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Bromate Formation by the Oxidation of Bromide in the Electrochemically Activated Persulfate Process: Mechanism and Influencing Factors

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In this study, an electrochemically activated persulfate (EAP) process using boron-doped diamond (BDD) as the anode was adopted for the activation of peroxydisulfate (PDS) to treat bromide-containing water. In this EAP process, the activation of PDS to generate $SO_4^{\bullet-}$ is mainly caused by direct electron transfer at the cathode. The synergetic oxidation by the free radical oxidants, including OH• electrogenerated on the BDD anode and $SO_4^{\bullet-}$ produced on the cathode, is the major driving force to oxidize bromide to bromate through the continuous stepwise reaction. The cathodic reduction of high-valent bromine compounds coexisting in the EAP process could also affect the distribution of bromine by-products. The bromate formed in the EAP process decreased when humic acid coexisted in the bromide-containing water because the active bromine (Br• and HOBr) could react with organic matter to form brominated by-products. Bromate formation was increased with increasing PDS dosage, initial bromide concentration and current density. An acidic environment is beneficial for inhibiting the formation of bromate, but it might also increase the risk of formation of brominated by-products.

Keywords: persulfate; electrochemical activation, bromate formation; transformation of bromine

1. INTRODUCTION

In recent years, activated persulfate water treatment technology, one kind of advanced oxidation process (AOP) based on sulfate radicals ($SO_4^{\bullet-}$), has received extensive attention in the field of organic micro-polluted water treatment. Its essence is to break the peroxide bond of peroxydisulfate (PDS) or peroxymonosulfate (PMS) and produce $SO_4^{\bullet-}$ to oxidize the pollutants in water [1]. Because of its higher solubility, lower dissociation energy of peroxide bonds, and lower price, PDS is more favoured than PMS in the selection of activated precursors [2]. To date, many activation methods have been verified by researchers, such as thermal activation, photoactivation, and transition metal ion activation [3-5]. Electrochemical methods, which have the advantages of ease of control and environmental compatibility, have also been tested to activate PDS for water treatment [6].

When the electrochemically activated persulfate (EAP) process was used in water treatment, the electrodes could be set in situ in polluted water mixed with PDS. On the one hand, the electrode can exert its own electrochemical oxidation and reduction effects; on the other hand, it can activate PDS continuously and controllably to produce $SO_4^{\bullet-}$ for the synergetic degradation of pollutants [2]. Compared with the iron anode, which has the disadvantage of producing Fe^{3+} precipitates, a boron-doped diamond (BDD) anode that does not generate waste and has a strong corrosion resistance has been used for the electrochemical activation process.

The BDD electrode is well known as an electrocatalytic oxidation anode in the field of water treatment. Boron-doped diamond thin films with excellent conductivity and stability on the electrode surface can efficiently produce physically adsorbed OH• to oxidize pollutants unselectively [7]. At present, different mechanisms of the electrochemical activation of persulfate using an electrode system consisting of a BDD anode have been proposed. Although the activation process on the cathode, in which PDS can accept electrons directly to transfer to $SO_4^{\bullet-}$ (Eq. 1), is widely recognized, researchers have different opinions on the activation process on anodes. Bu et al. [8] suggested that PDS could react with the OH• produced on the BDD anode to generate superoxide and singlet oxygen. Farhat et al. [6][9] stated that the mechanism of electrochemical activation of PDS at a BDD anode might be similar to the mechanism of activation of PDS by a carbon material. Song et al. [10] proposed that there may be several simultaneous effects on the BDD surface in the process of electrochemical activation of PDS; the electrochemically activated PDS molecule (PDS*), electrogenerated OH•, direct electron transfer (DET), and electrogenerated $O_2^{\bullet-}$ contributed to the degradation of organic matter. Although there are different views of the activation mechanism on the BDD anode, it is certain that, unlike the electrochemical AOPs based on OH• and other activated persulfate AOPs based on $SO_4^{\bullet-}$ (such as thermal and photoactivation), the EAP process using the electrode system consisting of the BDD anode is a typical composite AOP of OH• and $SO_4^{\bullet-}$. When this type of composite AOP is applied to treat water containing bromide (Br^-), there will also be a high risk of formation of the by-product bromate (BrO_3^-).

