Ozonation of endocrine disrupting chemical BHA under the suppression effect by salt additive—With and without H_2O_2

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Abstract

The oxidation of fresh and saline wastewater containing an endocrine disrupting chemical (butylated hydroxyanisole, BHA) under different reaction conditions by ozonation and O_3/H_2O_2 was investigated at various pH levels. The observed pseudo-first-order reaction kinetics was justified through a combined direct ozone and indirect radical oxidation approach for the ozonation process. The BHA decay rates increased with the increase of the solution pH, but decreased as the NaCl concentration increased because of the consumption of ozone by chloride. A kinetic model was therefore derived for predicting BHA degradation at various initial pH levels and NaCl concentrations. For the O_3/H_2O_2 and $O_3/H_2O_2/Cl^-$ processes, the rate of BHA removal was investigated at hydrogen peroxide concentration ranged from 0.5 to 5 mM at pH 7. Different optimal H_2O_2 dosages and decay rates were found for both processes due to the participation of reactions among O_3, H_2O_2, $OH^\bullet$ and Cl^- as discussed in the paper.
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1. Introduction

Butylated hydroxyanisole (BHA) is recognized as an endocrine disruptor chemical (EDC) in animal experiments [1–3]. It is a synthetic antioxidant which has been widely used to preserve and stabilize the freshness, nutrition, flavour and colour of food and animal feed products [4]. It was also added to edible fats and fat-containing food as an antioxidant, which prevents food from becoming rancid and developing objectionable odours. However, its use is not permitted in some countries such as Japan, because BHA could be tumour promoter [5]. Recently, numerous studies have shown the carcinogenicity of BHA in rat and hamster fore stomach, disturbance in mitochondrial electron transport, slightly oestrogenic to breast cancer cells, binds rainbow trout oestrogen receptor and claimed to stimulate transcriptional activity of the human oestrogen receptor [4,6].

In this study, BHA is selected as the probe for the investigation of the treatability by an advanced oxidation process (AOP): O_3/H_2O_2 system. Karimi et al. [7] has defined the AOP as processes which involved the generation of hydroxyl radicals in sufficient quantity, such as O_3/OH^-, O_3/H_2O_2, Fe^{2+}/H_2O_2, UVC/H_2O_2, UVC/O_3 and UVA/TiO_2 [8]. Kamenev et al. [9] investigated the effect of H_2O_2 concentration, $[H_2O_2]$, on the removal of phenol in O_3/H_2O_2 process and did not observe any significant impact on the oxidation efficiency for H_2O_2 doses ranging between 0.29 and 0.88 mM. It is postulated that these concentrations were relatively high comparing to the low concentrations of phenol (0.04 mg/L or 0.42 μM). Therefore, the effects of H_2O_2 could not be observed. On the other hand, Gulyas et al. [10] reported that the significant influence of H_2O_2 concentration on the removal of triethylene glycol dimethylether during O_3/H_2O_2 oxidation process. Therefore an optimum dosage of H_2O_2 towards ozonation is necessary for investigation.

Sodium chloride is commonly used as retarding agents or exhausting agents in textile industries with a concentration ranging from 5 to 100 ppt (part per thousand salinity or g/L) [11,12]. In Hong Kong, seawater is used for flushing purpose. The wastewater received by treatment works is usually salty (salinity of seawater is about 30 ppt) with an average pH level of 8 [13]. The chloride ions in wastewater may exert

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interference toward the performance of ozonation either in acidic or alkaline conditions. Muthukumar and Selvakumar [14] reported that presence of salts content in the acid dye effluent increase the complete decolouration time and hence decrease the decolouration efficiency of ozone. Therefore, the presence of NaCl in the treatment was simulated in this study as well.

2. Materials and methods

The butylated hydroxyanisole (BHA) was obtained from Sigma–Aldrich® (98.1% Purity, CAS: 25013-16-5). Sodium chloride and hydrogen peroxide (30%, w/w) were obtained from VWR International Ltd. and Junsei Chemical Co. Ltd. (Japan), respectively. All the solutions were prepared by 18 MΩ deionized distilled water from a Bamstead NANO pure water treatment system. All chemicals and solvents are of HPLC grade, and they are used without further purification. For pH adjustment, 0.1 M sulphuric acid or 0.1 M sodium hydroxide was used. All experiments were carried out at a controlled room temperature at $23 \pm 2\,°C$.

