_2$ experimental conditions

| Experiment set | Adjusted parameters | Fixed parameters |
|---|---|---|
| UV irradiation alone | UV dosage 30 W l$^{-1}$ | BPA 10 mg l$^{-1}$ |
| $H_2O_2$ dosage | 1.2, 5.8, 11.6, 23.3 mM | PBA 10 mg l$^{-1}$, UV dosage 30 W l$^{-1}$ |
| BPA initial concentration | 1.0, 3.4, 4.6, 8.9 mg l$^{-1}$ | UV dosage 30 W l$^{-1}$, $H_2O_2$ dosage 23.3 mM |
| pH | 3, 5, 7, 9, 11 | UV dosage 30 W l$^{-1}$, $H_2O_2$ dosage 23.3 mM, PBA 10 mg l$^{-1}$ |
| Anions | $NO_3^-$, $SO_4^{2-}$, $Cl^-$ (1.0M) | UV dosage 30 W l$^{-1}$, $H_2O_2$ dosage 23.3 mM, PBA 10 mg l$^{-1}$ |
| Scavenger | Ethanol, TBA (0.5M) | UV dosage 30 W l$^{-1}$, $H_2O_2$ dosage 23.3 mM, PBA 10 mg l$^{-1}$ |
| Water source | Surface water, groundwater | UV dosage 30 W l$^{-1}$, $H_2O_2$ dosage 23.3 mM, PBA 10 mg l$^{-1}$ |

Table 1(b)
UV/persulfate experimental conditions

| Experiment set | Adjusted parameters | Fixed parameters |
|---|---|---|
| Sodium persulfate dosage | 0.79, 1.58, 3.15, 6.3 mM | PBA 10 mg $l^{-1}$, UV dosage 30 W $l^{-1}$ |
| BPA initial concentration | 1.6, 2.6, 4.5, 9.5 mg $l^{-1}$ | UV dosage 30 W $l^{-1}$, sodium persulfate dosage 6.3 mM |
| pH | 3, 5, 7 | UV dosage 30 W $l^{-1}$, sodium persulfate dosage 6.3 mM, PBA 10 mg $l^{-1}$ |
| Reaction volume | 1.0, 2.5, 5.0, 10.0 l | UV dosage 30 W $l^{-1}$, sodium persulfate dosage 6.3 mM, PBA 10 mg $l^{-1}$ |
| Anions | $NO_3^-$, $SO_4^{2-}$, $Cl^-$ (1.0M) | UV dosage 30 W $l^{-1}$, sodium persulfate dosage 6.3 mM, PBA 10 mg $l^{-1}$ |
| Scavenger | Ethanol, TBA (0.5M) | UV dosage 30 W $l^{-1}$, sodium persulfate dosage 6.3 mM, PBA 10 mg $l^{-1}$ |
| Water source | Surface water, groundwater | UV dosage 30 W $l^{-1}$, sodium persulfate dosage 6.3 mM, PBA 10 mg $l^{-1}$ |

## 3. Results and discussion

### 3.1. UV irradiation and photo-degradation of BPA

In order to present the photo-degradation behavior of BPA by only applying UV irradiation, the experiment without oxidant addition was conducted in our experimental set-up. The photo-degradation of target pollutant, BPA, is presented in Fig. 2. The operating parameters were set at the initial BPA concentration of 10 mg $l^{-1}$, no oxidant added, and UV light intensity of 15 W $l^{-1}$ at wavelength of 254 nm in 120 min of reaction. In Fig. 2, the removal curve shows that UV irradiation can degrade BPA to 38.7% in 120 min irradiation time. This demonstrates that BPA molecule can be photo-degraded to moderate level. However, the UV irradiation is not able to further mineralize the organic carbons of intermediates and photo-degradation products. Therefore, barely change on TOC is observed. This implies more powerful approaches need to be conducted to fully degrade and mineralize BPA in wastewater.

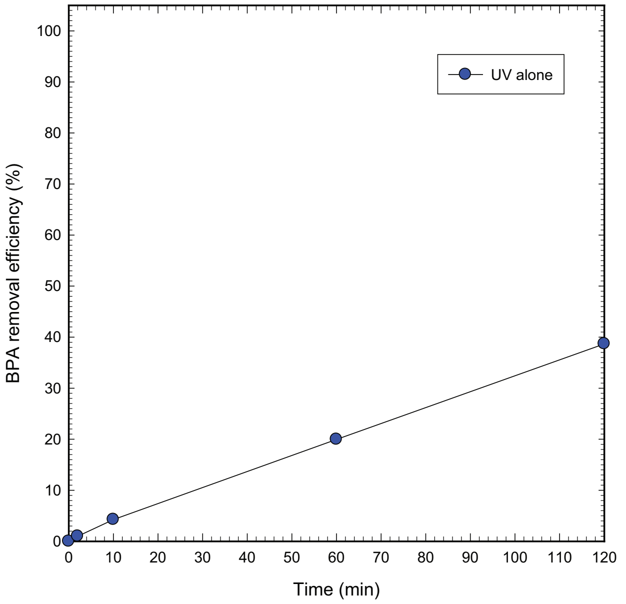

Fig. 2. The degradation of BPA by UV irradiation process alone. The conditions were initial BPA concentration of 10 mg $l^{-1}$, UV dosage 15 W $l^{-1}$ and reaction time during 120 min.

### 3.2. Effect of oxidant dosage

Theoretically, the higher hydrogen peroxide dosage applied under same UV irradiation intensity the higher hydroxyl radical concentration will be obtained in a UV/$H_2O_2$ process as shown in Eq. (1). However, there is usually an optimal hydrogen peroxide dosage exist for improve the degradation rate of pollutants. That is because when one applies hydrogen peroxide over the optimal dosage, the excess hydrogen peroxide will compete with pollutants for hydroxyl radicals. The above mentioned observation was presented in our previous study [53]. On the other hand, as presented in Eq. (2), more sulfate radicals formed with higher persulfate dosage utilized in a UV/persulfate process. And an optimal dosage of persulfate was also performed in previous UV/persulfate study [54].

$$H_2O_2 \xrightarrow{hv} 2OH. \tag{1}$$

$$S_2O_8^{2-} \xrightarrow{hv} 2SO_4^- \tag{2}$$

To demonstrate the effect of oxidant dosage on removal of BPA by proposed AOPs, i.e. UV/$H_2O_2$ and UV/persulfate, two sets of experiments were performed. The effect of oxidant dosage on the degradation of BPA was studied at initial BPA concentrations of 10 mg $l^{-1}$, hydrogen peroxide dosage of 1.2–23.3 mM, persulfate dosage of 0.79–6.3 mM, and 15 W $l^{-1}$ UV light intensity for a period of 120 min. Fig. 3(a) shows the degradation of BPA as a function of hydrogen peroxide dosage. Results present that the BPA removal efficiency achieves 63.2% and 99.5% in 4 min when the hydrogen peroxide dosage increasing from 1.2 to 23.3 mM, respectively. This concludes that the higher the hydrogen peroxide dosage reaches higher BPA removal efficiency. The results suggest that the higher hydrogen peroxide dosage under UV irradiation can produce more hydroxyl radicals which contribute to the degradation of BPA molecules. Therefore, the removal efficiency and degradation rate increases with increasing of hydrogen peroxide dosage.