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{\bullet-} + SO_4^{2-} \qquad (1)$$

Since the International Agency for Research on Cancer (IARC) listed bromate as a potential carcinogen in 1990, the formation of BrO_3^- during the treatment of bromide-containing water has attracted considerable attention. It is generally believed that bromide (0.01 mg/L ~1.0 mg/L), the precursor of bromine by-products and widely present in natural water bodies, is not harmful to the human body. However, it is easily oxidized by strong oxidants to form active bromine (Br•, $Br_2^{\bullet-}$, HOBr/OBr^-, etc.) in the process of water treatment, especially the process of AOPs. These bromine intermediates may be further oxidized to form the inorganic by-product bromate (BrO_3^-) and easily react with natural organic matter (NOM) common in raw water to produce brominated by-products. Moreover, once these by-products are formed, it is difficult to remove them from the water in subsequent processes, which greatly increases the cost of water treatment. Therefore, for the EAP process using the BDD anode with great application potential, it is necessary to study the formation mechanism of BrO_3^- and the transformation characteristics of bromine by-products before its scale application. In the existing literature, there have been many studies on bromate formation by AOPs based on single OH• or $SO_4^{\bullet-}$ [7, 11]. However, a similar topic has not been discussed in detail in the EAP process of composite free radicals.

In this study, an EAP process was established consisting of a BDD anode and a Ti cathode. Sodium peroxydisulfate (PDS) was chosen as the activation precursor, and the synthetic bromide solution was used as the reaction target. Based on the results of electrochemical behaviour characterization, electron spin resonance measurements, and free radical quenching experiments, the mechanism of BrO_3^- formation in the EAP process was analysed. By monitoring the concentration distribution of the main bromine by-products, the transformation process of bromine in the EAP process was investigated. The effects of operating conditions, including the dose of PDS, the initial Br^- concentration, the initial pH, the current density, and co-existent NOM, on BrO_3^- formation were discussed. The experimental results will provide a theoretical reference for the application of the EAP process in the field of micro-polluted water treatment.

2. MATERIALS AND METHODS

2.1. Chemicals

Synthetic bromide-containing water was prepared with analytically pure potassium bromide (KBr) from Tianli (Tianjin, China) and ultrapure water (conductivity ≥ 18.25 $M\Omega cm^{-1}$). Sodium peroxydisulfate ($Na_2S_2O_8$, PDS), purchased from Aladdin (Shanghai, China), was used to obtain and activate $SO_4^{\bullet-}$. All the other chemicals used in this study were analytical grade and utilized without further purification, and all aqueous solutions were prepared with ultra-pure water.

2.2. Experimental setup and procedures

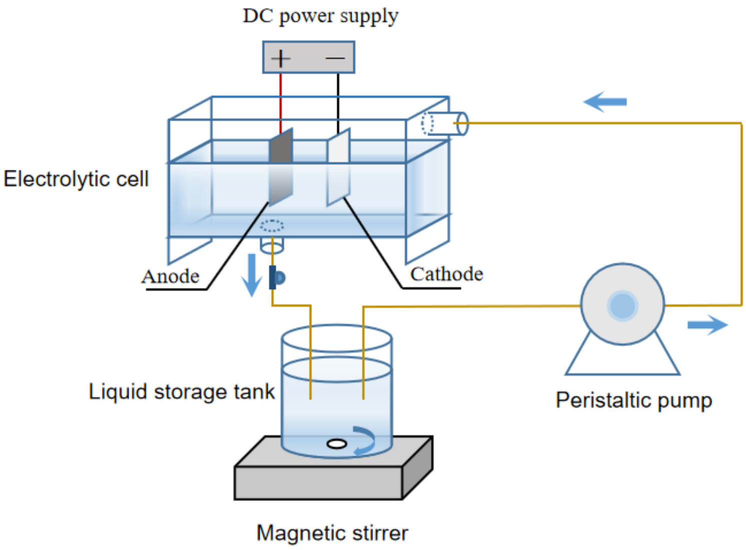

Figure 1. Schematic diagram of single-cell experimental setup

The electrochemical activation experiments were carried out in the continuous single-cell device shown in Fig. 1. A homemade organic glass reactor (14 cm × 5 cm × 10 cm) was used as the main reactor, and a 1 L beaker was used as a liquid storage container. A peristaltic pump was adopted to circulate the solution between the reactor and the liquid storage container at a specific flow rate. A BDD electrode (25 mm × 50 mm, Neo-Coat, Swiss) was chosen as the anode, and a Ti plate (25 mm × 50 mm, TJaida, China) was chosen as the cathode. The immersion area of both the anode and cathode was 10 cm^2, and the electrode distance was 1.5 cm. During the experiment, a DC potentiostat (Atten, voltage range 0-30 V, current range 0-5 A) was employed as the power supply.

