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Kinetics of Degradation of Bisphenol A by Ozonization in Aqueous Solution

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The degradation of bisphenol A in aqueous solution by ozonization was investigated at the laboratory scale. The primary factors that influenced the removal efficiency of bisphenol A were investigated, including the pH, the initial concentration of bisphenol A, the ozone gas concentration and the reaction temperature. Ozone enabled the efficient removal of bisphenol A and the maximum removal efficiency was achieved at pH 7. An accurate kinetic model of the chemical reaction and mass transfer was described by an exponential relationship between the pseudo-first-order rate constant and the operational parameters. The intrinsic kinetic constants for the reaction of bisphenol A with ozone were also determined using a competitive kinetics method with phenol as a reference compound. The results revealed that the pH exerted a strong influence on the kinetic constants and that the rate constants increased exponentially from 3.27×10^3 M^{-1} s^{-1} to 1.23×10^9 M^{-1} s^{-1} as the pH was increased from 3 to 11, respectively.

Keywords: Bisphenol A, Ozonation, Influencing factors, Removal efficiency, Kinetics model.

INTRODUCTION

In recent years, research on endocrine disrupting chemicals (EDCs), which interfere with the endocrine systems of humans and animals and affect both health and reproduction, has increased considerably[1]. Bisphenol A (BPA) is an endocrine disruptor that can mimic estrogen and consequently lead to negative health effects[2,3]. Adverse health effects caused by exposure to bisphenol A during pregnancy and development have been observed[4,5], and relevant evidence also suggests that bisphenol A can cause estrogenic effects[6], liver damage[7], obesity-promoting effects[8], pancreatic β-cell function[9] and thyroid hormone disruption[10]. Bisphenol A has drawn increasing scrutiny due to its potential threats to the human body and its increasing application in consumer products for food and drink packaging[11]. In 2010, Department of the Environment of Canada declared bisphenol A to be a "toxic substance" and the European Union, Canada and, most recently, the United States have banned bisphenol A use in baby bottles.

As an important raw chemical material, bisphenol A is extensively used in the production of epoxy resins, phenolic resins, polyacrylate, polycarbonate products[12] and many other plastics and resins. The world-wide production capacity of this compound was 3.2 million metric tons annually in 2005[13]. The long-term use, abrasion, heating and acidic exposure of plastic products can promote ester bond breakage of the polymer and release the bisphenol A monomer[14,15]. Bisphenol A is relatively stable and non-biodegradable. Moreover, large volumes of wastewater containing high concentrations of bisphenol A can be discharged locally during the production process without effective treatment, leading to the environmental exposure of humans and wildlife. Qiang *et al.*[16] found that the four most common wastewater treatment processes were unable to completely remove six predominant endocrine disrupting chemicals during a sampling survey of 20 rural wastewater treatment facilities located in eastern China. Therefore, there is a pressing demand for low-cost and high-efficiency bisphenol A removal methods that can achieve complete purification. Various chemical and physical treatment processes have been proposed for the removal of bisphenol A, including electrochemical methods[17,18], photodegradation[19,20], chemical oxidation[21], ultrafiltration and other non-destructive physical treatments[22,23]. These methods are limited by their low removal efficiency, their high cost or the incomplete oxidation of bisphenol A to CO_2 and water.

Ozonization is an emerging water treatment technology that has attracted attention because of its safety, efficiency and lack of secondary pollution. Ozone is strongly oxidizing and causes the majority of organic matter to be completely oxidized to CO_2 and water. Certain studies[24,25] have reported that the degradation of bisphenol A by the ozonization is highly effective. Additionally, related investigations of the reaction kinetics, reaction mechanisms and influencing factors during the oxidation process have also been studied. For example, Deborde *et al.*[26] investigated the direct ozonization rate constant of bisphenol A and concluded that the rate constant increased exponentially as the pH was increased from 3 to 12. Lee *et al.*[27] obtained similar results for the rate constant, but the degradation of bisphenol A was independent of pH at values of 2, 7 and 12. Garoma and Matsumoto[11] reported that the removal rate of bisphenol A reached a maximum at pH 7 and that there were no significant changes with pH. Ozone reacts selectively with certain functional groups, primarily C=C, -OH, $-CH_3$ and $-OCH_3$[28], and bisphenol A is first decomposed into complex phenolic derivatives. Therefore, the complete removal of the chemical oxygen demand (COD) would be more representative of bisphenol A removal and it should thus be considered. However, the majority of authors only studied the loss of bisphenol A rather than its mineralization.

The control and treatment of concentrated effluents are much more efficient, economical and green than the treatment of contamination after pollution has occurred. Considering the practical application and higher costs of ozonization, more experimental studies are needed to confirm and perfect the kinetics of ozonization and to optimize the operating parameters, especially pH. In this work, we studied the main factors that influence both the ozonization of high-concentration bisphenol A wastewater and the removal efficiency of the chemical oxygen demand. A simple kinetics model involving the operating parameters was derived for prediction of the rate constant during the degradation process. Meanwhile, the intrinsic kinetic constants of the reaction of bisphenol A with ozone at various pH values were determined to provide theoretical guidance for further research and application in industry.

EXPERIMENTAL

Bisphenol A (99 %) was obtained from Aladdin Reagent Co., Ltd. (China) and was used without further purification. Phenol, *tert*-butanol, potassium iodide, sodium thiosulfate, sodium hydroxide, sulfuric acid, methanol, potassium bromate, potassium hydrogen phosphate and potassium dihydrogen phosphate were purchased from Yongda Chemical Co., Ltd. (China) and all reagents were analytical grade except for the HPLC-grade methanol. Ozone was generated using a corona discharge ozone generator (NPF3W, Shandong Nippon Photoelectricity Equipment Co., Ltd., China) that was supplied with oxygen gas (97 %). Deionized water was prepared from a combination of electrodialysis and ion exchange resins.