In most of the AOPs studies, the reaction kinetics is proposed to follow pseudo first-order reaction. Therefore, the initial stage of BPA degradation reaction under UV/$H_2O_2$ and UV/persulfate processes can be described as follows:

$$C_{BPA} = C_{BPA,0} \times e^{-k_1 t} \tag{3}$$

where, $k_1$ denotes the pseudo first-order reaction rate constant ($min^{-1}$), t is the reaction time (min), CBPA, 0 designates the initial concentration (mg $l^{-1}$) of BPA and CBPA is the concentration (mg $l^{-1}$) of BPA at time t. In order to calculate rate constant, $k_1$, Eq. (3) can be further transformed as follows:

$$-\ln\left(\frac{C_{BPA}}{C_{BPA,0}}\right) = k_1 \times t \qquad (4)$$

By applying pseudo first-order reaction kinetics, the first-order rate constants can be obtained as shown in Fig. 3(b) by linear regression technique. The curve fitting of experimental results by Eq. (4) can be used to obtain first-order rate constants. The observed pseudo first-order rate constants for UV/$H_2O_2$ process are 0.280 and 1.324 $min^{-1}$ at BPA initial concentration of 10 mg $l^{-1}$, and $H_2O_2$ dosage of 1.2 and 23.3 mM, respectively. It is about 5 times increase on first-order rate constant for 20 times of hydrogen peroxide dosage increasing. The regressions are with good agreement ($r^2$ = 0.989–0.998). The results indicate that in our AOP reactor the rate constants are far higher than 0.0011 to 0.0054 $min^{-1}$ for BPA in previous UV/$H_2O_2$ study conducted by Sharma et al. [51].

The TOC value represents the total organic carbon concentration in the solution. It is an important indicator of mineralization. At beginning of the hydroxyl radical oxidation reaction, solution TOC cannot be destroyed easily. At time region less than 30 min, large molecules were degraded to lower molecule weight intermediates which still contributed to TOC measurement. Therefore, at this region, TOC removal efficiency may persist almost unchanged. After this lag phase (30 min), TOC can be removed proportionally to the reaction time observable. In Fig. 3(c), under low hydrogen peroxide dosage as 1.2–5.8 mM, the results show that TOC is hardly mineralized by UV/$H_2O_2$ process. For higher hydrogen peroxide dosage of 11.2 mM, TOC removal efficiency increases to about 25.5% in 120 min. For the highest dosage of 23.3 mM, the TOC mineralization efficiency increases from 11.1% to 50.1% for reaction time of 30 and 120 min, respectively. In general, AOPs with long reaction time can mineralize the TOC from pollutants effectively. However, for the case of BPA, the UV/$H_2O_2$ process shows not so vigorous for mineralizing BPA.

A parallel study was performed to demonstrate the persulfate dosage effect on the BPA degradation by UV/persulfate process. The results of BPA degradation and mineralization are summarized in Fig. 4(a) and 4(b). Fig. 4(a) shows the degradation of BPA as a function of persulfate dosage. Results present that the BPA removal efficiency increases from 84.6% to 99.7% in 4 min when the persulfate dosage increasing from 0.79 to 6.3 mM, respectively. The results reveal that the UV/persulfate process is a very powerful technology to degrade BPA in wastewater even in very limited persulfate dosage of 0.79 mM. And UV/persulfate process is more powerful than that of UV/$H_2O_2$ process. Similar oxidant dosage effect is obtained for UV/persulfate process as well as UV/$H_2O_2$ process. That is the higher the persulfate dosage reaches higher BPA removal efficiency. The results imply that the higher persulfate dosage under UV irradiation can produce more sulfate radicals which contribute to the degradation of BPA

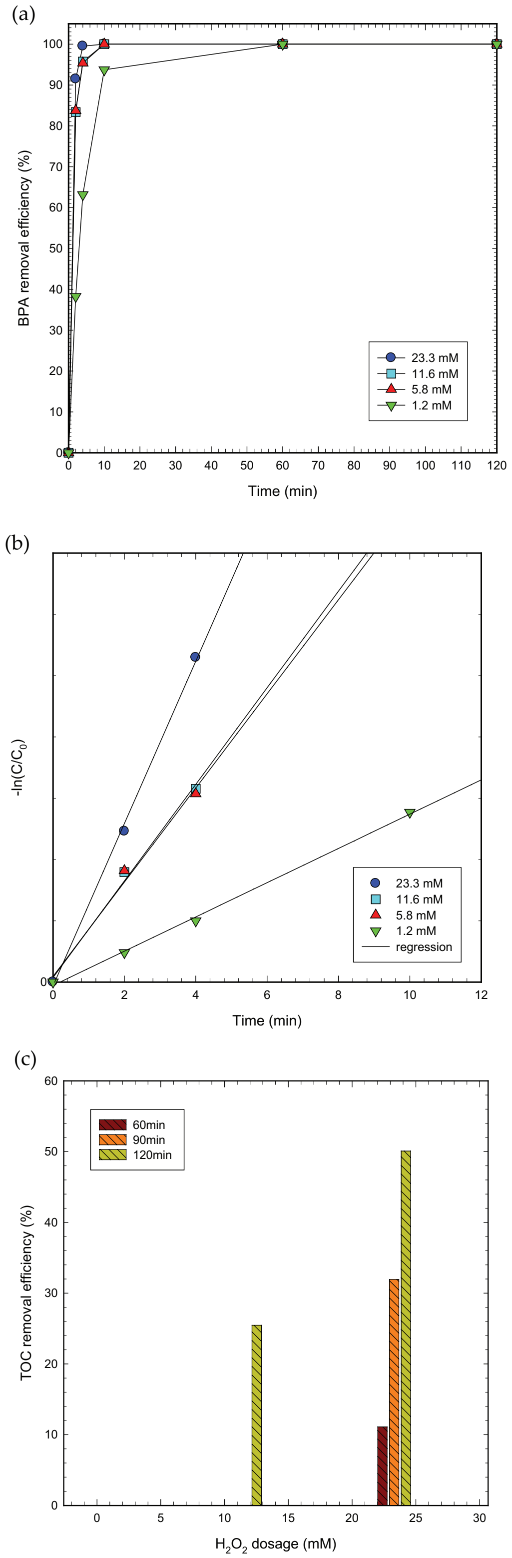

Fig. 3. Effect of oxidant dosage on (a) BPA removal, (b) first order kinetics, (c) TOC removal, by UV/$H_2O_2$ process. The conditions were initial BPA concentration of 10 mg $l^{-1}$, hydrogen peroxide dosage of 1.2–23.3 mM, UV light intensity of 15 W $l^{-1}$ and reaction time during 120 min.