For the ozonation process, the experiments were carried out in a 1000 ml cylindrical contact tower, where the deionized water solution was pre-ozonated for 10 min (to reach saturation of ozone). Ozone gas was fed continuously into the reactor throughout the reaction with a glass sparger for better gas transfer and mixing. The OZAT® ozone generator (CFS-1A from Ozonia Ltd.) using oxygen as the source generated 0.018 mM (0.88 mg/L) saturated ozone at a flowrate of $1\,L\,min^{-1}$. The dissolved ozone concentration was determined by Indigo spectrometric method.

Sample analysis by HPLC was carried out using a chromatograph equipped with a pump (Waters 515), an ISCO injector (with a 20 μl loop), a C8, 250 mm × 4.6 mm, 5 μm particle size Restek® Pinnacle II column, and a Waters™ 486 Tunable Absorbance Detector. The mobile phase was 70% (v/v) acetonitrile and 30% distilled-deionised water, and the flow rate was 1.0 ml/min. The detection wavelength for BHA was 226 nm, which were pre-determined as the maximum absorption wavelengths (λ_{max}) by a Spectronic Genesys 2™ UV–vis Spectrophotometer.

In each test, 0.2 mM of BHA (36 mg/L) in a continuous ozone purging mode was applied to investigate the reaction kinetics of BHA ozonation (i.e. $0.024\,mg\,O_3/mg\,BHA^{-1}$). Three initial pH levels at 3, 7, and 11 were used to examine the consequence of the initial pH levels to the overall reaction rates. Samples were collected from the base of the contact tower at specific time intervals (0, 1.5, 3, 5, 8, 10 and 20 min) and reaction was quenched by excess sodium thiosulphate [15,16]. For those experiments involving H_2O_2, different concentration of H_2O_2 (0.5–5 mM) has been spiked simultaneously before the reaction start, in order to quench the residual hydrogen peroxide in the sample, excessive methanol [17] is previously added into the vials in a 1:1 ratio. Experiments involving the salt were carried out by addition of 10, 20, 30 ppt NaCl to the pre-ozonated solution and followed by the introduction of BHA.

3. Results and discussion

3.1. Quantitative prediction: decay kinetics of BHA under different conditions

The ozonation of BHA at different initial pH levels and NaCl concentration was examined. More than 98% of 0.2 mM BHA could be removed by continuous feeding of ozone at 0.018 mM in 20 min when no NaCl was present in the solution, where the decay rates of BHA were found to follow pseudo-first-order kinetics (Fig. 1). In the presence of NaCl, the interfering effect causing the drop of ozonation efficiency was observed at three different salinities (10, 20, and 30 ppt NaCl), and Fig. 2 (solid lines) shown one of the typical example (i.e. 30 ppt). The kinetic rate constants of ozonation reduced by 10%, 13% and 16% after the addition of 10, 20, and 30 ppt of NaCl, respectively. Therefore, it should be useful to establish a model that predicted the suppression effect for the proper reactor design when
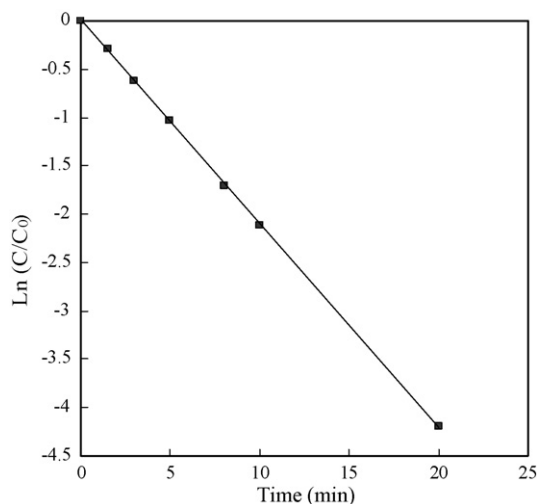

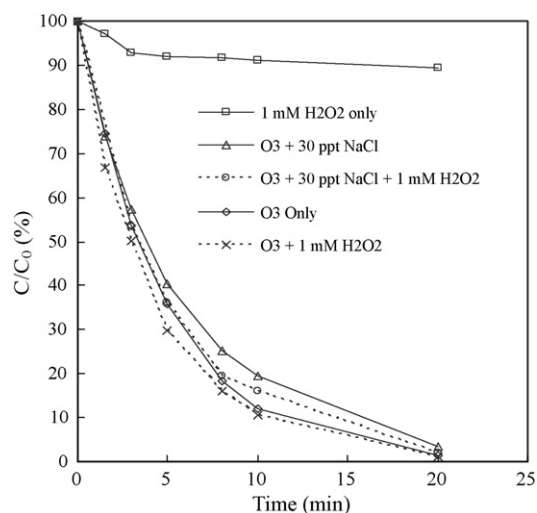Fig. 1. Ozonation of 0.2 mM BHA at pH 7 in a pseudo-first-order kinetics.

