



The impact of humic acid on the removal of bisphenol A by adsorption and ozonation

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ABSTRACT

This study investigates the removal of bisphenol A (BPA) by either adsorption or oxidation when humic acid was presented. For adsorption, three types of activated carbon (A, B, and C) were used. BPA adsorption with the presence of humic acid (4.5 mg L^{-1}) showed that Freundlich constant (K) was reduced in the range of 31–68%, compared to K without humic acid. Moreover, the relatively greater influence of humic acid on BPA adsorption was observed when activated carbon with the larger portion of micropore (i.e. activated carbon B) was used. BPA oxidation was tested using ozone solutions ($0.5\text{--}4 \text{ mg L}^{-1}$). The presence of humic acid (5 mg L^{-1}) reduced BPA oxidation in the range of 16–26%. The presence of bicarbonate increased BPA oxidation, but no significant influence of bicarbonate concentration (from 46 to 180 mg L^{-1}) was observed. The increasing pH increased BPA oxidation, and BPA (7 mg L^{-1}) was completely removed when 4 mg L^{-1} of ozone solution was used at the pH of 4–10. In addition, the appearance of degradation by-products depended on both concentration of ozone solution and the pH.

Keywords: Bisphenol A; Humic acid; Activated carbon; Ozone solution; The pH

1. Introduction

Bisphenol A (2,2-bis(4-hydroxyphenyl)propane, BPA) has been known as a basic component to synthesize polycarbonate (i.e. a raw material of infant bottles, plastic plates, and glass lens) and epoxy resin (i.e. packing material). Moreover, it has also been used as a coating chemical to increase the resistance against corrosion [1]. Toxicity of BPA has been well known, and especially, it has been classified as endocrine disrupting chemicals (EDCs) [2].

Adsorption has been noticed as one of the effective technologies to remove BPA [3–8]. Bautista-Toledo et al. [5] observed the high BPA adsorption with the zero surface charge of activated carbon, and they concluded that the adsorption capacity depended on the chemical nature of the surface and the solution pH. Choi et al. [6] reported that the surface charge was also important to BPA adsorption, but the pore volume of activated carbon mainly influenced the adsorption capacity. Moreover, the long-term operation caused the residing of microbes on carbons, and the adsorption of the specific EDC (i.e. amitrol) was better on the used

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carbons than the virgin carbons [6]. Tsai et al. [7] tested BPA adsorption on various adsorbents including mineral adsorbents, and they observed that the adsorption capacity of activated carbon was significantly larger than those of mineral adsorbents. Based on that, BPA adsorption depended on the surface area and the surface polarity [7]. Sui et al. [8] investigated BPA adsorption on the synthesized mesoporous carbon and they observed that adsorption capacity decreased as temperature increased from 10 to 40°C, while BPA adsorption was not influenced by the pH changes from 3 to 9.

Competitions of natural organic matter (NOM) were also reported [9]. Yu et al. [9] investigated the effect of NOM on adsorption of the selected pharmaceuticals (naproxen and carbamazepine) and endocrine disrupting compound (nonyphenol). They revealed that the granular activated carbon with the wider pore size distribution had greater NOM loading, resulting in lower adsorption of the selected pharmaceuticals and endocrine disrupting compound.

As alternatives, chemical oxidations have been adapted as BPA removal technology [10–12]. Especially, ozonation has been intensively studied [13–17]. Garoma and Matsumoto [14] studied ozonation under different operational conditions (i.e. ozone doses, BPA concentrations, pH, and bicarbonate ion concentrations), and they concluded that BPA was effectively degraded at the pH of 7.0. On the other hand, Tay et al. [15] showed that the maximum rate constant was calculated under basic conditions (pH > 10). Even though the suggested optimum pH has been reported differently, no significant effect of inorganic ions was agreed with by most researchers [14,15]. In addition, Deborde et al. [16] identified the major transformation products (i.e. catechol, orthoquinone, muconic acid derivatives of BPA, benzoquinone, and 2-(4-hydroxyphenyl)-propan-ol) with the additional minor transformation products.