In each experiment, 1 L of a bromide solution was used to simulate the bromide-containing water, and a certain amount of PDS was added. Sodium perchlorate (700 mg/L; $NaClO_4$) was used in all experiments as the supporting electrolyte to maintain the necessary conductivity. Samples were collected at regular time intervals and then subjected to BrO_3^-, Br^- and HOBr/OBr^- analysis. The analysis of BrO_3^- quenched using excessive sodium nitrite at a nitrite-to-persulfate dose ratio of approximately 3:1 [12]. All analyses were conducted in triplicate, and the results were reported as the mean and standard deviation.

To determine the mechanism of BrO_3^- formation in the EAP process, the electrochemical behaviour of the substances in the solution was characterized by cyclic voltammetry (CV). To discern the reactive species generated in the EAP process, the presence of free radicals was directly detected by electron spin resonance (ESR), and the contribution of different free radicals to the synergetic oxidation was evaluated by degradation of a radical probe (carbamazepine, CBZ) with radical scavenging (methanol or tert-butanol). The radical quenching experiments were carried out in the split-cell reactor. The split-cell reactor was divided by a cation exchange membrane (Nafion115), and the effective volumes of the anode and cathode chamber were both 100 mL; an anolyte and a catholyte with the same composition were circulated between the respective electrode chamber and liquid storage tank by a dual-channel peristaltic pump. During the quenching experiment, samples were taken every 10 min, and the concentration of CBZ was analysed immediately.

To investigate the effect of operating parameters on the formation of BrO_3^-, single factor experiments were carried out. The parameters, including PDS dose (0.1-20 mM), Br^- concentration (0.1-2.0 mg/L), current density (5-100 mA/cm^2) and initial pH (3.0-11.0), were varied one parameter at a time while the others were kept constant. During the experiment, the initial pH of the solution was adjusted using acetic acid (0.1 M) and sodium hydroxide (0.1 M) solutions. To study the effect of coexisting NOM on BrO_3^- formation, 3.0 mg/L humic acid (as TOC, HA) was added to the synthetic solution; the concentrations of the main brominated by-products (including Br-THMs and Br-HAAs) were measured, and the total amount of inorganic bromine (TIBr) was calculated by summarizing the molar concentrations of Br^-, HOBr/OBr^- and BrO_3^-.

2.3. Analytical Methods

Bromate was quantified by an ion chromatograph (IC, CIC-D120, SHINE, China) equipped with a conductivity detector and continuous automatic regenerated microfilm anion suppressor; the mixed eluent of 2.0 mM Na_2CO_3 and 8.0 mM $NaHCO_3$ was used with a flow rate of 1 mL/min. The samples were filtered through a 0.2 μm filter before injection. The concentration of Br^- was determined by a spectrophotometric method in the presence of phenolsulfonphthalein [13]. The $HOBr/OBr^-$ concentration was identified using DPD spectrophotometry [11]. The formation of Br-THMs and Br-HAAs was analysed according to Chinese standard methods HJ620-2011 [14] and HJ758-2015 [15], respectively, using a GC-4000A gas chromatograph (GC, EWAI, China) equipped with an electron capture detector and KB-1701 capillary column (30 m × 0.53 mm × 1.5 μm film thickness). The Br-THM samples were injected with an automatic headspace sampler; Br-HAAs were concentrated by liquid-liquid extraction using MTBE and methylated with 10% sulfuric acid in methanol.

High-performance liquid chromatograph (HPLC, LC100, Wufeng, China) equipped with a UV detector (operating at 286 nm) and C18 column (ID = 4.6 mm, length = 150 mm) was used to analyse the concentration of CBZ. The measurement was performed with a mobile phase of methanol/acetonitrile = 6/4 (v/v) at a flow rate of 0.8 mL/min.

The cyclic voltammetry (CV) curve of the electrode was recorded by a CHI600 electrochemical workstation (CH instruments, China). A three-electrode system was used, in which the BDD anode and Ti cathode were alternately used as the working and auxiliary electrodes, and the saturation mercury electrode (SCE) was used as the reference electrode. Before the electrochemical measurement, dissolved oxygen was removed by purging with N_2 gas.