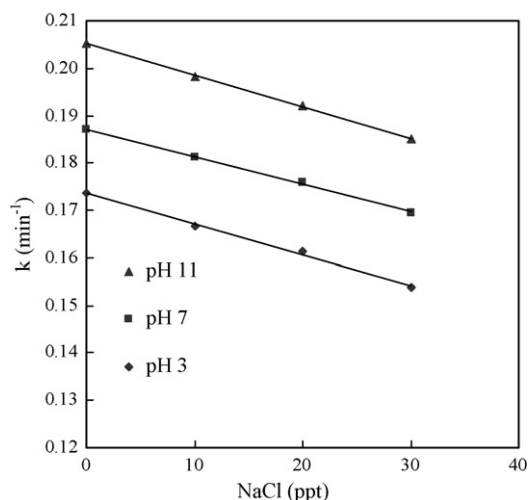Fig. 2. Removal efficiency of 0.2 mM BHA by different ozonation conditions at pH level of 7.

Fig. 3. The correlation between the BHA decay rate constant of the pseudo-first-order kinetics (k) and the [NaCl] at different initial pH.

salty wastewater was involved. It was interesting to note that the ozonation of BHA in the presence of NaCl can be described by a simple pseudo-first-order kinetics and the rate constants are highly correlated to either initial pH level or NaCl concentration, see Figs. 3 and 4.

According to our previous studies [15], the ozonation in a continuous purging mode can be formulated by Eq. (1), in which the oxidising ability of ozone is the combination of direct oxidation by molecular ozone and indirect oxidation by hydroxyl free radicals. The concentration of hydroxyl radicals [OH•] is pH dependent and can be related to the hydroxide ion [OH−] and [O₃] in solution [18]. In addition, the hydroxyl radicals and ozone concentration in the solution can be assumed to be constants through the continuous ozone supply:

$$\frac{d[BHA]}{dt} = -k_0[O_3][BHA] + k'_{OH}[OH^-][O_3][BHA] \qquad (1)$$

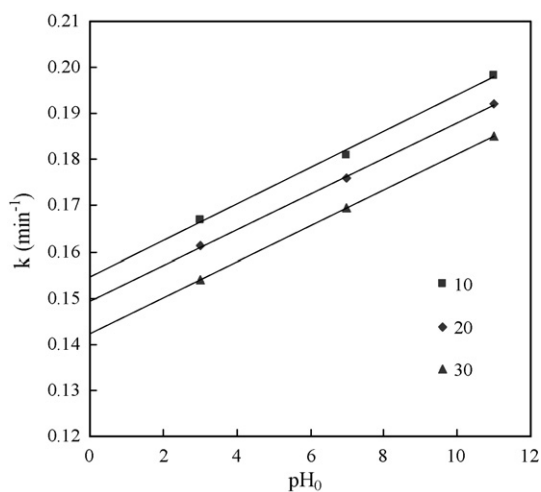Fig. 4. The correlation between the BHA decay rate constant of the pseudo-first-order kinetics (k) and the initial pH levels at different [NaCl] concentrations (ppt).

where [BHA], [O₃] and [OH−] are the concentrations of BHA, ozone and hydroxide ion, and k_0 and k'_{OH} are their corresponding kinetic rate constants. In this study, the change of pH levels during the reaction was found insignificant, so the variation of transaction rate from O₃ to OH• during the process can be neglected. This will simplify the modeling work, and the initial pH level was therefore used as the determining parameter in simulating the process.