This study investigated the removal of BPA using either adsorption or ozone oxidation when humic acid (i.e. a possible representative of NOM) was presented. For adsorption, three types of activated carbon were used and the influence of humic acid on BPA adsorption was evaluated. In addition, the effects of ozone concentration in aqueous solution, humic acid, bicarbonate, and the pH on BPA degradation were evaluated. Moreover, degradation by-products were identified.

2. Experimental

2.1. Materials

BPA and humic acid were purchased from Sigma Aldrich. BPA dissolved in acetone was prepared as a

stock solution, and BPA concentration in the stock solution was 5,000 mg L⁻¹. HPLC grade reagent of methanol, dichloromethane, and acetone were purchased from Merck.

Three types of coal-based activated carbon (i.e. A, B, and C) were selected and their characteristics are presented in Table 1.

Those activated carbons had a similar Brunauer–Emmett–Teller (BET) surface area ranged from 980 to 991 m² g⁻¹. Specifically, activated carbon A had a larger portion of mesopore, while activated carbon B had a larger portion of micropore.

2.2. BPA adsorption with humic acid

Activated carbons were prepared as follows. Those were ground using a mortar until the activated carbons pass through 325-mesh sieve and stored in a desiccator.

A bottle-point technique was used for adsorption isotherm. The weight of activated carbon with ± 0.3 mg was measured for the isotherm test, and total volume of the bottle was 330 mL. After the injection of BPA (i.e. 384 ± 17 (avg. ± st.dv.) µg L⁻¹) either without or with humic acid (i.e. 1.4 and 4.5 mg L⁻¹), the bottles were mounted on a tumbler at 10 rpm and the samples were retrieved from the tumbler after 5 d. To analyze BPA in aqueous phase, the samples were filtered to remove activated carbon by 0.45 µm membrane.

2.3. Bisphenol A oxidation by ozone solution

The ozone-saturated water was prepared by purging O₃ gases, which was generated from ozone generator (model PC57-10, Ozonetech) with diffuser. The ozone solution was used for experiments, and it was prepared by a dilution of the ozone-saturated solution with the de-ionized water. The concentrations of the ozone solution were checked by an indigo method [18]. After that, the effects of ozone (i.e. 0.5, 1, 2, and 4 mg L⁻¹), humic acid (i.e. 1, 3, and 5 mg L⁻¹), the pHs (i.e. 2, 4, 6, and 10), and bicarbonate (i.e. 46, 90, and 180 mg L⁻¹) on BPA degradation were investigated. Concentration of BPA was 7.0 ± 0.18 mg L⁻¹.

2.4. Analysis

The BET surface area and total pore volume were determined using ASAP 2020 instrument (Micromeritics). Approximately 0.2 g of the sample was degassed for 12 h at 140°C. The BET surface area was calculated in the relative pressure range of 0.05–0.2, and total

Table 1
The surface area and pore volume of the tested activated carbons

Types	Surface area ($\text{m}^2 \text{g}^{-1}$)			Pore volume ($\text{cm}^3 \text{g}^{-1}$)		
	Total	Micro ($d < 2 \text{ nm}$)	Meso ($d > 2 \text{ nm}$)	Total	Micro ($d < 2 \text{ nm}$)	Meso ($d > 2 \text{ nm}$)
A	991	889	103	0.558	0.379	0.179
B	980	953	26	0.426	0.395	0.030
C	985	924	61	0.466	0.360	0.085

pore volume was calculated at the relative pressure (P/P_0) of 0.99.

The pH was measured by the pH meter (Model 420A, ORION). Concentration of humic acid was checked by measuring dissolved organic carbon, which was detected by Multi N/C 3000 (AnalytikJena). The method of non-purgeable organic carbon was used, and the detector was a non-dispersive infrared detector. A fresh standard solution of potassium hydrogen phthalate ($\text{C}_6\text{H}_4(\text{COOK})(\text{COOH})$) was prepared before the analysis, and it was regularly used to check the sensitivity.