Ozonization experiments: Ozonization experiments were conducted semi-continuously under heterogeneous conditions in a bubble column and an experimental setup consisting of an oxygen tank, an ozone generator, an ozone concentration detector and a thermostatic system, as shown in Fig. 1. The bubble column was a 1300 mL cylindrical glass vessel with a 55 cm length and 5.5 cm diameter that was equipped with a ceramic sand core diffuser plate (G5, 5 mm height) at the bottom for the feeding of the ozone gas and an outlet at the top for the exit of the gas and for sampling. Solutions of bisphenol A that ranged from 60 to 140 mg L^{-1} were prepared directly in deionized water with moderate heating. The solution was adjusted to the desired pH using 0.1 M potassium phosphate-buffered saline and either sodium hydroxide or sulfuric acid. In each batch, 1000 mL of the prepared solution was loaded into the bubble column with or without the addition of other reagents as necessary for experimental purposes. The concentration of generated ozone gas, a mixture of ozone and oxygen, for fixed gas flow was determined by passing it through the ozone concentration detector and adjusting the flow meter. Then, the stabilized gas was continuously bubbled into the solution through the sand core diffuser plate. The gas flow rate was adjusted to 0.4 L min^{-1} with an ozone inlet concentration between 15 and 30 mg L^{-1}. Because the holes of the diffuser plate were densely concentrated and because the apertures were small, the gases and liquids could be easily mixed completely. During the ozonization process, a 1 mL aliquot of solution was removed from the reactor at specified time intervals and was quenched immediately in a small beaker with three drops of 0.1 M sodium thiosulfate to eliminate the residual ozone and $^{\bullet}OH$ radicals. Then, the samples were measured according to experimental purposes after filtration.

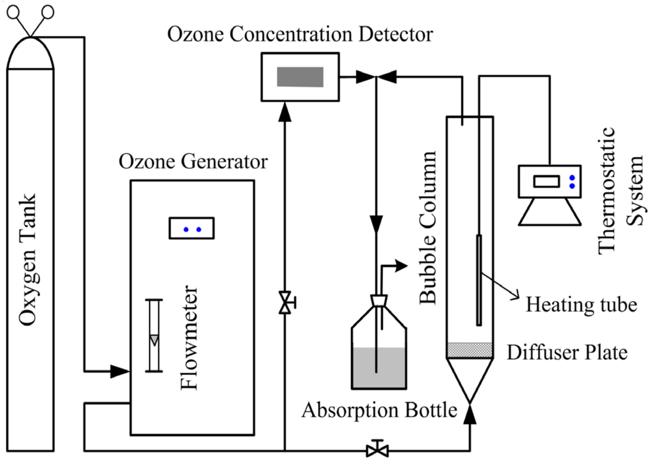

Fig. 1. Experimental setup for ozonization

Analysis: The concentrations of bisphenol A and phenol in the aqueous solution were analyzed using a high-performance liquid chromatograph (HPLC, LC-20AT, Shimadzu, Japan) that was equipped with a multiple UV wavelength detector (SPD-M20A, 190-800 nm). A 20 μL volume of solution was injected manually for each sample and the UV detector was set at 278 nm for all analyses. The analytes were separated using a C18 HPLC column (150 × 4.6 mm, 5 μm, Dikma Diamonsil) with an elution flow rate of 1 mL min^{-1} and the mobile phase consisted of methanol:water in 70:30 and 65:35 volume ratios for the bisphenol A and phenol analyses, respectively. The retention times for bisphenol A and phenol were approximately 5 and 8 min, respectively. Neither compound was detected in deionized water. The chemical oxygen demand of the solution was determined by spectrophotometry using potassium dichromate as the oxidant and silver sulfate as the catalyst in a sulfuric acid medium. The mixture solution was digested with a chemical oxygen demand digester at 165 ± 2 °C for 15 min and the absorbance was then measured using a UV-visible spectrophotometer (722N) at 610 nm. Finally, the chemical oxygen demand was calculated from the calibrated standard curve. The ozone concentration in the gas mixture was detected directly using an ozone concentration detector

(IDEAL-2000, Zibo Ideal Computer Software Co., China). The pH was measured using a PHS-3D pH meter that was equipped with an E-201-9 composite electrode that had been previously calibrated.

RESULTS AND DISCUSSION

Influencing factors and efficiency of bisphenol A removal: The practical application of ozonization to wastewater treatment must be conducted under conditions of heterogeneous contact. Due to the strong oxidative abilities of O_3, the reaction rate is fast and greatly exceeds the mass transfer rate. However, under practical conditions, mass transfer likely becomes the rate-determining step of the reaction due to insufficient ozone that is provided for this rapid reaction. The factors that impact the solubility, self-decomposition rate and mass transfer rate of ozone will also influence the removal of bisphenol A. Therefore, the effects of the main reaction conditions, including the pH, the initial bisphenol A concentration, the ozone gas concentration and the reaction temperature on the bisphenol A removal efficiency were investigated in subsequent experiments to determine the optimum operating conditions (Fig. 2).

