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The photochemical decomposition and detoxification of bisphenol A in the VUV/H_2O_2 process: Degradation, mineralization, and cytotoxicity assessment

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ABSTRACT

The present study investigates the novel advanced process of VUV/H_2O_2 for oxidation of bisphenol A (BPA) known as an endocrine disrupting compound (EDC) which is released from the human and industrial activities. The effect of water pH, H_2O_2 and BPA concentrations, reaction time and presence of anions and scavengers were examined on the BPA degradation and mineralization in the VUV/H_2O_2 batch process. The optimum values of solution pH and H_2O_2/BPA mass ratio were found to be 3 and 4, respectively. The oxidation with hydroxyl radicals was the main mechanism involved in the BPA degradation. The rate of BPA degradation under optimum conditions observed to be increased from 20.5 to 50.8 mg/L.min when the BPA concentration was increased from 20 to 100 mg/L. The main anions did not majorly affect the BPA degradation in the VUV/H_2O_2 process. 97.6% of BPA was mineralized within 60 min in the VUV/H_2O_2 process under optimum conditions. The cytotoxicity of the BPA significantly decreased after treating in the VUV/H_2O_2 process. The complete degradation of BPA was obtained in the continuous-flow VUV/H_2O_2 process at a hydraulic retention time (HRT) as short as 8 min whereas only 48.2% of BPA could be degraded in the single VUV under similar experimental conditions. The electrical energy consumed per order (EE/O) of degraded BPA was 2.4 and 4.2 kWh/m^3 for initial BPA concentrations between 20 and 100 mg/L. Accordingly, the VUV/H_2O_2 process is found to be a very efficient and cost-effective process for oxidation of BPA.

1. Introduction

The pharmaceuticals, personal care products, endocrine disrupting compounds (EDCs), etc. are a main family of the environmental emerging contaminants possessing several concerns for the human health and the ecosystem [1]. EDCs are among the prime municipal driven emerging contaminants, which are released into the environment mainly through the discharge of industrial and municipal wastewater [2]. EDCs are xenobiotic substances that disrupt the normal function of endocrine system resulting in the adverse health and reproductive effects in the contaminated organism [3]. Bisphenol A (BPA), which is widely used for manufacturing different types of polymeric and petrochemical products, is a well-known EDC [2,3]. A BPA concentration ranging from a few to tens milligram per litter is usually found in the effluent from the petrochemical plants. Although the biological processes are the most accepted method of choice for treating the municipal and most of industrial wastewaters, EDCs are toxic and refractory substances that are not efficiently treated in the biological treatment processes [2,3]. Therefore, many efforts have been paid by the researchers to develop new methods for efficient degradation of such toxic compounds as BPA. Advanced oxidation process (AOP) is a very efficient technique used for oxidation of organic contaminants by reactive free hydroxyl ($HO^{\cdot}$) and sulfate ($SO_4^{-\cdot}$) radicals [4]. Several AOPs have been tested for degradation of BPA including UV-$Na_2S_2O_8$/H_2O_2-Fe process [2], photocatalytic process [5,6], Fenton process and its derivates [7–10], catalytic ozonation [11], UVC/peroxymonosulfate [12], UVC/persulfate [13], UV/O_3 [14], and UVC/H_2O_2 [13,15–17].

Due mainly to high efficiency, simplicity, no ozone dosing and thus no off-gas treatment requirement, no need to separate solid materials and having the potential for field-scale application, the homogeneous UVC/H_2O_2 photochemical oxidation processes are among the most attractive AOPs being increasingly investigated for water and wastewater treatment [18,19]. In the UVC/H_2O_2 process, H_2O_2 is irradiated with UVC radiation resulted in the generation of very reactive oxidative radical species of $HO^{\cdot}$ [18]. The efficacy of UVC/H_2O_2 process in

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degradation of BPA was investigated by different researchers who observed a degradation rate between 0.14 and 3.30 g/L.min [12,13,15–17]. The VUV irradiation process in which $HO^{\cdot}$ is generated through photoionization and homolysis of water molecules has recently received many attentions for treatment of different types of water organic contaminants [20–23]. Therefore, adding H_2O_2 as a strong initiator for generation of $HO^{\cdot}$ [13] to the VUV reactor provides a novel UV-based AOP variant of VUV/H_2O_2 in which the formation of $HO^{\cdot}$ and thus improve the contaminant(s) degradation process is accelerated.

It was found from reviewing the literature that no study has been conducted to date on degradation of BPA in the VUV/H_2O_2 process. Accordingly, this study was designed to evaluate the efficacy of the VUV/H_2O_2 process in degradation and mineralization of BPA under different experimental conditions. The kinetics of BPA degradation and mineralization in the VUV/H_2O_2 process was evaluated. The detoxification of the fresh and treated (under optimum experimental conditions) BPA solutions was also determined.

2. Materials and methods

2.1. Materials

The working BPA solution was prepared from dissolving a given amount of BPA in distilled water, unless otherwise specified. All chemical reagents used were of analytic grade and purchased from Sigma–Aldrich Co.

2.2. Experimental setup

The experiments were conducted in a bench-scale setup shown in Fig. 1. As observed in Fig. 1, the experimental setup consisted of a glass column (inner diameter of 25 mm and height of 400 mm) as photoreactor, a sample vessel (recirculation tank), a peristaltic pump, and the valves, tubing and fittings. A quartz sleeve (outer diameter of 15 mm) was installed in center of the column. For the VUV and VUV/H_2O_2 experiments, a 5.7 W low-pressure UV lamp (Heraeus Co.) was placed inside the sleeve. The UVC lamp emitted radiation both at 254 nm (~90%; flux of 56 $\mu W/cm^2$ at 1 cm from the lamp surface) and at 185 nm (~10%; flux of 5 $\mu W/cm^2$ at 1 cm from the lamp surface). A 6 W low-pressure UVC lamp (OSRAM Co.) emitting the radiation at 254 nm (flux of 59 $\mu W/cm^2$ at 1 cm from the lamp surface) was used in the UVC and UVC/H_2O_2 experiments, placed inside the sleeve. The photoreactor had a working volume of 120 mL.