BPA was analyzed by a modified method consisting of solid-phase extraction followed by gas chromatography coupled to mass spectrometry (GC-MS) [19,20]. Cartridges (Oasis HLB 6 cc cartridge, Waters) were conditioned with 4 mL of methanol and 4 mL of de-ionized water. A solution sample (250 mL) was percolated through the cartridge equipped with a manifold (waters) at a flow rate of 10 mL min^{-1} . After that, BPA was extracted from the cartridge consecutively by 0.5 mL of methanol, 1 mL of methanol:dichloromethane (1:1), and 4 mL of methanol:dichloromethane (1:3). This extractant was evaporated under nitrogen gas, and reconstituted to 1 mL with acetone.

GC-MS (6890N-5975B, Agilent Technologies) was used for BPA detection. The injection temperature was 250°C , and helium was used as a carrier gas. A HP-5 ($30 \text{ m} \times 0.25 \text{ mm}$ i.d. with $0.25 \mu\text{m}$ film thickness) was used and the oven temperature was programmed from 80°C (1 min) to 280°C (4 min) at the rate of 8°C min^{-1} . An injection volume of $2 \mu\text{L}$ was used in the splitless mode. Electron impact mode was used for the ionization of samples and the mass spectra were acquired with m/z ranging from 60 to 300.

3. Results and discussion

3.1. Effect of humic acid on BPA adsorption

The linearized Freundlich isotherm was shown in Fig. 1 when BPA adsorption either with or without humic acid was conducted with three types of activated carbons (i.e. A, B, and C).

Even though BPA adsorption with activated carbon B was not much affected by humic acid (1.4 mg L^{-1}), BPA adsorption decreased with increasing concentration of humic acid, regardless of the types of activated carbons. Therefore, this could imply the competition that humic acid in the solution could act as competitive compounds to BPA for the adsorption.

Freundlich isotherm (i.e. $q = KC^{1/n}$), where K is a constant related to adsorption capacity and n is related to adsorption intensity was used to explain the experimental data [21,22]. The values of Freundlich constants (i.e. K and $1/n$) are presented in Table 2.

According to adsorption capacity constant (K) from BPA adsorption without humic acid, the lower BPA adsorption was observed with activated carbon A, while the higher BPA adsorption was observed with activated carbon C. Moreover, BPA adsorption was greatly reduced by humic acid when activated carbon B was used.

Specifically, BPA adsorption with the presence of humic acid (4.5 mg L^{-1}) revealed that the higher reduction of K (i.e. 68% reduction comparing to K without humic acid) was calculated at activated carbon B. Moreover, at a certain condition ($[\text{C}]_{\text{HA}} = 1.4 \text{ mg L}^{-1}$), $1/n$ of activated carbon B was suddenly increased. According to the characteristics of activated carbons, activated carbon B had the larger portions of micropore and the lower portions of mesopore. Therefore, BPA adsorption was greatly influenced by humic acid when activated carbon that had a large portion of micropore was blocked by humic acid. With limitation, the surface chemistry of activated carbons might influence the adsorption especially in diluted solutions [5,6,23]. It was reported that the favorable conditions for the adsorption of BPA was those in which the net charge density of activated carbon was zero and BPA was in molecular form [5].

3.2. BPA oxidation by ozone solution

3.2.1. Effects of humic acid and bicarbonate on BPA oxidation

Effects of humic acid and bicarbonate on BPA oxidation are shown in Fig. 2 when the concentrations of ozone solution ranged from 0.5 to 4 mg L^{-1} .