It has previously been reported that the reaction between bisphenol A and O_3 follows second-order reaction kinetics overall and first-order kinetics with respect to each reagent. Considering the two pathways for oxidation, direct ozone oxidation and hydroxyl radical ($^{\bullet}OH$) oxidation, the overall ozonization rate constants for bisphenol A can be expressed by eqn. 1 as follows.

$$-d[BPA]/dt = (k_{O_3,BPA}[O_3] + k_{\bullet OH,BPA}[^{\bullet}OH]) \times [BPA] \quad (1)$$

where $k_{O_3,BPA}$ and $k_{\bullet OH,BPA}$ represent the second-order kinetic constants for the bisphenol A reaction with O_3 and $^{\bullet}OH$, respectively.

Because ozone gas was continuously fed, we assumed that the concentrations of the ozone and hydroxyl radicals were unchanged during the reaction and that they could therefore be merged into a second-order reaction rate constant to create a pseudo-first-order kinetic equation, as shown in eqn. 2. The experimental results verified this assumption based on the plot of ln ($[BPA]_n/[BPA]_0$) *versus t*, which demonstrated a linear relationship with a slope that was equal to the pseudo-first-order reaction rate constant (k_{obs}).

$$-d[BPA]/dt = k_{obs}[BPA] \quad (2)$$

Effect of pH: A 100 mg L^{-1} bisphenol A solution was prepared for the degradation experiment at various pH values buffered by 0.1 M phosphate solution. The effect of pH on the bisphenol A removal rate is displayed in Fig. 2(A). As shown in Fig. 2(A), the pH affected the removal of bisphenol A, as the percent removal varied from 81.7 to 95.2 % after 60 min of ozonization depending on the pH. The degradation rate of bisphenol A increased with the pH from pH 3 to 7 and the maximum degradation rate was obtained at pH 7, with a rate constant of 0.0475 min^{-1}. However, the degradation rate began to decrease at pH values greater than 7. The removal rates of bisphenol A decreased from 95.2 to 81.7 % from pH 7 to pH 10.20, respectively. Deborde *et al.*[26] and Tay *et al.*[29] reported that the intrinsic kinetic constant for the reaction of bisphenol A with O_3 was greater under alkaline conditions due to the

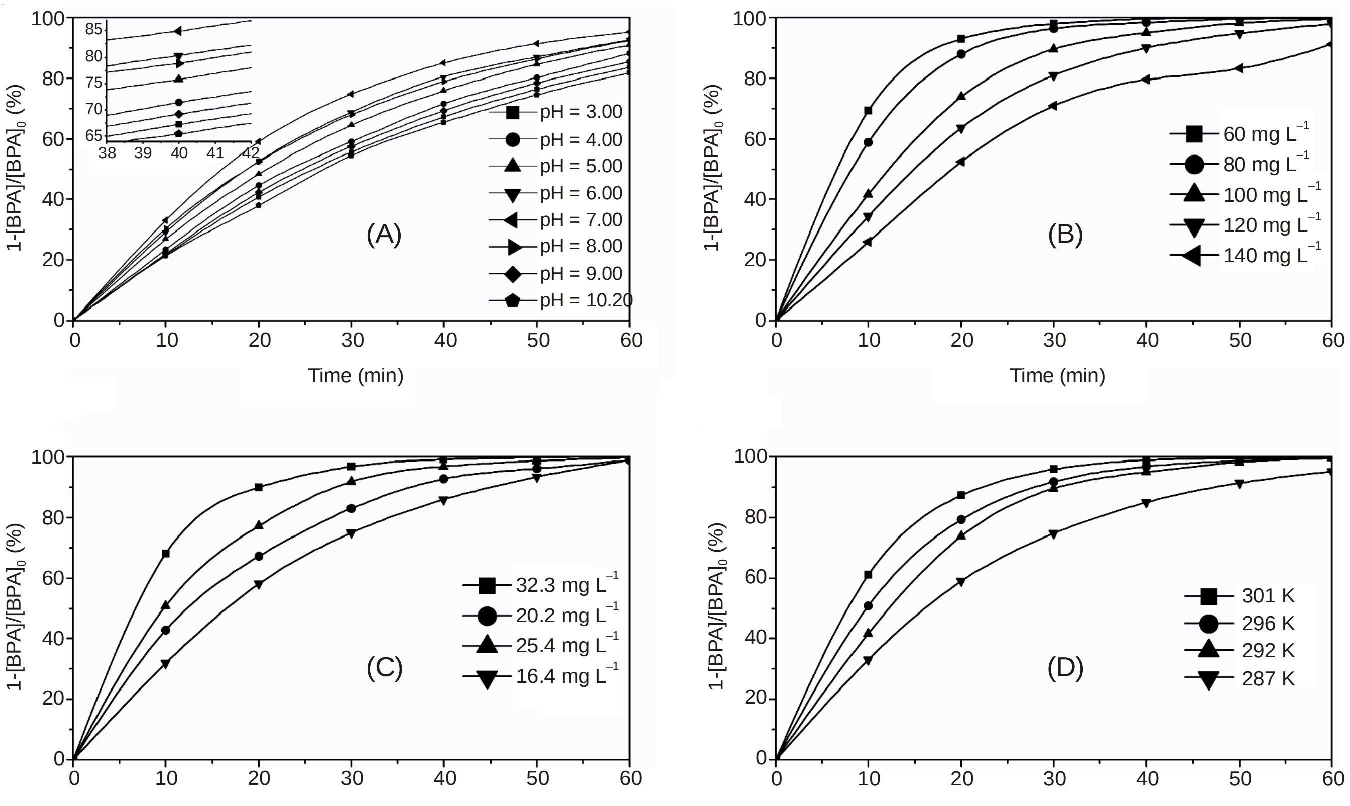

Fig. 2. Effect of reaction conditions on the bisphenol A (BPA) removal percentage. (A) Effect of pH, runs 1-8; (B) effect of bisphenol A initial concentration, runs 9-13; (C) effect of ozone gas concentration, runs 14-17; (D) effect of reaction temperature, runs 18-21

dissociation of bisphenol A. Here, the lower removal rates in alkaline conditions were attributed to the relatively minor impact of bisphenol A dissociation compared with the insufficient provision of ozone. The mass transfer rate of ozone was slower and was the rate-determining step of the reaction. Additionally, ozone readily decomposes in water and the increased alkalinity destabilized the ozone. Thus, more ozone was decomposed, leading to a reduction in the bisphenol A removal efficiency. Therefore, a pH of 7 or even slightly acidic conditions provided optimal reaction conditions for the practical degradation of bisphenol A.