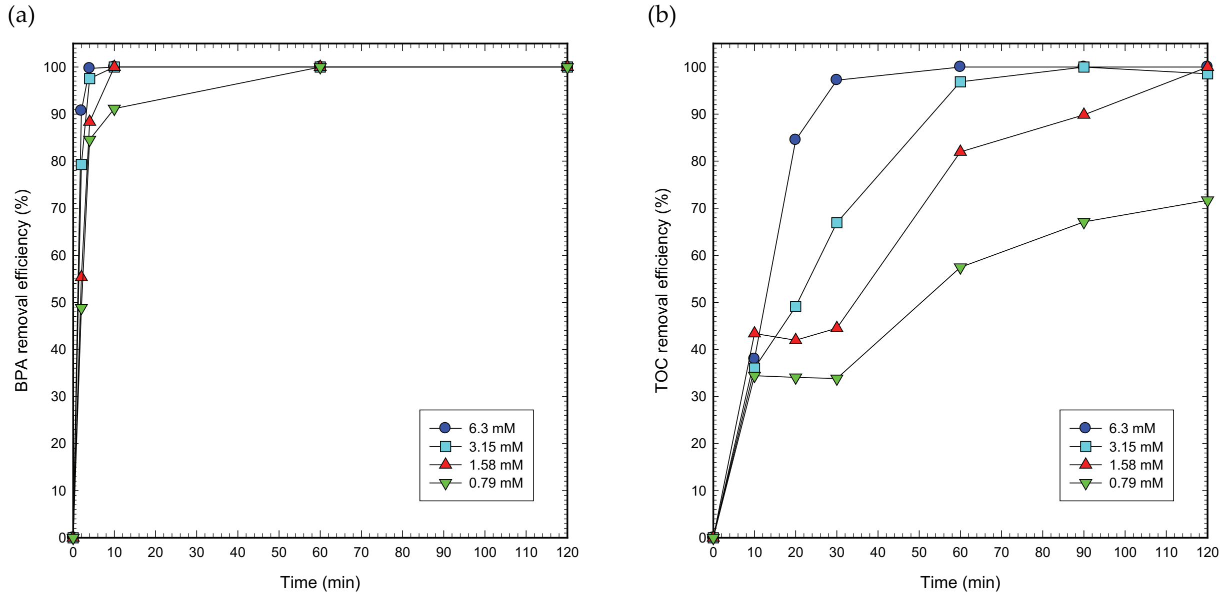

Fig. 4. Effect of oxidant dosage on (a) BPA removal, (b) TOC removal by UV/persulfate process. The conditions were initial BPA concentration of 10 mg $l^{-1}$, persulfate dosage of 0.79–6.3 mM, UV light intensity of 15 W $l^{-1}$ and reaction time during 120 min.

molecules. However, in both processes, i.e., UV/$H_2O_2$ and UV/persulfate, there is no optimal dosage at designed dosage range. In contrast, the optimal persulfate dosage was observed by Sharma et al. [51] for degrading BPA at 5.7:1 persulfate/BPA ratio by UV/persulfate process. That is because the excess amount of persulfate reacts with sulfate radicals to form less reactive species such as persulfate ions. The first-order rate constants can be obtained by applying pseudo first-order reaction kinetics to the experimental data as well as UV/$H_2O_2$ process. The observed pseudo first-order rate constants for UV/persulfate process are 0.467 and 1.445 $min^{-1}$ at BPA initial concentration of 10 mg $l^{-1}$, and persulfate dosage of 0.79 and 6.3 mM, respectively. The results also demonstrate the rate constants from our UV/persulfate photochemical reactor are far higher than 0.0021 to 0.0094 $min^{-1}$ for BPA in UV/persulfate process study reported by Sharma et al. [51].

To compare the TOC mineralization capabilities of UV/persulfate and UV/$H_2O_2$ process, TOC removal efficiencies for UV/persulfate process are demonstrated in Fig. 4(b). From the Fig., TOC removal efficiencies can be reached to 98.6–100% for persulfate dosage of 1.58–6.3 mM for reaction time 120 min under UV/persulfate process. At lowest persulfate dosage of 0.79 mM, 71.7% TOC removal efficiency can be achieved at 120 min. The UV/persulfate process shows stronger capability for mineralizing BPA's TOC than that of UV/$H_2O_2$ process. With the highest persulfate dosage of 6.3 mM, UV/persulfate process takes only 20 and 30 min to obtain 84.5 and 97.2% TOC removal efficiencies, respectively. The persulfate dosage of 0.79–6.3 mM is rather lower than that of 1.2–23.3 mM hydrogen peroxide for UV/$H_2O_2$ process. In contrast, UV/persulfate process demonstrates more thoroughly mineralization of TOC than the UV/$H_2O_2$ process. Results in Fig. 4(b) indicate that the TOC removal was more sensitive than BPA removal on persulfate dosage. To simultaneously degrade BPA and mineralize TOC, one should choose higher persulfate dosage to full fill both BPA and TOC removal requirements. At the meantime, TOC mineralization performance of the UV/$H_2O_2$ process is more sensitive and limited by oxidant dosage than that of UV/persulfate process.

The BPA in wastewater was demonstrated to be almost totally degraded by UV/persulfate process and mineralized to carbon dioxide to result very low detection of TOC. In this set of experiments, we sampled reaction liquid at medium region of the reaction at 10 min of reaction time and analyzed with GC/MS. An m/z = 207 compound was identified for both UV/$H_2O_2$ and UV/persulfate system. It may be the similar structure compound as identified by other previous study with m/z = 206 of phenol,3,5-bis(1,1-dimethyl(ethyl)) or phenol,2,4-bis(1,1-dimethyl ethyl) [55]. Furthermore, with longer reaction time the TOC can be thoroughly mineralized to ensure degradation of organics in wastewater and reduce its toxicity to minimal.

The comparison of pseudo first-order rate constants for various oxidant dosages on UV/persulfate and UV/$H_2O_2$ processes are illustrated in Fig. 5. The results show that first-order rate constant increases proportionally to the oxidant dosage for both AOPs. Furthermore, UV/persulfate process shows lower oxidant demand to achieve same rate constant level. And in all oxidant dosage range, UV/persulfate process presents higher reaction rate than UV/$H_2O_2$ process. The correlations of first-order rate constant with oxidant dosage for both AOPs can be expressed as empirical Eqs. (Eqs. (5) and (6)) as follows:

$$k_{\mathrm{UV/persulfate}} = 0.3022 + 0.1833 \times \mathrm{D}_{\mathrm{persulfate}} \tag{5}$$

$$k_{\mathrm{UV/H_2O_2}} = 0.3427 + 0.0427 \times \mathrm{D}_{\mathrm{H_2O_2}} \tag{6}$$

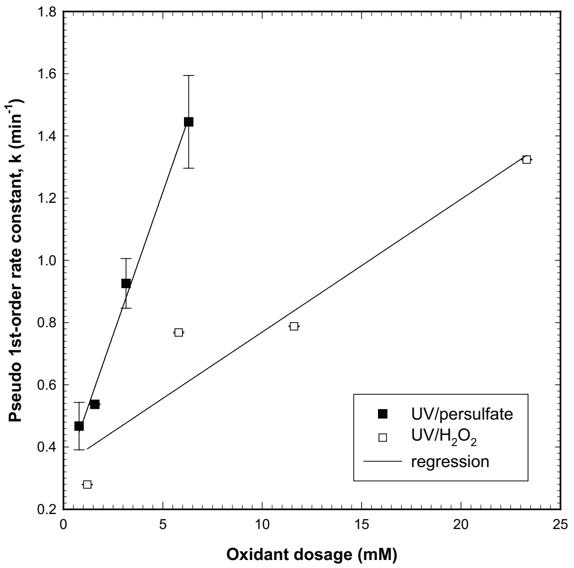

Fig. 5. The comparisons of pseudo first-order rate constants for various oxidant dosages on UV/persulfate and UV/$H_2O_2$ processes. The conditions were the same as Fig. 3 and 4.

where, $k_{UV/persulfate}$ and $k_{UV/H_2O_2}$ denote the pseudo first-order rate constants of UV/persulfate and UV/$H_2O_2$ processes in min$^{-1}$, respectively. $D_{persulfate}$ and $D_{H_2O_2}$ denote persulfate dosage and $H_2O_2$ dosage in mM, respectively.