In the ESR measurement, an electron paramagnetic resonance spectrometer (EMXPLUS10/12, Bruker, Germany) was employed. The microwave power was 20 mW, the modulation frequency was 100 kHz, the centre field was 3510.00 G, the scan width was 100.0 G, the scanning time was 60 s, and the gain was 30 dB. DMPO (5.5 dimethyl-1-pyrroline-N-oxide) was chosen as the free radical trapping agent, and the final concentration of DMPO was 200 mM.

3. RESULTS AND DISCUSSION

3.1. Bromate formation mechanism

3.1.1 Analysis of electrochemical behaviour in the EAP process

To explain the formation mechanism of BrO_3^- in the EAP process, the electrochemical behaviour of the main substances in the bulk solution on the surface of the anode and cathode was investigated. As a typical non-active electrode, the BDD anode has a weak ability for direct oxidation on the surface and can produce physical-adsorption state OH• more efficiently by water dissociation (Eq. 2) [10]. Fig. 2 shows that when either Br^- or PDS was added to the electrolyte, no obvious direct oxidation peaks were observed during scanning from 0.5 V to 2.5 V compared with the CV curve without coexisting substances. This indicates that the transformation of Br^- could be caused by indirect oxidation of the active substances in the EAP process, and that the activation of PDS is also not achieved by anodic direct electron transfer.

$$\mathrm{BDD} + \mathrm{H_2O} \rightarrow \mathrm{BDD(OH\bullet)} + \mathrm{H^+} + \mathrm{e^-} \qquad (2)$$

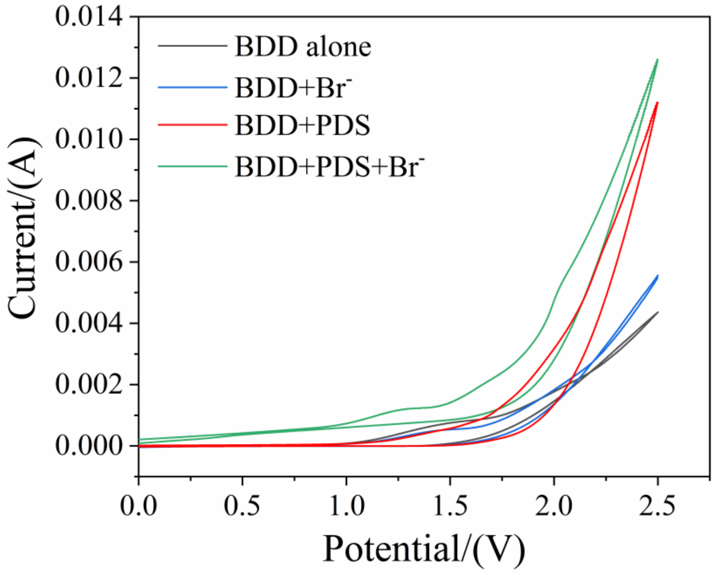

Figure 2. Cyclic voltammetry curve of the BDD electrode. Reaction conditions: [$NaClO_4$] = 2 mM, [Br^-] = 1 mg/L, [PDS] = 5 mM.

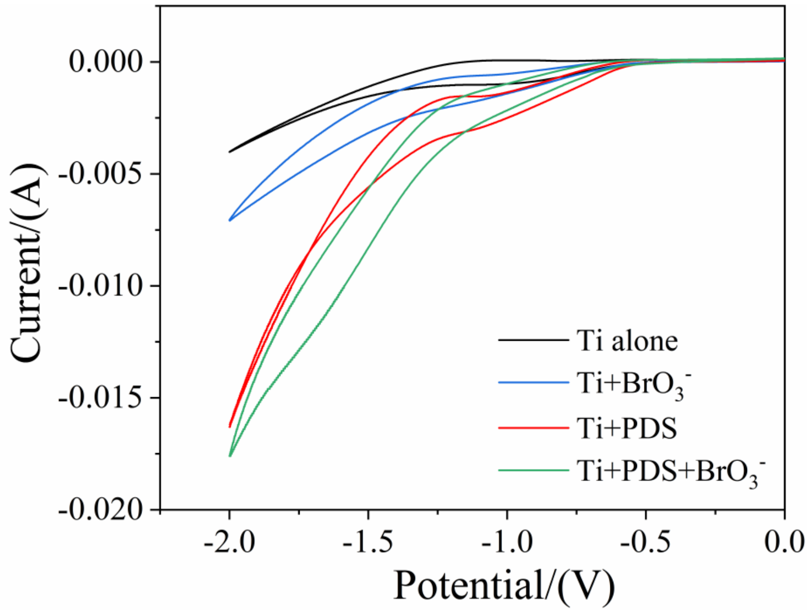

Figure 3. Cyclic voltammetry curve of the Ti electrode. Reaction conditions: [$NaClO_4$] = 2 mM, [BrO_3^-] = 1 mg/L, [PDS] = 5 mM.