2.3. Experimental procedure

The VUV/H_2O_2 process was operated in both batch and continuous modes. In batch experiment, the effect of solution pH (3–10), H_2O_2 concentration (H_2O_2/BPA mass ratio = 0–5), BPA concentration (25–100 mg/L) and reaction time (1–60 min) were evaluated in oxidation of BPA. For each test, 150 mL of BPA solution with a given composition (in terms of pH, H_2O_2 and BPA concentrations, etc.) was transferred to the sample vessel (Fig. 1) and the recirculation pump was switched on. When the reactor was filled, the UV lamp was switched on and the solution was recirculated through the reactor. The solution was sampled at the desired intervals from the sample vessel (recirculation tank). The lamps were allowed to warm up before starting the tests. The degradation of BPA in the VUV/H_2O_2 process was also tested at the presence of salicylic acid (50 mg/L) as a strong $HO^{\cdot}$ scavenger to confirm the generation of $HO^{\cdot}$. The para-chlorobenzoic acid (pCBA) was used as the probe of measuring the concentration of $HO^{\cdot}$. The concentration of $HO^{\cdot}$ was measured from Eq. (1) in which $pCBA_0$ and $pCBA_t$ represent pCBA concentration (mg/L) at the beginning and time t of the reaction, and $k_{HO^{\cdot}}$ is the second order reaction rate constant of pCBA with $HO^{\cdot}$ ($5 \times 10^9\ M^{-1}\ s^{-1}$) [25].

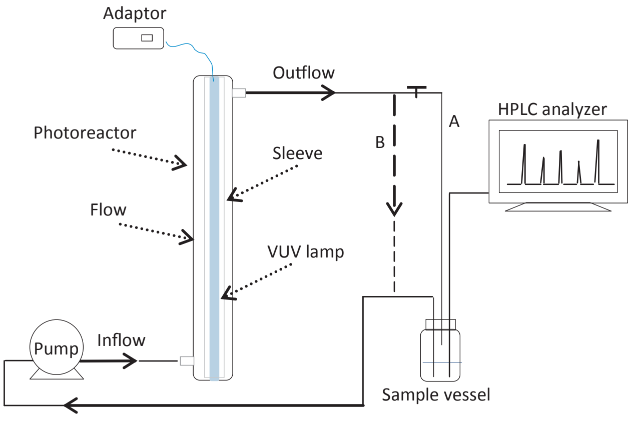

Fig. 1. The schematic of VUV/H_2O_2 experimental setup.

$$[HO^{\cdot}] = \frac{\ln\left(\frac{pCBA_t}{pCBA_0}\right)}{k_{HO^{\cdot}} \cdot t} \tag{1}$$

The effect of anions including chloride, bicarbonate, sulfate, nitrate, phosphate individually and in tap water (main composition: pH = 7.9, TDS = 214 mg/L, Cl^- = 58 mg/L, SO_4^{2-} = 16 mg/L, alkalinity = 16 mg/L as $CaCO_3$, and temperature = 23 °C) as a mixture was also examined on the BPA degradation in the VUV/H_2O_2 process. The second-order reaction rate constant of BPA with $HO^{\cdot}$ was determined according to the competition kinetic method with pCBA as the reference compound, during which the degradation of both BPA and pCBA was simultaneously investigated in the process under the optimum experimental conditions [25]. The same procedure was adopted in the continuous flow experiments, except outlet stream of the reactor was transferred to a separate effluent tank. All experiments were conducted in duplicate and the average results were reported.

2.4. Analytical methods

The concentration of BPA was determined using an Agilent HPLC (Eclipse Plus C18 column; 3.5 µm, 4.6 × 100 mm) with a UV detector at a wavelength of 217 nm. The mobile phase was a mixture of water and acetonitrile with a volumetric ratio of 50/50 with an injection flow rate of 0.5 mL/min. The degradation percentage of BPA in the process was measured as the disappearance of BPA.

The concentration of TOC was measured with TOC analyzer (Shimadzu Co.) and the degree of BPA mineralization in the VUV/H_2O_2 process was determined from Eq. (2).

$$\text{BPA mineralization (\%)} = \left(\frac{TOC_0 – TOC_t}{TOC_0}\right) \times 100 \tag{2}$$

where TOC_0 and TOC_t represent the TOC concentrations (mg/L) in the solution at the beginning and time t of the reaction H_2O_2 concentration was measured using titration with potassium permanganate [24]. The pH was measured by SenseIon 37.58, Hach pH-meter.

The kinetic of BPA degradation was evaluated based on the Eqs. (3)–(6).

$$\frac{d[BPA]}{dt} = -k_{HO^{\cdot}}[HO^{\cdot}][BPA] \tag{3}$$

$$-k_{HO^{\cdot}}\ [HO^{\cdot}] = k_{obs} \tag{4}$$

$$\frac{d[BPA]}{dt} = r_{obs} = -k_{obs}[BPA] \tag{5}$$

The observed degradation rate (r_{obs}) of BPA was calculated from the PFO reaction rate given in Eq. (5). The PFO degradation rate constant (k_{obs}) of BPA was determined from fitting the experimental data with