### 3.3. Effect of initial BPA concentration

To present the effect of initial BPA concentration on the UV/$H_2O_2$ processes and UV/persulfate process, experiments were implemented at BPA initial concentrations of 1–10 mg l$^{-1}$, hydrogen peroxide dosage of 23.3 mM, persulfate dosage of 6.3 mM and 15W l$^{-1}$ UV light intensity for a period of 120 min. Fig. 6(a) presents the results of BPA degradation as a function of reaction time at various initial BPA concentrations. Results demonstrate that the degradation of BPA is fast and complete in all BPA concentration levels tested. As summarized in Fig. 6(b), the TOC removal efficiencies are 97.0% and 50.1% in 120 min for initial BPA concentration of 4.6 and 8.9 mg l$^{-1}$, respectively for UV/$H_2O_2$ process. Results indicate that the TOC removal is more difficult than that of BPA degradation. At lower BPA concentration such as 1.0 and 3.4 mg l$^{-1}$, the mineralization of TOC is difficult to be observed during the reaction.

Similar behavior of BPA degradation by UV/persulfate process can be presented in Fig. 7(a). The degradation of BPA in UV/persulfate is even faster than UV/$H_2O_2$ process, the degradation of BPA is also complete in all BPA level tested. From Fig. 7(b), as for TOC mineralization experiments, by utilizing UV/persulfate process, the TOC can be mineralized thoroughly in most of the cases, i.e., 2.6–9.5 mg l$^{-1}$. For the lowest BPA concentration of 1.6 mg l$^{-1}$, the TOC removal efficiency reaches 92.8% in comparing to 100% for higher BPA concentrations. It may be caused by sulfate radicals hardly target low concentration organic carbons in aqueous phase. However, the mineralization of BPA is far more efficient by UV/persulfate than UV/$H_2O_2$ process.

In Fig. 8, the first-order rate constants for all initial BPA concentrations by both AOPs are summarized. In UV/persulfate process, it is expected to find that the first-order rate constant, *k*, declines linearly by raising initial BPA concentration from 4.5 to 9.5 mg l$^{-1}$. The results are consistent to the observations by pervious work that the pseudo first-order rate constant decreases with increasing of initial dye concentration [54]. However, for lower BPA concentration from 1.6–2.6 mg l$^{-1}$, the reaction is too fast to measure experimental data and calculate the first-order rate constant. On the other hand, for UV/$H_2O_2$ process, the first-order rate constant, *k*, declines by raising initial BPA concentration from 1.0 to

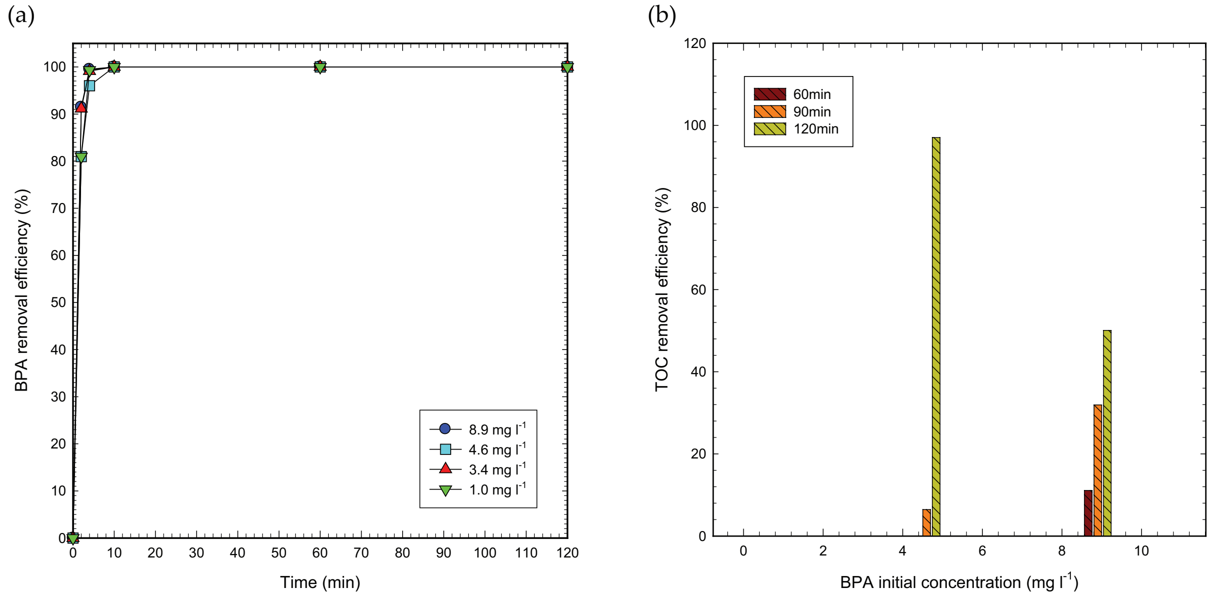

Fig. 6. Effect of initial BPA concentration on (a) BPA degradation and (b) TOC removal efficiency by UV/$H_2O_2$ process. The conditions were hydrogen peroxide dosage of 23.3 mM, light intensity of 15 W l$^{-1}$ and reaction time 120 min.

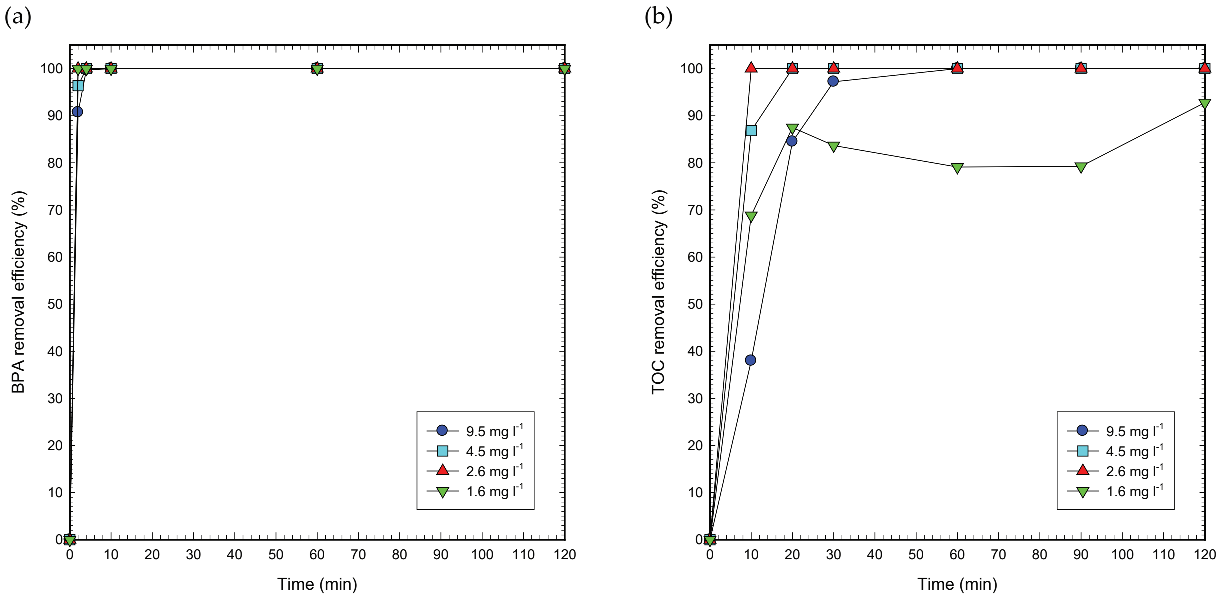

Fig. 7. Effect of initial BPA concentration on (a) BPA degradation and (b) TOC removal efficiency by UV/persulfate process. The conditions were persulfate dosage of 6.3 mM, light intensity of 15 W $l^{-1}$ and reaction time 120 min.