As shown in Fig. 3, a Ti cathode was used as the working electrode, and CV scanning was performed in the range of 0 V to -2 V. In the base electrolyte, the main observed processes are the onset of water electrolysis to produce hydrogen at approximately -1.4 V to -1.7 V. When PDS was added, the response current increased significantly between -0.5 V to -1.25 V (red curve). This indicates that PDS probably underwent a reduction reaction on the Ti electrode surface. This is consistent with the recognized mechanism that $SO_4^{\bullet-}$ could be generated by PDS activation at the cathode (Eq. 1) [16]. Unlike in other PDS activation methods, the conversion of the bromine element in the EAP process could also be affected by the coexisting cathodic reduction. The addition of BrO_3^- made the current at -1.0 V to -1.40 V very low and gave rise to rather broad waves extending from -1.4 V to -2.0 V (green curve). Bromate could be converted to a low-value state through direct electron transfer at the cathode [17]. It is worth noting that when BrO_3^- coexists with PDS, the reduction peak of PDS appears to be weakened, indicating that BrO_3^- reduction may compete with PDS activation for cathode electrons.

It could be inferred based on the analysis of CV curves that in the EAP process consisting of the BDD anode, except for the cathodic DET, the active species produced in the bulk solution, such as OH• and $SO_4^{\bullet -}$, should play an important role in the transformation of bromine.

3.1.2 Estimation of active species in the EAP process

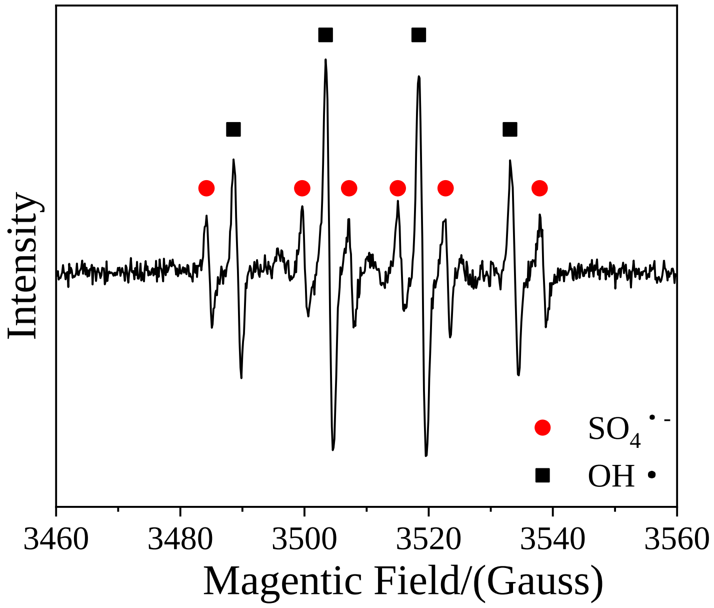

Figure 4. ESR atlas of free radicals generated during the EAP process in a single-cell reactor; reaction conditions: [PDS]/[DMPO] = 1/40, t = 5 min, pH = 7, [PDS] = 5 mM, [$NaClO_4$] = 700 mg/L, *I* = 20 mA/cm^2, T = 30±2°C.

To identify the primary free radicals generated in the EAP process, ESR experiments were carried out. Fig. 4 shows the main free radical adduct signals captured in the EAP process. The obvious quadruplet with a peak height ratio of 1/2/2/1 represents the DMPO-OH• adduct of the trapping agent DMPO and OH• (α (N) = α (H) = 14.9 G). The lower six peaks represent the DMPO-$SO_4^{\bullet -}$ adduct of DMPO and $SO_4^{\bullet -}$ (α(N) = 13.2 G, α(H) = 9.6 G, α(H) = 1.48 G, α(H) = 0.78 G). The results illustrate that both $SO_4^{\bullet -}$ and OH• exist in bulk solution, and the EAP process is indeed a typical composite AOP of OH• and $SO_4^{\bullet -}$. Determined roughly through the peak height of the two groups, the ratio of OH• in mixed free radical active species was significantly higher than that of $SO_4^{\bullet -}$. To further estimate the contribution of $SO_4^{\bullet -}$ and OH• in mixed oxidants, free radical scavenging experiments were conducted.