It was known that the presence of Cl− will consume O₃ and form the less reactive O₂ in solution as shown below [19]:

$$Cl^- + O_3 \rightarrow ClO^- + O_2 \qquad (2)$$

Because Cl− acts as a catalyst and can be regenerated in the solution, the attenuation effect to the available ozone concentration should be closed to a constant in a continuous ozonation process, therefore the Eq. (1) can be modified as below:

$$\frac{d[BHA]}{dt} = -(k_0[O_3]_m + k'_{OH}[OH^-][O_3]_m)[BHA] \qquad (3)$$

where [O₃]ₘ is the modified ozone concentration in the solution. When the terms in the bracket $(k_0[O_3]_m + k'_{OH}[OH^-][O_3]_m)$ are all constants, the Eq. (3) can be simplified to

$$\frac{d[BHA]}{dt} = -k[BHA] \quad \text{or} \quad [BHA] = [BHA]_0 \, e^{-kt} \qquad (4)$$

where t is the reaction time, [BHA]₀ the initial BHA concentration and k is the overall pseudo-first-order rate constant. By cross examining the kinetic data of BHA decay, it was found that the BHA decay always followed pseudo-first-order kinetics no matter the NaCl was involved or not, so the assumption in deriving Eq. (4) is valid. As a result, the overall rate constant k is likely dominated by both the initial pH level and sodium chloride concentration.

3.2. Prediction of the NaCl suppressing-effect

To validate the dependency of the rate constants to the two proposed determining parameters, an analysis of the rate constants in terms of the pH and [NaCl] was conducted as shown in Figs. 3 and 4. These figures showed a precise linear correlation between k versus pH and k versus [NaCl]. This suggests that the pseudo-first-order rate constant can be predicted by a linear increment or reduction of either the pH level or the [NaCl] in the solution. In addition, all the correlations are parallel lines with non-zero intercepts on y-axis, while the trends declining and inclining with [NaCl] and pH level, respectively. Therefore, the combined effects can be simulated by using multiple-regression via a graphical approach and a general form of this model is defined below:

$$k = m_1(pH) + m_2[NaCl] + c \qquad (5)$$

By incorporating the y-intercepts from Figs. 3 and 4, the overall slopes (i.e. m_1 and m_2) and intercept (c) in Eq. (5) could be derived, as shown in Fig. 5. The linear model for pseudo-first-order rate constant for various pH and NaCl conditions,
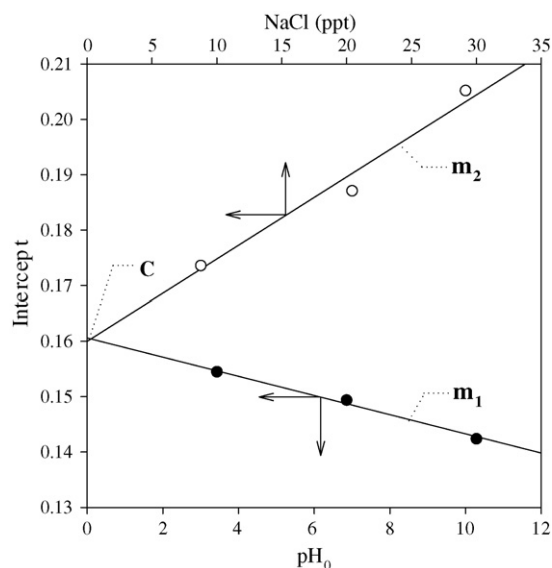
Fig. 5. A graphical approach to analyze the proposed linear model m_1 and m_2 are the slopes and c is the intercept for Eq. (5).
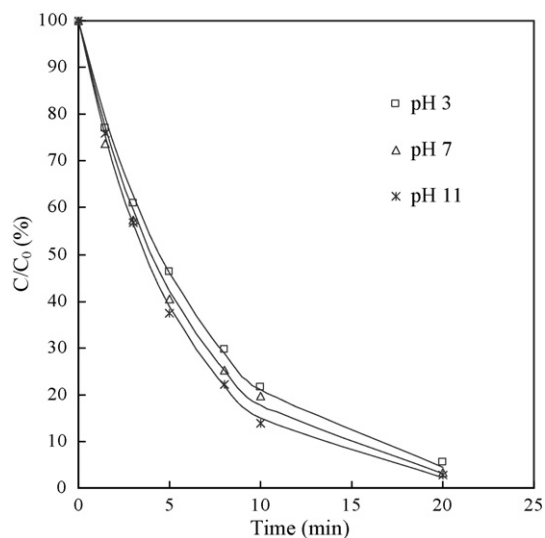

Fig. 6. A comparison of experimental data and predicted BHA decay curves using Eq. (7) at different pH levels (with addition of 30 ppt NaCl).

therefore, is derived:

$$k = 4.32 \times 10^{-3} \, (\text{pH}) - 5.94 \times 10^{-4} \, [\text{NaCl}] + 0.1606 \qquad (6)$$