Effect of the initial concentration of bisphenol A: The initial concentrations of contaminants exert a significant effect on the practical application of ozonization by directly impacting the removal efficiency of the targets and the time necessary for processing. To investigate the effect of the initial bisphenol A concentration on the degradation process, experiments were conducted with varying initial bisphenol A concentrations. As shown in Fig. 2(B), the overall removal rates of bisphenol A decreased and the pseudo-first-order rate constants decreased from 0.1390 to 0.0377 min^{-1} as the initial concentration of bisphenol A increased from 60 to 140 mg L^{-1}, respectively. At the beginning of the reaction, the ozone concentration remained nearly constant with the same ozone dosage. The increase in the initial bisphenol A concentration enhanced the reaction driving force and facilitated the forward reaction direction, leading to bisphenol A elimination and increased ozone utilization. However, the percentage of bisphenol A degradation decreased due to the reduction in the molar ratio of ozone to the relative excess of bisphenol A. The utilization rate of ozone increased with increasing initial concentrations of bisphenol A and complete bisphenol A removal required correspondingly longer reaction times.

Effect of ozone gas concentration: The ozonization of bisphenol A was investigated by changing the ozone gas concentrations to determine the effect of ozone dosage on the degradation efficiency of bisphenol A. The effect of ozone dosage on the degradation of bisphenol A can be observed in Fig. 2(C). Increasing the ozone gas concentration significantly accelerated the rate of removal of bisphenol A and this influence was particularly evident at the initial stage of the reaction or at high concentrations of bisphenol A. After a 20 min reaction, the bisphenol A removal rate increased from 58.1 to 89.9 % as the ozone concentration increased from 16.4 to 32.3 mg L^{-1}, respectively. Increasing the ozone gas concentration led to increases in the ozone partial pressure in the mixed gas, which enhanced the mass transfer driving force of ozone between the gas-liquid phases and which then strengthened the ozone mass transfer rate. Thus, the degradation rates of bisphenol A were limited by the ozone supply. As a result, increasing the ozone gas concentration and supply could accelerate the oxidation rates. Increasing the ozone gas concentration is recommended within certain limits, because increasing the ozone gas concentration also leads to lower ozone utilization, according to reports from Garoma and Matsumoto[11] and Arslan-Alaton & A.E. Caglayan[30].

Effect of reaction temperature: The effect of the reaction temperature on the bisphenol A ozonization was also investigated between 287 and 301 K. The results are shown in Fig. 2(D). The reaction temperature exerted a strong impact on the ozonization process because increases in the temperature accelerated the degradation of bisphenol A within a certain temperature range. Temperature increases exerted a more dramatic effect at low temperature ranges than at high ranges. The percent removal of bisphenol A increased from 74.7 to 89.6 % as the temperature was increased from 287 to 292 K, respectively, after a 0.5 h reaction. But the overall removal only increased to 95.8 % as the temperature was further increased to 301 K. Temperature exerts a significant impact on the reaction rate constants and self-decomposition of ozone. According to the van't Hoff approximate rule, rate constants increase an average of 2- to 4-fold with each 10 K increase in temperature. However, temperature increases can also accelerate the self-decomposition rate of ozone in gas and water and reduce the solubility of ozone in water. As a result, the ozone mass transfer driving force was reduced, impeding the ozonization of bisphenol A. The former effect was more pronounced than the latter, making higher temperatures conducive to the ozonization of bisphenol A within a certain temperature range.

Removal efficiency of bisphenol A: Ten additional ozonization experiments were conducted at pH values of 5-8, initial bisphenol A concentrations of 80-120 mg L^{-1}, an ozone dosage of 20-25 mg L^{-1} and a reaction temperature of 290-300 K and the removal of bisphenol A reached a considerable efficiency of greater than 95 % after 60 min for all reactions. For the treatment of organic wastewater, the reduction of chemical oxygen demand is a necessary consideration. Under typical operating conditions, the removal of chemical oxygen demand was investigated simultaneously with the elimination of bisphenol A. A representative degradation result is shown in Fig. 3. As shown in Fig. 3, the removal rates of chemical oxygen demand and bisphenol A exhibited large differences during the ozonization process. The removal of bisphenol A reached 99.8 % completion after 70 min. However, only a 52.2 % reduction of chemical oxygen demand was achieved within the same time frame. The asynchronism between these two variables indicated that bisphenol A was not completely mineralized and that intermediate products were first generated by the oxidation of bisphenol A Keykavoos *et al.*[31] reported that bisphenol A could be completely degraded within 4 min in single ozonization systems, but only a 35 % conversion of the total organic carbon (TOC) was achieved within 60 min. This lagging total organic carbon removal rate, as measured by UV absorption at 280 nm, also revealed that the initial degradation products were primarily aromatic organic compounds that contained benzene rings, which were then further oxidized to aliphatic hydrocarbons as inferred from the chemical oxygen demand removal trend. Deborde *et al.*[24] investigated the byproducts of bisphenol A ozonization by LC-UV, LC-MS and MS/MS methods and identified five major transformation byproducts. Tay *et al.*[29] identified eight degradation byproducts, including hydroquinone and 4-hydroxyacetophenone. Due to the generation of byproducts were more stable and exhibited lower reaction rates with ozone, organic compounds could not be completely mineralized within a short time and only a 71.3 % reduction of chemical oxygen demand was obtained after 100 min.