Methanol (MeOH) is a commonly used quencher of $SO_4^{\bullet-}$ and OH• ($k_{MeOH\text{-}SO_4^{\bullet-}} = 1.23 \times 10^7\ M^{-1}s^{-1}$, $k_{MeOH\text{-}OH\bullet} = 2.8 \times 10^8\ M^{-1}s^{-1}$ [18]), and tert-butanol (TBA) is a unique quencher of OH• ($k_{TBA\text{-}OH\bullet} = 6.0 \times 10^8\ M^{-1}s^{-1}$, $k_{TBA\text{-}SO_4^{\bullet-}} = 2.0 \times 10^6\ M^{-1}s^{-1}$ [19]). In the EAP process, a large amount of OH• will be appended to the electrode plate. A low concentration of quenching agent cannot quench the OH• completely. To ensure that the results are closer to reality, excess MeOH or TBA was added, and the quenching effects were approximately equal to the effects of pure MeOH or TBA [10].

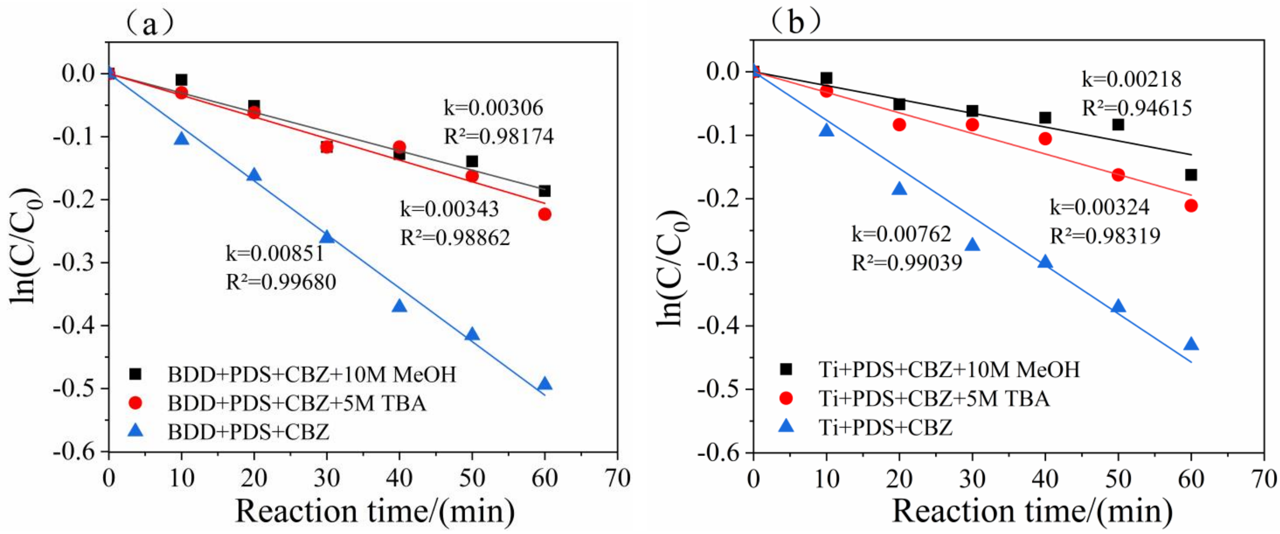

Figure 5. Effect of the addition of free radical scavenging agents (TBA and MeOH) on the degradation of CBZ in a split-cell reactor. (a) BDD anode, (b) Ti cathode. Reaction conditions: pH=7, [PDS] = 5 mM, [CBZ] = 0.01 g/L, I = 20 mA/cm^2, T = 30 ±2 °C.