The slopes (m_1 and m_2) are the weight coefficients of the initial pH and NaCl concentration, respectively. The positive and negative signs before the slopes indicate the overall k will increase and decrease with the pH and NaCl in the solution, which agrees with our observations. A common intercept (c) for correcting the two slopes was determined to be 0.1606 with a minimal error as indicated in Fig. 5. By substituting Eq. (6) into Eq. (4), the kinetic model in predicting the BHA decay at various pH levels and NaCl concentrations could be derived as follows:

$$[\text{BHA}] = [\text{BHA}]_0 \exp\{-4.32 \times 10^{-3} \, (\text{pH}) - 5.94$$
$$\times 10^{-4} \, [\text{NaCl}] + 0.1606)t\} \qquad (7)$$

Eq. (7) has been verified by the experimental data as shown in Fig. 6, where the predicted pseudo-first-order decay curves and the experimental data at different initial pH levels and NaCl concentrations fitted very well. This indicates that the proposed model is capable of predicting the decay of BHA through the proposed kinetic approach and the assumptions made in the derivation procedures are valid.

3.3. Effect of hydrogen peroxide concentration

Hydrogen peroxide was suggested as a ubiquitous compound present in natural waters at low levels generally ranging from 0.015 to 0.412 μM in seawater and 0.03–0.882 μM in fresh water [20]. According to a control test of applying 1 mM H_2O_2, see Fig. 2, the removal of BHA was very low (only 10% removal), which suggests the level of natural-occurring H_2O_2 is difficult initiate noticeable degradation of BHA.

Since hydrogen peroxide is not an effective oxidant for the removal of BHA, the use of H_2O_2 together with ozone could be a better alternative for the same purpose. H_2O_2 can be used

as the source in generating $OH^\bullet$ in the O_3/H_2O_2 process; however, it may also perform as a scavenger for hydroxyl radicals if overdosed. Hence it is critical to determine the optimal H_2O_2 concentration for application purpose.

Therefore ozonation process in the presence of H_2O_2 was investigated, and two typical BHA decay curves (with and without NaCl) were shown and compared with other processes at Fig. 2 (dotted lines). The degradation of BHA by using O_3/H_2O_2 still follows the pseudo-first-order decay kinetics, while O_3/H_2O_2 resulted in the fastest BHA decay among the other processes. The NaCl again can induced a suppression effect in the O_3/H_2O_2 process due to the consumption of ozone, which results in a ranking of the rates in the descending order of O_3/H_2O_2, O_3, $O_3/H_2O_2/Cl^-$, and O_3/Cl^-. Because the rate reduction due to the presence of NaCl is apparently not avoidable, it is suggested to lessen such an interfering effect of salt by improving the process performance through the adjustment of H_2O_2 dosage. To quantify the rate enhancing and/or retarding effects of adding H_2O_2 in the ozonation process, a typical case of the BHA degradation at pH 7 with and without 30 ppt NaCl was chosen for detail investigation so as to simulate the case of seawater using for flushing in Hong Kong.

The ozonation of BHA was therefore conducted at various H_2O_2 dosages ranging from 0.5 to 5.0 mM, and the variation of kinetics rate constants are illustrated at Fig. 7. It was noticed that both ozonation (i.e. without using H_2O_2) and O_3/H_2O_2 processes exhibited two distinct phases, no matter NaCl was involved or not. In general, an increment of rate was observed as $[H_2O_2]$ increased, but the rate would be retarded when the $[H_2O_2]$ was overdosed. It was interesting to note that the observed optimal dosages of H_2O_2 were different at 1.5 and 1.0 mM with a 99 and 97% removal of 0.2 mM BHA at 20 min for the case without and with NaCl, respectively.

The BHA decay rate improvement at lower $[H_2O_2]$ is simply due to the formation of more hydroxyl radical using H_2O_2 as the source (where hydroperoxide ions is the major promoter of the
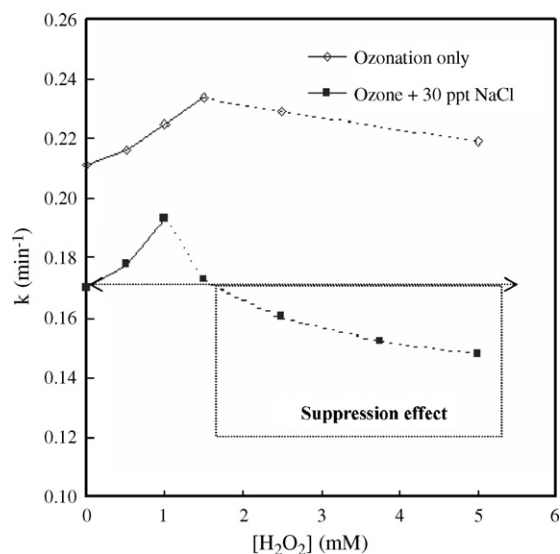
Fig. 7. The backward-shifting optimum H_2O_2 dosage via comparison of the decay rate constant of BHA ozonation with and without addition of NaCl at pH 7 (—); incremental stage; (- - -) retardation stage; the zone of suppression effect in dashed box).