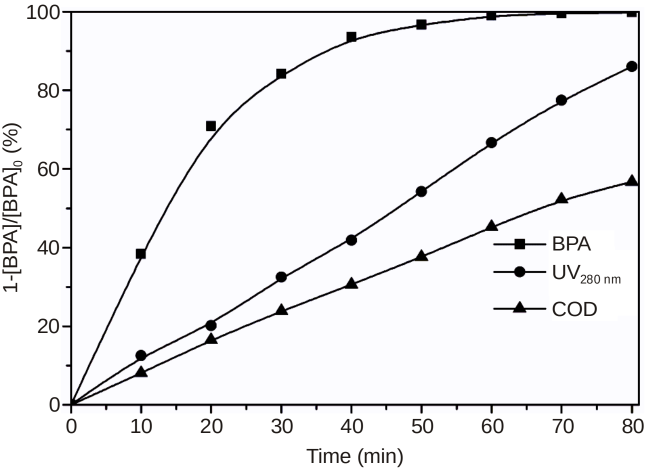

Fig. 3. Removal percentage based on different indicators. Experimental conditions: T = 301 K, pH = 7, $[BPA]_0$ = 100 mg L^{-1} and C_{O_3} = 21.6 mg L^{-1}

Kinetics model of bisphenol A ozonization and stability: The process of ozonization consists of a chemical reaction and mass transfer, with the latter being the rate-determining step. Our experiments revealed that the reaction rates of ozonization of bisphenol A depend on the solution pH, the initial bisphenol A concentration, the concentration of ozone and the reaction temperature. The complex influences of the chemical reaction and mass transfer on the ozonization process can be represented by a simple relationship between the pseudo-first-order rate constant (k_{obs}) and the above parameters, as expressed by the exponential empirical equation in eqn. 3[32,33].

$$k_{obs} = A\exp(-E_{a,obs}/RT)C_{O_3}^{\alpha}C_0^{\beta}[OH^-]^{\gamma} \quad (3)$$

A logarithmic transformation can be used to obtain eqn. 4.

$$\ln k_{obs} = \ln A - E_{a,obs}/RT + \alpha \ln C_{O_3} + \beta \ln C_0 + \gamma \ln [OH^-] \quad (4)$$

A linear fit was calculated between $\ln k_{obs}$ and T^{-1}, $\ln CO_3$, $\ln C_0$ and $\ln [OH^-]$ based on Table-1 and the results are shown in Fig. 4.

The fitting results demonstrated that the rate constants and the operating parameters followed a linear relationship. According to the slope of the straight line, $-E_{a,obs}/R$, α, β and γ could then be obtained.

$-E_{a,obs}/R = -4893$ and $E_{a,obs} = 40{,}680$ J mol^{-1}

$\alpha = 1.3448$, $\beta = -1.4681$, $\gamma_1 = 0.0567$ (pH = 3-7), $\gamma_2 = -0.078$ (pH = 7-11)

Substituting into eqn. 3 to obtain eqn. 5,

For pH = 3-7,

$$k_{obs} = A\exp(-40680.4/RT)C_{O_3}^{1.3448}C_0^{-1.4681}[OH^-]^{0.0567} \quad (5,a)$$

Based on the data from Table-1, A was calculated to have an average value of 3.36 × 10^7. Using substitution to obtain the kinetics model in eqn. 6,

$$C = C_0\exp(-k_{obs}t) = C_0\exp(-3.36\times10^7 \exp(-40680.4/RT)C_{O_3}^{1.3448}C_0^{-1.4681}[OH^-]^{0.0567}t) \quad (6, a)$$

For pH = 7-11,

$$k_{obs} = A\exp(-40680.4/RT)C_{O_3}^{1.3448}C_0^{-1.4681}[OH^-]^{-0.078} \quad (5, b)$$

$$A = 3.86 \times 10^6$$

$$C = C_0\exp(k_{obs}t) = C_0\exp(-3.86\times10^6 \exp(-40680.4/RT) C_{O_3}^{1.3448}C_0^{-1.4681}[OH^-]^{-0.078}t) \quad (6, b)$$

To verify the accuracy of the model, several additional experiments were conducted using operating parameters within the above ranges. The simulated and measured concentrations of bisphenol A after specific reaction times are listed in Table-2. The results confirmed that the kinetics model was accurate within an error range of 12 %.