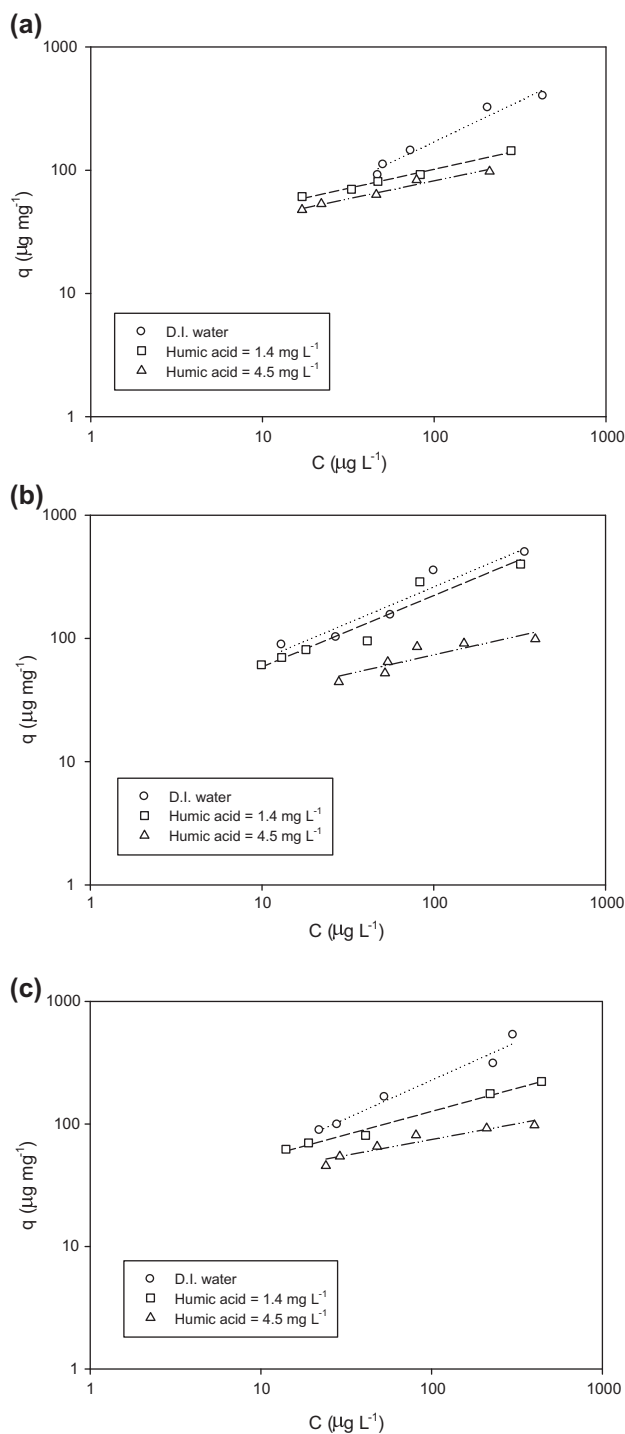


Fig. 1. Effects of humic acid on BPA removal by activated carbon (a) A, (b) B, and (c) C.

BPA oxidation increased with increasing the concentrations of ozone solution, and BPA (7 mg L^{-1}) was effectively oxidized with 4 mg L^{-1} of ozone solution.

The increasing concentration of humic acid decreased BPA oxidation. Moreover, BPA was completely oxidized with 4 mg L^{-1} of ozone solution when humic acid was below 3 mg L^{-1} . Compared to BPA oxidation without humic acid, the presence of humic acid (5 mg L^{-1}) reduced BPA oxidation in the range of 16–26%. Mostly, BPA oxidation was reduced as much as 26% when the concentration of ozone solution was 2 mg L^{-1} . The reason to reduce the oxidation of BPA at high concentrations of humic acid was that parts of ozone were used to oxidize the humic acid.

The results of BPA oxidation with bicarbonate indicated that no significant effect was observed on varying bicarbonate concentrations in the range of 45–180 mg L^{-1} . It was agreed that the gradients of bicarbonate (from 61 to 488 mg L^{-1}) did not affect BPA oxidation by ozone [14], and it was explained that no significant effect of bicarbonate was due to the higher reactivity of BPA with hydroxyl radical ($1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) [24]. Moreover, BPA oxidation with and without bicarbonate indicated that the existence of bicarbonate increased BPA oxidation. This might be explained by the carbonate radical ($\cdot\text{CO}_3^-$). The reaction of hydroxyl radical with bicarbonate in ozonation could produce carbonate radical, and the oxidation by carbonate radical might be effective for compounds bearing easily oxidizable moieties like phenols [25,26]. In addition, Tay et al. [15] reported that various inorganic anions (phosphate, nitrate, chloride, and sulfate ions) did not affect BPA oxidation when the inorganic anions at concentration levels in the wastewaters were used.