4.6 mg $l^{-1}$. But, for the highest BPA concentration of 8.9 mg $l^{-1}$, the first order rate constant is 1.324 $min^{-1}$ which is the highest among all initial BPA concentrations. This may be due to the increase of collision opportunity between sulfate radicals and BPA molecules at highest BPA concentration of 8.9 mg $l^{-1}$.

### *3.4. Effect of pH*

Fig. 9(a) shows BPA degradation by UV/$H_2O_2$ process as a function of time at various pH values. Results indicate that at original pH of 7, the BPA removal efficiency reaches 99.5% in 4 min of UV/$H_2O_2$ reaction. At acidic pH of 3, 5 and alkaline pH of 9, 11 conditions, the BPA degradation efficiencies all reach 100% but with lower reaction rates. This implies that adjusting pH by either HCl or NaOH will result disadvantage effects on BPA degradation by UV/$H_2O_2$ process. Furthermore, the solution initial pH presents observable effect on BPA degradation under UV/$H_2O_2$ system as shown in Fig. 8(a). Fig. 8(b) shows the TOC removal efficiency as a function of pH value for UV/$H_2O_2$ process. Results indicate that at original pH 7 the TOC removal efficiencies are 11.1, 31.9 and 50.1% for reaction time of 60, 90 and 120 min, respectively. The highest TOC removal efficiency is 50.1% at 120 min for pH 7. In all pH values tested, the TOC mineralization is in moderate region and cannot reach total mineralization. On the other hand, the UV/persulfate process demonstrates better BPA degradation performance as shown in Fig. 10(a). Degradation reactions at pH 3, 5 and 7 conditions were investigated and showed powerful degradation capability. Additionally, the TOC mineralization by UV/persulfate process is quite effective as shown in Fig. 10(b). The TOC removal efficiencies are from 91.8% to 100% which are far effective than that of UV/$H_2O_2$ process for only less than 50.1%. The pH value of 7 shows the best TOC mineralization with shortest reaction time. It takes only 30 min to achieve 97.2% TOC removal. Fig. 10 presents the comparisons of pseudo first-order rate constants of UV/persulfate and UV/$H_2O_2$ processes at various pH conditions. UV/persulfate process remains higher rate constants than UV/$H_2O_2$ process for pH 3–7. Both UV based AOPs demonstrate highest rate constants at pH 7, and the first-order rate constants are in the range of 0.198 to 1.445 $min^{-1}$.

### *3.5. Effect of treatment volume and volumetric UV dosage*

Based on the results of various operating conditions, UV/persulfate process shows the lower oxidant demand

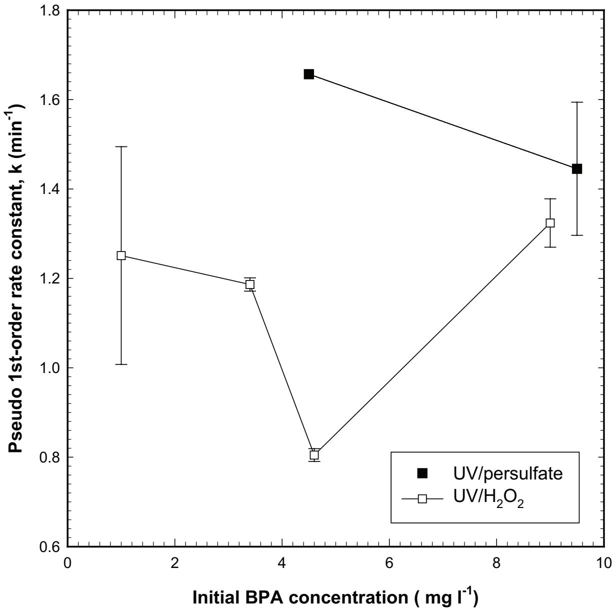

Fig. 8. The comparisons of pseudo first-order rate constants for various initial BPA concentrations on UV/persulfate and UV/$H_2O_2$ processes. The conditions were the same as Fig. 6 and 7.

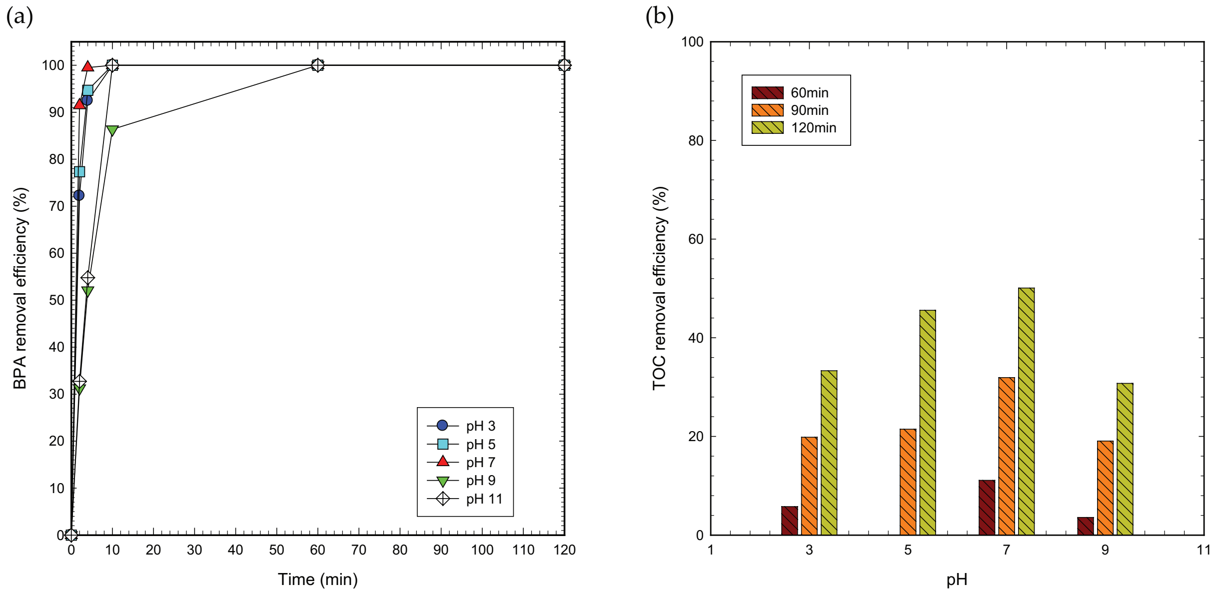

Fig. 9. Effect of pH on (a) BPA degradation, (b) TOC removal by UV/$H_2O_2$ process. The conditions were initial BPA concentration of 10 mg $l^{-1}$, hydrogen peroxide dosage of 23.3 mM, UV light intensity 15 W $l^{-1}$ and reaction time during 120 min.