chain reaction or via the dissociation reaction of O_3 to oxygen atom as the precursor of hydroxyl radical formation) as indicated in Eq. (8), detailed intermediate reaction can be found in other studies [16,21]:

$$2O_3 + H_2O_2 \rightarrow 2OH^\bullet + 3O_2 \quad (8)$$
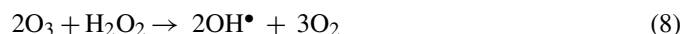
The reason causing the rate retardation ay higher [H_2O_2] is because the consumption of hydroxyl radical by H_2O_2, which forms weaker radicals (such as $HOO^\bullet$) in the solution [22,23]. This mechanism will become more significant if high [$OH^\bullet$] and [H_2O_2] are both present simultaneously, which reduces the effective level of both hydrogen peroxide and hydroxyl radical in the solution and, therefore, the decay rate of BHA. In addition, a slightly shifting of optimal [H_2O_2] to the lower side was observed in the presence of salt, which is likely due to the consumption of ozone by chloride ion as indicated in Eq. (2). Under these circumstances, the effective ozone concentration in the solution is lowered and results in a higher H_2O_2/O_3 ratio comparing to that without Cl^-. Because the free H_2O_2 not reacting to the ozone is relatively increased for the case with NaCl, the overdose of H_2O_2 shows up earlier at a lower dose.

In the $H_2O_2/O_3/Cl^-$ process, a significant reduction of all the rate constants than that of H_2O_2/O_3 process through out the tested H_2O_2 dosages was observed as expected, however, it is surprise to note a suppression effect, in which the addition of high dose of H_2O_2 results in a lower BHA decay rate than that without using H_2O_2 (see Fig. 7).

The chloride in the saline solution apparently not only consumes ozone but also reacts with hydroxyl radicals (Eqs. (9) and (10)), where the available hydroxyl radical for the oxidation of BHA will be largely reduced. In addition, other than the generation of weak $HOO^\bullet$ as indicated before, another weak oxidant Cl_2 will be generated in the system (the oxidation potential of ozone and chlorine is 2.08 and 1.36 V, respectively) [24] by con-

suming ozone via the reaction with hydroxyl radical. Because the overdose of H_2O_2 can induce faster generations of chlorine and $HOO^\bullet$ and results in lower ozone and hydroxyl radical concentrations in the solution, the overall oxidation capability of the system (and therefore the removal of BHA) is significantly reduced at higher H_2O_2 levels:

$$Cl^- + OH^\bullet \rightarrow Cl^\bullet + OH^- \quad (9)$$

$$Cl^- + Cl^\bullet \rightarrow Cl_2 + e^- \quad (10)$$

4. Conclusions

The ozonation of BHA with or without the presence of NaCl follows pseudo-first-order kinetics and it shows that ozonation is an effective approach to remove one typical EDC compound (BHA). The presence of NaCl in the solution reduces the efficiency of BHA degradation by ozonation in all the pH ranges. Kinetic study reveals that the reaction rate constant is dominated by NaCl concentration and initial pH level. A kinetic model was proposed and found feasible to be used in predicting BHA-contaminated wastewater at different salinity through such a kinetic approach.

In this study, H_2O_2-aided ozonation, as one of the advanced oxidation processes has shown its advantages in improving the removal efficiency of BHA, not only to the fresh water solution but also to the saline water. Optimum concentrations of hydrogen peroxide of 1.5 and 1.0 mM were observed for fresh and saline water systems, respectively, for a system of 0.024 mg O_3/mg BHA. The reactions of chloride to the ozone and hydroxyl radicals (that generated from either O_3 or O_3/H_2O_2) are the main reason to cause the retardation of BHA decay. However, the adverse effect of NaCl could be minimized by the addition of properly selected dose of hydrogen peroxide.

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