3.2.2. Effects of the pH on BPA oxidation and degradation by-products

BPA oxidations by ozone solution in varying pHs are shown in Fig. 3.

As a result, BPA oxidation without the pH adjustment was similar to that at pH 6, and BPA oxidation was increased with the increasing pH of solution. It has been known that the decomposition of ozone is initiated by the reaction of ozone and hydroxide ion (OH^-), and this initiation reaction produces hydroxyl radical through a consecutive series of reactions [14,27]. In pure water, the degradation of the target compounds by direct reaction with ozone is favored at lower pH levels, and that with hydroxyl radical is favored at higher pH levels [14]. Because the redox potential of hydroxyl radical (2.8 V) was stronger than that of ozone (2.07 V), higher BPA oxidation occurred at higher pH. In addition, the reactive oxygen species other than hydroxyl radical might react with BPA at

Table 2

Freundlich constants (i.e. K and $1/n$) of BPA adsorption with humic acid

Types	$[C]_{\text{HA}}^a = 0 \text{ mg L}^{-1}$			$[C]_{\text{HA}} = 1.4 \text{ mg L}^{-1}$			$[C]_{\text{HA}} = 4.5 \text{ mg L}^{-1}$		
	K	$1/n$	r^2	K	$1/n$	r^2	K	$1/n$	r^2
A	15.6	0.53	0.96	13.5	0.42	0.98	10.7	0.41	0.98
B	24.2	0.52	0.99	11.6	0.57	0.94	7.67	0.47	0.96
C	27.3	0.52	0.90	15.5	0.40	0.98	10.3	0.41	0.94

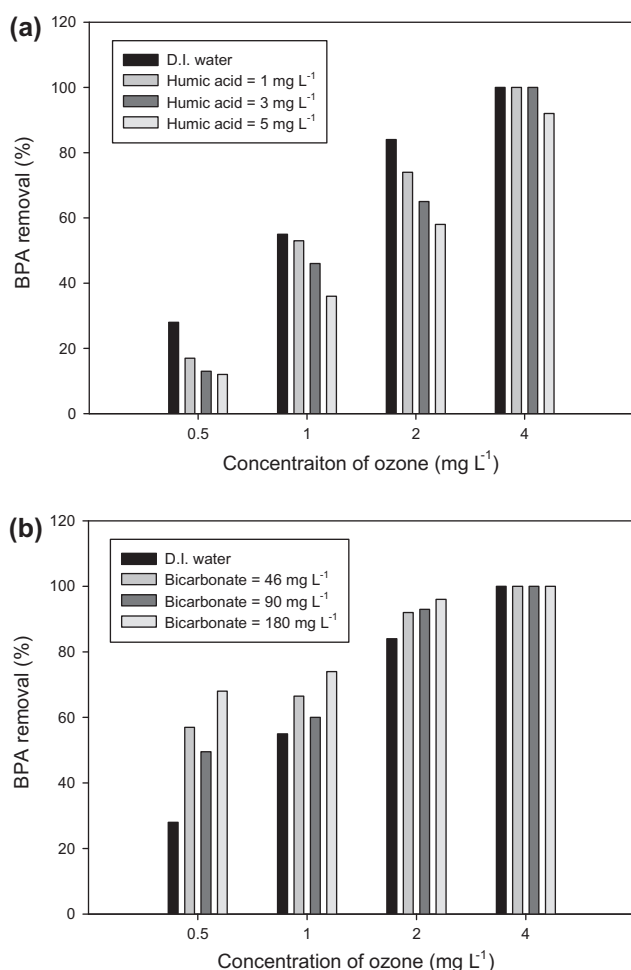
^a $[C]_{\text{HA}}$ = concentration of humic acid.