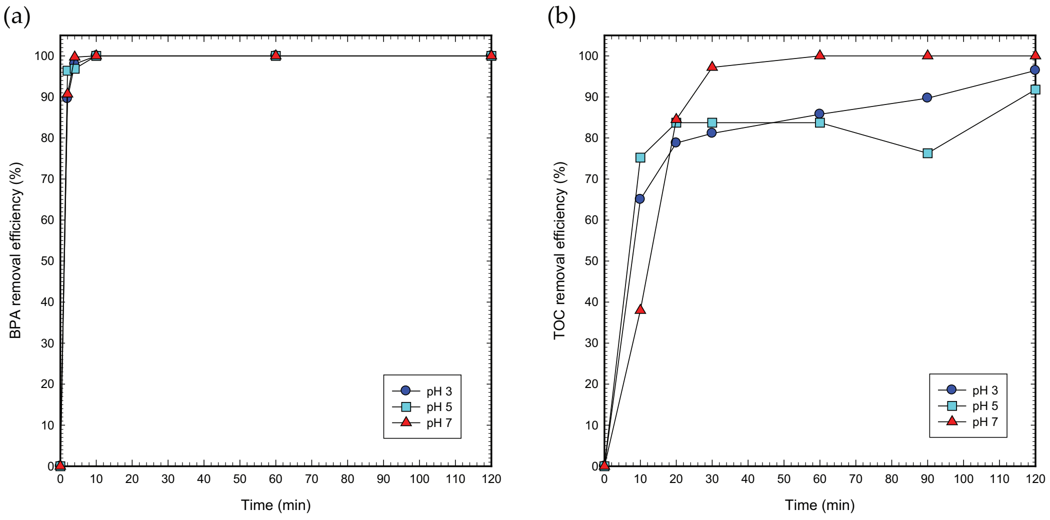

Fig. 10. Effect of pH on (a) BPA degradation and (b) TOC removal efficiency by UV/persulfate process. The conditions were initial BPA concentration of 10 mg $l^{-1}$, persulfate dosage 6.3 mM, light intensity of 15 W $l^{-1}$ and reaction time 120 min.

and faster degradation rate of BPA than that of UV/$H_2O_2$ process. The reaction time required for total degradation of BPA is very short in all cases. Therefore, for scale up purpose, a scale up photochemical reactor with higher UV intensity lamp (30 W input power) is conducted for treating more volume of wastewater up to 10 L. Fig. 12(a) shows BPA degradation by high power UV/persulfate process as a function of time at various treatment volumes. Results reveal that the BPA removal efficiencies reach >99.7% in 60 min for 1–10 L treatment volume by UV/persulfate reaction. In the case of lowest volume, i.e., 1 L treatment volume, presents superior BPA degradation efficiency. It takes only 4 min to reach 100% BPA degradation and 30 min for 98.7% TOC mineralization (Fig. 12b). In contrast, it takes 60 min to obtain 98.6% of BPA degradation efficiency and 120 min to achieve only 32.8% of TOC mineralization for the highest treatment volume of 10 L. Among scale up tests, 5 L treatment volume with 99.5% BPA degradation in 30 min and 84.3% TOC mineralization in 120 min performances may be the suitable case for sense of balance on BPA (and TOC) removal and operation cost. Furthermore, this UV/persulfate process is estimated to have a treatment capacity of 0.4–3.6 $m^3$/d for 95% BPA removal. On the other hand, in order to demonstrate the effect of volumetric UV dosage, the UV power input divided by treatment volume (W $l^{-1}$) is conducted to present with first-order rate constant. As shown in Fig. 13, the first-order rate constant increases exponentially with increasing of volumetric UV dosage in W l$^{-1}$. And an empirical equation. (Eq. (7)) can be derived as follows,

$$k_{\text{UV/persulfate}} = 0.0821 \times e^{0.1134 \times D_{\text{UV}}} \tag{7}$$

where, $k_{\text{UV/persulfate}}$ denotes the pseudo first-order rate constant of UV/persulfate process in min$^{-1}$. $D_{\text{UV}}$ denotes the volumetric UV dosage in W l$^{-1}$.

### 3.6. Effect of co-existing anions and scavengers

There are various anions existing in the aqueous phase in surface water as well as in wastewater. Therefore, an experimental set on the effects of nitrate, sulfate and chloride anions was demonstrated to reveal the inhibition effect of anions on the performance of BPA degradation by UV/$H_2O_2$ and UV/persulfate processes. In this series of tests, 1.0 M, significant high concentration of generally existing anions, i.e., nitrate, sulfate and chloride were prepared with 10 mg l$^{-1}$ BPA in UV/$H_2O_2$ and UV/persulfate processes. The results of BPA degradation are illustrated in Fig. 14(a) and 14(b) for

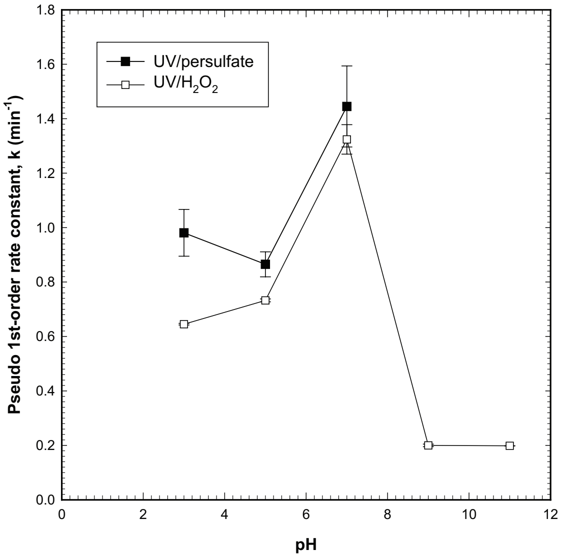

Fig. 11. The comparisons of pseudo first-order rate constants for various pH values on UV/persulfate and UV/$H_2O_2$ processes. The conditions were the same as Fig. 9 and 10.

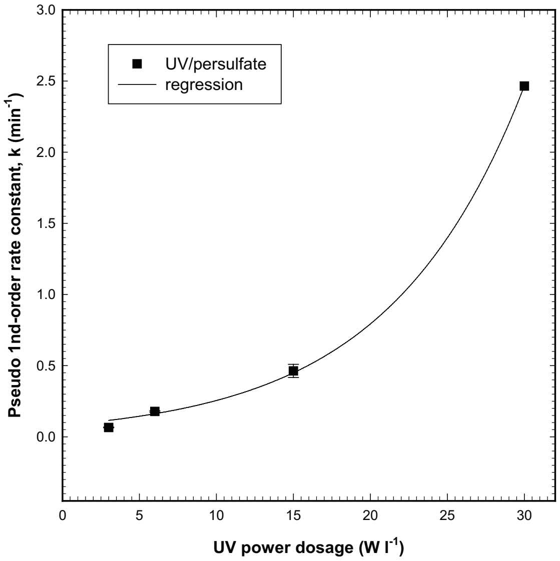

Fig. 13. The effect of volumetric UV dosage on first-order rate constant for BPA degradation by UV/persulfate process. The conditions were the same as Fig. 12.