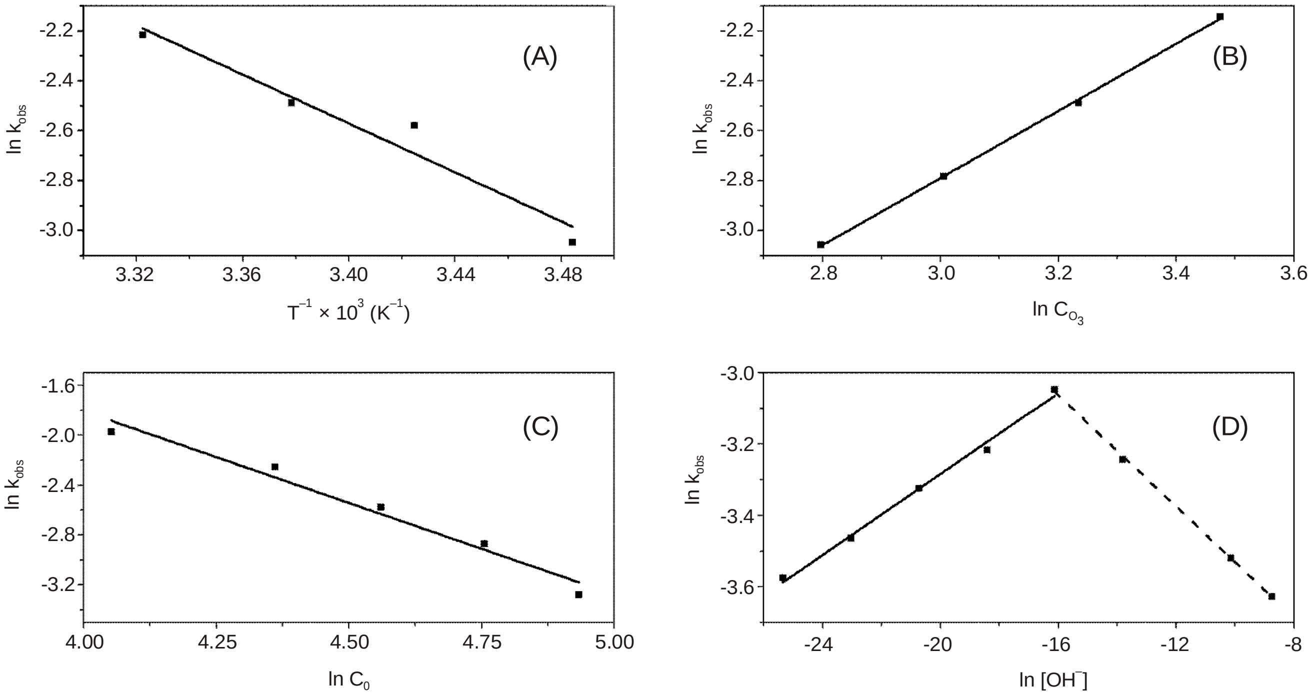

Fig. 4. Linear fitting of $\ln k_{obs}$ with (A) T^{-1}, (B) $\ln C_{O_3}$, (C) $\ln C_0$ and (D) $\ln [OH^-]$

TABLE-1
EXPERIMENTAL PARAMETERS AND PSEUDO-FIRST-ORDER RATE CONSTANTS

Run	pH	C_{BPA} (mg L^{-1})	C_{O_3} (mg L^{-1})	T (K)	k_{obs} (min^{-1})	ln (k_{obs})	r
1	3.00	95.58	25.9	287	0.0280	-3.576	0.9966
2	4.00	97.62	25.8	287	0.0313	-3.464	0.9953
3	5.00	96.56	25.6	287	0.0360	-3.324	0.9946
4	6.00	95.48	25.7	287	0.0401	-3.216	0.9968
5	7.00	95.86	25.7	287	0.0475	-3.047	0.9957
6	8.00	96.76	26.0	287	0.0390	-3.244	0.9979
7	9.60	95.59	26.0	287	0.0296	-3.520	0.9953
8	10.20	96.28	25.8	287	0.0266	-3.627	0.9961
9	7.00	57.51	25.9	292	0.1390	-1.973	0.9982
10	7.00	78.34	25.8	292	0.1050	-2.254	0.9963
11	7.00	95.68	25.7	292	0.0759	-2.578	0.9909
12	7.00	116.16	25.5	292	0.0567	-2.870	0.9922
13	7.00	138.78	25.6	292	0.0377	-3.278	0.9879
14	7.00	99.29	16.4	296	0.0470	-3.058	0.9925
15	7.00	98.77	20.2	296	0.0619	-2.782	0.9886
16	7.00	98.71	25.4	296	0.0831	-2.488	0.9917
17	7.00	98.58	32.3	296	0.1174	-2.142	0.9978
18	7.00	95.86	25.7	287	0.0475	-3.047	0.9957
19	7.00	95.68	25.7	292	0.0759	-2.578	0.9909
20	7.00	98.71	25.4	296	0.0831	-2.488	0.9917
21	7.00	97.53	24.6	301	0.1089	-2.217	0.9936

TABLE 2
STABILITY OF THE KINETICS MODEL

pH	C_{BPA} (mg L^{-1})	C_{O_3} (mg L^{-1})	T (K)	*t* (min)	C_{sim}^{a} (mg L^{-1})	C_{mea}^{b} (mg L^{-1})	E_r^{c} (%)
4	80.272	20.5	301	30	8.796	8.024	9.62
5	91.054	24.9	290	40	12.860	11.575	11.10
5	100.345	20.9	300	30	17.177	17.347	0.98
6	76.054	23.6	293	30	6.835	7.373	7.30
6	99.258	25.4	289	40	14.790	15.354	3.67
7	89.198	22.8	298	20	14.310	15.119	5.35
7	95.592	23.2	292	50	4.670	4.187	11.54
8	75.244	22.7	295	20	14.261	13.981	2.00
8	95.136	24.9	290	35	16.451	17.884	8.01
9	97.430	24.8	290	40	19.483	18.131	7.46