Fig. 2. Effects of humic acid and bicarbonate on BPA removal by ozone solution.

alkaline conditions. It has been proposed that the formation of superoxide anion ($\cdot\text{O}_2^-$) is favored at basic pH value [27]. Moreover, it was recently reported that superoxide anion involved the redox reactions with the target compounds, especially at high pH [28].

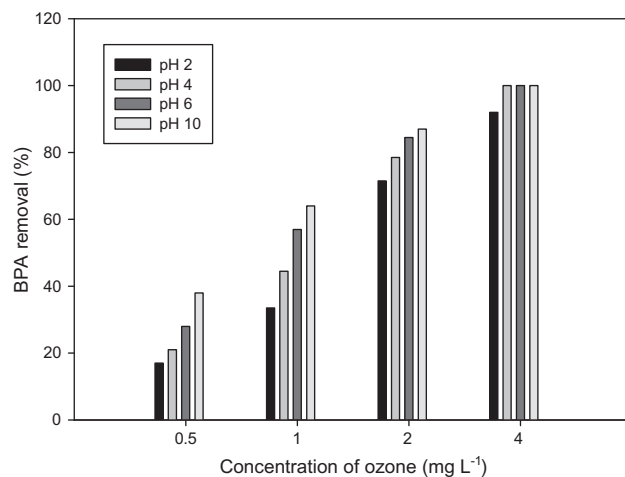


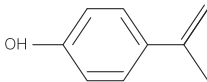
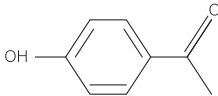

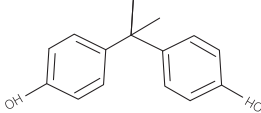
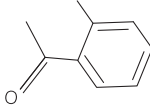
Fig. 3. BPA removals by ozone solution at various levels of pH.

The identified and proposed degradation by-products including BPA are in Table 3.

Identification of the degradation by-products (DBPs) at various levels of pH indicated that degradation by-products were observed when ozone solution (below 2 mg L^{-1}) was used at acidic conditions (i.e. pH 2 and 4). Moreover, the degradation by-products were not observed when the high concentration of ozone (4 mg L^{-1}) and the pH of 10 were applied. Regardless of ozone concentration, BPA oxidation at the high pH (i.e. pH 10) did not produce degradation by-products, possibly due to the reaction of BPA with the reactive oxygen species like hydroxyl radical.

Among degradation by-products, DBP1 was detected mostly, and both DBP2 and DBP3 were recognized irregularly. Those were agreed with other publications [15,29]. Moreover, the proposed degradation by-product, DBP4 appeared with over 90% abundance.

Table 3
The identified and proposed degradation by-products

Name (Level)	RT ^a (min) [<i>m/z</i>] ^b	MW	Molecular structure	
<i>Identified</i>				
4-(prop-1-en-2-yl)phenol (DBP1)	9.0 [1 3 4]	134		[15,29]
4-hydroxyacetophenone (DBP2)	10.4 [1 2 1]	136		[15,29]
Hydroquinone (DBP3)	8.4 [1 1 0]	110		[15]
BPA	21.0 [2 1 3]	228		[15,29]
<i>Proposed</i>				
1-(2-methylphenyl)ethanone (DBP4)	8.9 [1 3 4]	134		This study

^aRetention time.

^bMass to charge ratio.

4. Conclusions

The presence of humic acid affected both BPA adsorption and BPA oxidation. Based on Freundlich isotherm, using activated carbon with higher portion of micropore (i.e. activated carbon B in this study) led to a greater reduction of BPA adsorption at the presence of humic acid. BPA oxidation was affected by parameters (i.e. ozone, humic acid, and the pH), but no significant effect on BPA oxidation was observed with bicarbonate. BPA (7 mg L⁻¹) was completely removed at the conditions of ozone (4 mg L⁻¹), humic acid (below 3 mg L⁻¹), and above pH 4. Several degradation by-products were identified at the acidic conditions, and the possible degradation by-products were also proposed.

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