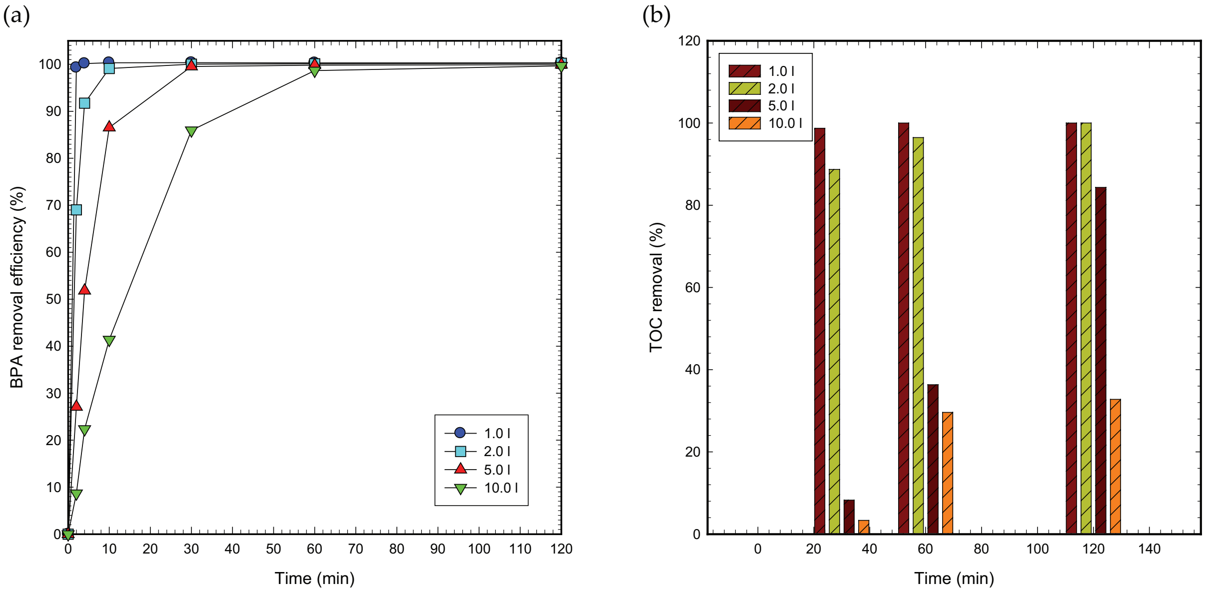

Fig. 12. Effect of treatment volume on (a) BPA degradation, (b) TOC removal by UV/persulfate process. The conditions were initial BPA concentration of 10 mg l$^{-1}$, persulfate dosage of 6.3 mM, UV light intensity 30 W l$^{-1}$ and reaction time during 120 min.

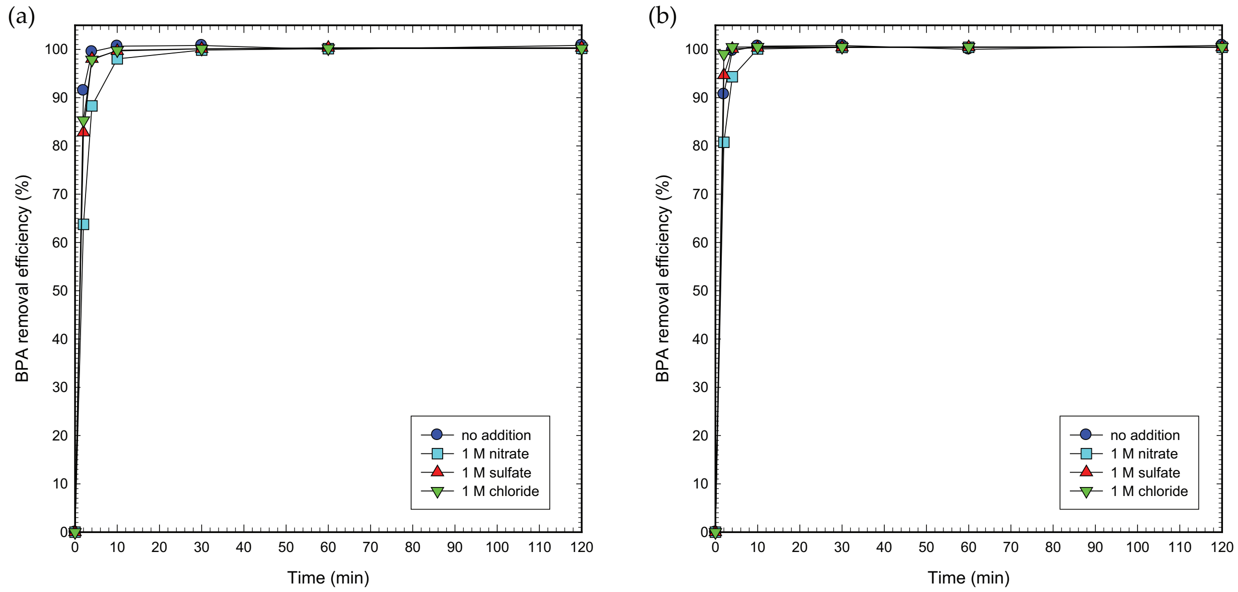

Fig. 14. Effect of anions on BPA degradation by (a) UV/$H_2O_2$ and (b) UV/persulfate processes. The conditions were initial BPA concentration of 10 mg $l^{-1}$, persulfate dosage 6.3 mM ($H_2O_2$ dosage 23.3 mM), light intensity of 30 W $l^{-1}$ and reaction time 120 min.

UV/$H_2O_2$ and UV/persulfate processes, respectively. From the results, the existing of anions such as nitrate, sulfate and chloride show no significant influence on BPA degradation for both processes. Only the presence of nitrate contributes to the slightly inhibition of BPA degradation rate. But for longer reaction time, the final removal efficiencies of BPA under nitrate anion influence show all reach 100% removal. It is different than at UV-C/peroxymonosulfate process reported by Sharma et al. [55] an inhibition in BPA degradation was observed for chloride concentration from 10 to 20 mM due to the formation of less reactive chlorine species. At the same time, TOC removal efficiencies are also monitored. In UV/persulfate process, the presence of sulfate ion shows no effect of inhibition of BPA's TOC removal and the presence of nitrate shows slightly effect on BPA's TOC removal after 60 min of reaction as well. In contrast, the presence of chloride, seriously reduce the removal efficiency of TOC from 100 down to about 50% throughout the reaction period (data not shown). For UV/$H_2O_2$ process, the original TOC removal is less effective. On the other hand, the presence of nitrate and chloride anions in UV/$H_2O_2$ process, the TOC mineralization shows no significant effects by additions of nitrate and chloride. However, the addition of sulfate ions can extremely benefit the TOC removal up to 93% in UV/$H_2O_2$ process.

Two very useful scavengers, i.e., ethanol and tert-butyl alcohol (TBA), were tested for BPA degradation in both UV/$H_2O_2$ and UV/persulfate processes. Therefore, a set of experiments were conducted for reveal scavenging effects of BPA degradation by UV/$H_2O_2$ and UV/persulfate processes in presences of ethanol and TBA. In this series of tests, 0.5 M, significant high concentration of scavengers, i.e., ethanol and TBA were prepared with 10 mg $l^{-1}$ BPA in UV/$H_2O_2$ and UV/persulfate processes. The results of BPA degradation are illustrated in Fig. 15(a) and 15(b) for UV/$H_2O_2$ and UV/persulfate processes, respectively. From the results shown in Fig. 15(a), 100% BPA removal can be reached for reaction time larger than 10 min without scavenger addition in UV/$H_2O_2$ process. However, in the presence of TBA, the BPA removal efficiency drops to about 45.2% for 10 min reaction. Similarly, in the existing of ethanol, the BPA removal efficiency decreases to about 38.2% for 10 min reaction. The ratio of scavenging rates of oxidants by TBA and ethanol varies between 1.3 and 3.5 for OH radicals and between 18 and 200 for sulfate radicals. For TBA, the rate constant is approximately 1000 fold greater for OH radicals than that for sulfate radicals [55]. Fundamentally, in UV/$H_2O_2$ process, OH radicals dominate the BPA degradation. The presence of TBA scavenges OH radicals strongly, thus resulting the significantly decline of BPA removal. On the other hand, the presence of ethanol, not only scavenging OH radicals, but also scavenging other oxidant species. Therefore, the decrease of BPA removal efficiency is more effective by ethanol than TBA. As shown in Fig. 15(b), 100% BPA removal can be reached for reaction time larger than 10 min without scavenger addition in UV/persulfate process. Furthermore, in the presence of TBA, the BPA removal efficiency remains very good for about 100% at 10 min reaction. This shows no significant scavenging effect between TBA and sulfate radicals. In a UV/persulfate process, the sulfate radicals dominate the degradation of BPA. The reaction rate constant of TBA to sulfate radicals is much less than that of OH radicals. Therefore, in UV/persulfate process, the scavenging effect of TBA is insignificant for BPA degradation. In contrast, with presence of ethanol, the scavenging effect is obviously illustrated. Only 56.8% of BPA removal is reached in 10 min reaction. The reaction rate of BPA degradation is much lower in the presence of ethanol than that of TBA. The observation also demonstrates the high selectivity of sulfate radicals for BPA degradation.