[a]Simulated concentration; [b]Measured concentration; [c]Relative tolerance

Intrinsic kinetic constants for the reaction of bisphenol A with O_3: During a typical ozonization process, the reduction of bisphenol A follows first-order kinetics for ozone and bisphenol A. Due to the fast reaction rate of ozonization and the instability of ozone in aqueous solution, fast reaction times are observed under homogeneous conditions, making it difficult to accurately detect changes in the concentrations of bisphenol A and ozone during the reaction. Furthermore, mass transfer between the gas-liquid phases makes it difficult to calculate the concentration of ozone and the reaction rate constants during heterogeneous reaction processes. Thus, the rate constants were determined using a competitive kinetics method with phenol as a reference compound in a semi-batch reactor through heterogeneous contact. In this series of experiments, solutions containing the same concentrations of bisphenol A and phenol were treated with ozone. A 52.04 mM concentration of *tert*-butanol was added in excess ([*tert*-butanol] > 100 [BPA]) as a radical scavenger of $^{\bullet}$OH to restrict the reaction of bisphenol A with $^{\bullet}$OH. Due to the elimination of $^{\bullet}$OH for both substances, eqn. 1 can be rearranged to eqn. 7.

$$-d[BPA]/dt = k_{O_3}, BPA[O_3][BPA] \quad (7,a)$$

$$-d[phenol]/dt = k_{O_3}, phe[O_3][phenol] \quad (7,b)$$

Integration and division are used to obtain eqn. 8.

$$\ln\left(\frac{[BPA]_n}{[BPA]_0}\right) = \frac{k_{O_3,BPA}}{k_{O_3,phe}} \ln\left(\frac{[phenol]_n}{[phenol]_0}\right) \quad (8)$$

where $[BPA]_0$ and $[phenol]_0$ represent the initial concentrations of bisphenol A and phenol before the reaction, respectively and $[BPA]_n$ and $[phenol]_n$ represent the corresponding concentrations during the reaction process. k_{O_3}, phe is the second-order kinetic constant for the total phenol reaction with O_3 and can be calculated using eqn. 9[27].

$$k_{O_3,phe} = k_{O_3,phenol}\left(\frac{10^{-pH}}{10^{-pKa}+10^{-pH}}\right) + k_{O_3,phenolate}\left(\frac{10^{-pKa}}{10^{-pKa}+10^{-pH}}\right) \quad (9)$$

where $k_{O_3,phenol} = (1.3 \pm 0.2) \times 10^{4}$ M^{-1} s^{-1}, $k_{O_3,phenolate} = (1.4 \pm 0.4) \times 10^{9}$ M^{-1} s^{-1} and pKa = 9.9[34]. Thus, $k_{O_3, phe}$ can be obtained under different pH values.

For a typical experiment at fixed pH, the ratio of the degradation rate constant of bisphenol A to that of phenol was determined by the slope of ln ($[BPA]_n/[BPA]_0$) *versus* ln ($[phenol]_n/[phenol]_0$) using experimental values measured with time. The second-order rate constants of bisphenol A with O_3 as a function of pH are shown in Fig. 5.

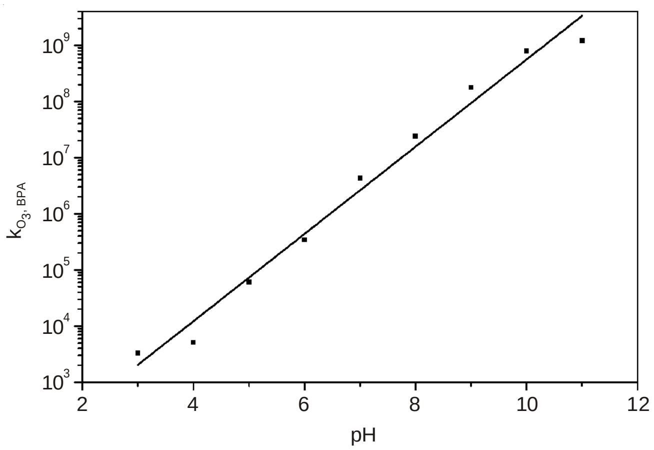

Fig. 5. Effect of pH on the second-order kinetic constant for the reaction of bisphenol A with O_3. Experimental conditions: T = 297 K, $[BPA]_0$ = 100 mg L^{-1}, $[phenol]_0$ = 0.439 mM and C_{O_3} = 22.6 mgL^{-1}

The second-order rate constants exhibited a strong dependence on pH. The reaction rate constants $k_{O_3,\ BPA}$ reached a minimum under acidic conditions and they increased with increasing alkalinity of the solution. In the range of pH 3 to 11, $k_{O_3,BPA}$ increased exponentially from approximately 3.27 × 10^3 M^{-1} s^{-1} (pH = 3) to 1.23 × 10^9 M^{-1} s^{-1} (pH = 11). Due to the shielding effect of *tert*-butanol for the hydroxyl radicals, bisphenol A and phenol primarily reacted directly with the ozone molecules. Bisphenol A contains two phenolic hydroxyl groups per molecule; therefore, it underwent a two-step ionization with pH that corresponded to the hydroxyl pK_a values of pK_{a_1} = 9.60 and pK_{a_2} = 10.20[29]. Various forms of bisphenol A were present in the aqueous solution. The undissociated species was predominant when the pH was less than 9 and bisphenol A was present primarily in an anionic or dianionic form at pH values greater than 9. The effect of pH on the results was consistent with the previous report by Deborde *et al.*[26], which reported rate constants of 1.71 × 10^4 M^{-1} s^{-1} (pH = 3) and 1.10 × 10^9 M^{-1} s^{-1} (pH = 11). The specific test methods, varying temperature or other conditions may have caused deviation from other previous results. The ionized bisphenol A fraction increased and the neutral fraction decreased with increasing pH until the ionized form of bisphenol A became the predominant species under alkaline conditions. Because of the high selectivity for the reaction of ozone molecules with organic matter, the reaction rates depend on molecular structure and the ionization of bisphenol A facilitated the ozone-based oxidation of bisphenol A due to the electrophilicity of ozone. Thus, the reaction between O_3 and anionic bisphenol A is faster than that between O_3 and neutral bisphenol A and the fastest reaction is observed between O_3 and dianionic bisphenol A. The effect of pH on removal of bisphenol A did not conform to the theoretical predictions and the maximum degradation rate was obtained at pH 7 because mass transfer was the rate-determining step during the practical ozonization process.

Effect of *tert*-butanol: The oxidation of organics with ozone can follow two pathways *i.e.*, the direct pathway, which involves molecular ozone and the radical pathway, which utilizes hydroxyl radicals derived from the ozone[34,35]. Molecular ozone direct oxidation exhibits greater selectivity for specific substances and functional groups. In contrast, hydroxyl radical oxidation is non-selective and it produces faster reaction rates. Additionally, many methods can be used to promote the generation of hydroxyl radicals to facilitate the ozonization process.

A greater number of ozone molecules can generate hydroxyl radicals with increasing pH and hydroxyl ion concentration and the fraction of hydroxyl radicals involved with indirect oxidation in organic ozonization processes increases as a result[36]. To study the importance of molecular ozone direct oxidation and hydroxyl radical indirect oxidation and to identify the major pathway in the degradation of bisphenol A, ozonization experiments were conducted either in the presence of excess *tert*-butanol (52.04 mM) or without *tert*-butanol. The effect of *tert*-butanol on the oxidative degradation process of bisphenol A at pH values of 7 and 11 is shown in Fig. 6.

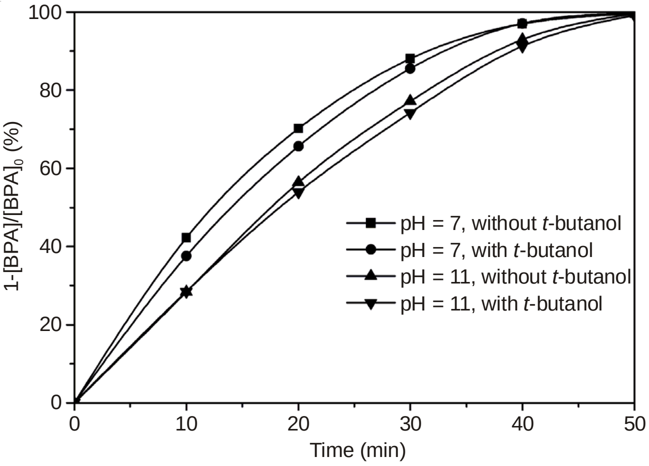

Fig. 6. Effect of *tert*-butanol on bisphenol A removal percentage. Experimental conditions: T = 297 K, pH = 7, $[BPA]_0$ = 100 mg L^{-1} and C_{O_3} = 22.6 mg L^{-1}

As shown in Fig. 6, the addition of *tert*-butanol caused a slight decrease in the degradation rate of bisphenol A. However, the difference in degradation rates with and without *tert*-butanol diminished as the reaction time increased and no difference was observed after 50 min. As a scavenger of hydroxyl radicals, *tert*-butanol preferentially reacted with the hydroxyl radicals and only weakly reacted with the ozone molecules because the rate of reaction with hydroxyl radicals (4.6 × 10^8 M^{-1} s^{-1}) is much greater than the rate of reaction with ozone (0.003 M^{-1} s^{-1})[34]. *tert*-Butanol did not affect the degradation rates of bisphenol A, indicating that the presence of hydroxyl radicals did not significantly influence the degradation of bisphenol A. It can be inferred, therefore, that the degradation of bisphenol A was primarily caused by direct ozonization with ozone molecules rather than by indirect oxidation and that a dominant fraction of bisphenol A was consumed by the direct reaction. This phenomenon may be due to the similar reaction rates for direct oxidation by ozone and indirect oxidation by hydroxyl radicals coupled with the much higher concentration of ozone molecules compared with that of hydroxyl radicals, even under alkaline conditions. As a result, the quenching of hydroxyl radicals by *tert*-butanol would exert less influence on the degradation of bisphenol A. Lee *et al.*[27] reported that ozone remained the principal oxidant at pH values as high as 12 by adding hydroxyl radical scavengers for comparison. Furthermore, the authors found that the addition of *tert*-butanol accelerated the reduction of bisphenol A at pH 2, which they attributed to the higher mass transfer rate of *tert*-butanol compared with that of ozone.

Conclusion

The effects of the main experimental parameters on the ozonization degradation of bisphenol A were studied under practical conditions. High ozone dosages and low initial concentrations of bisphenol A increased the reaction rates as well as the removal efficiency of bisphenol A. But the utilization rate of ozone was also reduced under these conditions. Increasing the reaction temperature also accelerated the removal of bisphenol A. A kinetic model for the ozonization of bisphenol A based on the operating parameters was established using multi-variable linear regression. Additionally, the removal of COD during ozonization was not efficient and lagged significantly behind the removal of bisphenol A.

The second-order kinetic constant for the reaction of bisphenol A with O_3 was investigated using a competitive kinetics method with phenol as a reference compound and a relative excess of *tert*-butanol as a scavenger for $^{\bullet}$OH radicals. The rate constants exhibited a strong dependence on the pH and increased exponentially from 3.27×10^3 M^{-1} s^{-1} to 1.23×10^9 M^{-1} s^{-1} as the pH was increased from 3 to 11, respectively.

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