### *3.7. Effect of water source*

In order to verify the effect of various water sources, a set of experiments were conducted with a surface water

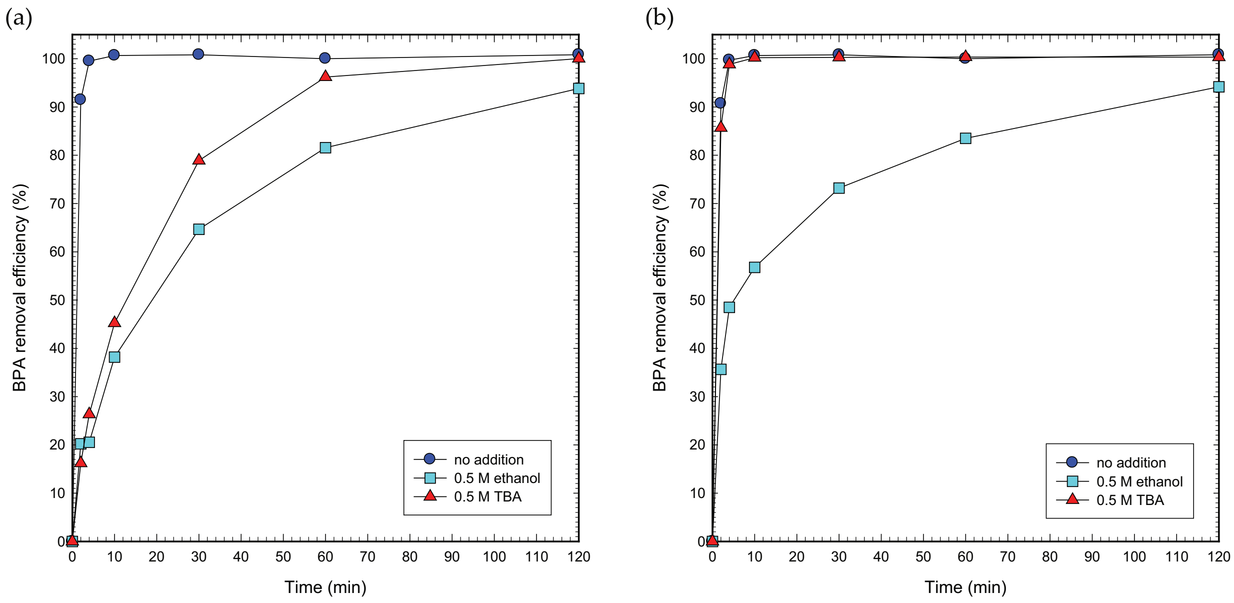

Fig. 15. Effect of scavengers on BPA degradation by (a) UV/$H_2O_2$ and (b) UV/persulfate processes. The conditions were initial BPA concentration of 10 mg $l^{-1}$, persulfate dosage 6.3 mM ($H_2O_2$ dosage 23.3 mM), light intensity of 30 W $l^{-1}$ and reaction time 120 min.

sample and a groundwater sample. In this series of tests, BPA was spiked into surface water and groundwater samples and prepared with 10 mg $l^{-1}$ BPA in UV/persulfate processes. The surface water sample was collected from central Taiwan downstream of Da-Ja River. The groundwater sample was collected from a well in central Taiwan Shalu area. From the results in Fig. 16, the degradation performances of BPA by UV/persulfate processes are all very powerful in DI water, surface water and groundwater prepared samples. This implies that in ours proposed UV/persulfate process, the operating conditions are suitable for BPA wastewater treatment, even with slightly pollution condition of surface water with about 10 mg $l^{-1}$ of TOC and 10-50 mg $l^{-1}$ level of sulfate, nitrate, chloride ions. The groundwater sample is low in organic carbons but with 100 mg $l^{-1}$ level of chloride and sulfate ions.

## 4. Conclusion

UV/$H_2O_2$ and UV/persulfate processes were demonstrated to be promising treatment technologies for degradation and mineralization of BPA in wastewater. The oxidant (persulfate or hydrogen peroxide) dosage was shown to be the most effective parameter to influence the BPA and TOC removal efficiencies among all operating parameters studied. In tested conditions, the highest oxidant dosage ensures the best removal efficiency for both UV/$H_2O_2$ and UV/persulfate processes. The first-order rate constant of BPA removal increased with oxidant dosage increasing for both UV/persulfate and UV/Oxone processes. No optimal oxidant dosage was observed in tested range for both AOPs. The initial pH of 7 was shown to be most effective condition on the BPA degradation for both AOPs. Overall, the UV/persulfate process demonstrates the better BPA removal and TOC mineralization than UV/$H_2O_2$ process. The test of various treatment volumes showed capability to scale up. Furthermore, the first-order rate constant was demonstrated to increase exponentially by increasing volumetric UV dosage. The anions, such as nitrate, sulfate and chloride, show insignificant effect on BPA degradation. The scavengers, such as ethanol and TBA, affect the UV/$H_2O_2$ process for BPA degradation. The UV/persulfate process dominates by sulfate radicals is more influenced by ethanol

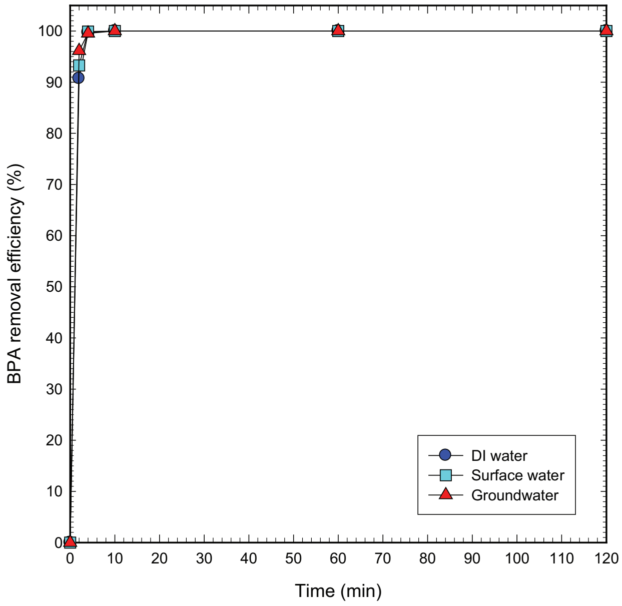

Fig. 16. Effect of water sources on BPA degradation by UV/persulfate processes. The conditions were initial BPA concentration of 10 mg $l^{-1}$, persulfate dosage 6.3 mM, light intensity of 30 W $l^{-1}$ and reaction time 120 min.

than that of TBA due to high selectivity of sulfate radicals. The water sources show no significant effect on BPA degradation for UV/persulfate process.

## Acknowledgements

The authors appreciate the research funding granted by the Taiwan Ministry of Science and Technology (MOST 101-2221-E-241-004-MY3).

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