Quenching experiments of CBZ degradation were carried out in the anode chamber and cathode chamber of the split-cell reactor. It is worth noting that, in Fig. 5(a), the inhibitory effect of 10 M MeOH on the degradation of CBZ (0.00306 min^{-1}) was close to that of 5 M TBA (0.00343 min^{-1}). Because the anode chamber is in an acidic environment, it is not conducive to the rapid conversion of $SO_4^{\bullet-}$ to OH• (Eq. 3 and 4) [20]. Therefore, this result indicates that the activation of PDS probably does not occur at the BDD anode, or at least the reaction rate is slow. Many researchers believe that PDS may have an excited transition form (PDS*) during anodic discharge, which also has high oxidation ability. PDS* might be generated on the surface of BDD anodes for non-free-radical oxidation, which could promote the anodic oxidation effect to a certain extent [10].

$$SO_4^{\bullet-} + H_2O \rightarrow H^+ + OH\bullet + SO_4^{2-} \qquad (k < 60\ M^{-1}s^{-1},\ pH=7) \tag{3}$$

$$SO_4^{\bullet-} + OH^- \rightarrow OH\bullet + SO_4^{2-} \qquad (k = 7.3 \times 10^7\ M^{-1}s^{-1},\ alk.) \tag{4}$$

In the cathode chamber (Fig. 5(b)), the inhibition effect of MeOH on CBZ degradation (0.00218 min^{-1}) was significantly higher than that of TBA (0.00324 min^{-1}), which verified the theory that PDS could receive electrons on the cathode and be activated to $SO_4^{\bullet-}$ (Eq. 1). In addition, according to the inhibition of TBA addition on CBZ degradation, it could be proven that a certain amount of OH• is also produced in the cathode system. This OH• is likely to be generated by sulfate radical conversion in an alkaline environment (Eq. 4).

Therefore, based on the above analysis, the transformation of bromine in the EAP process is expected to be mainly the result of the interaction of OH• and $SO_4^{\bullet-}$, and the production of $SO_4^{\bullet-}$ is caused by the cathodic electroactivation of PDS.

3.1.3 Transformation of bromine and formation of BrO_3^-

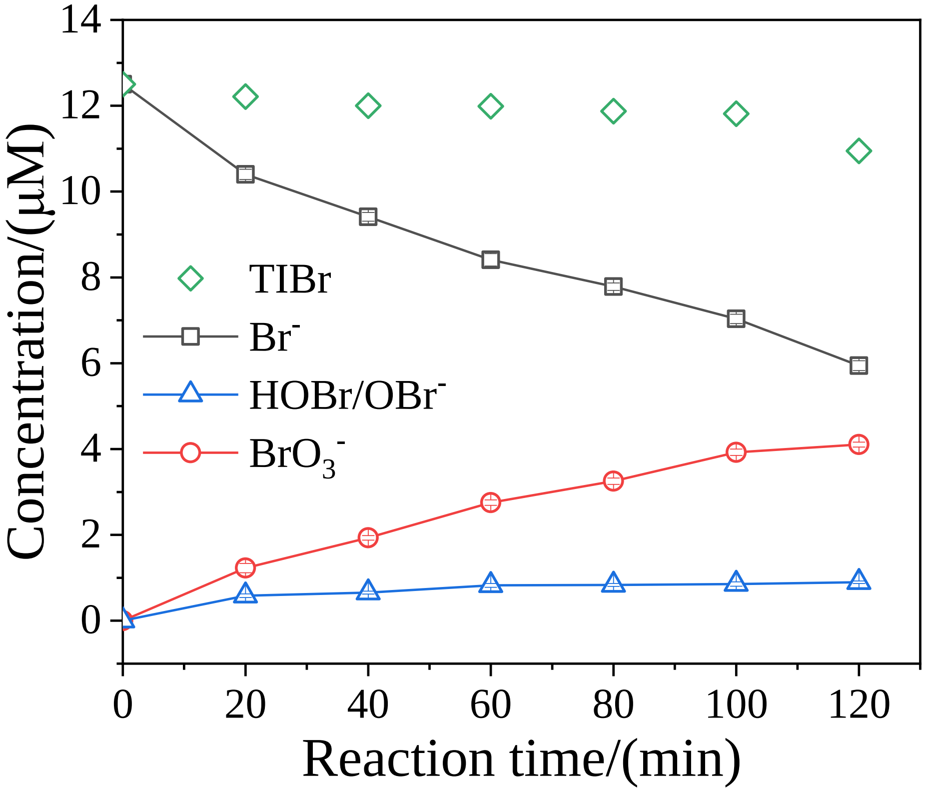

Figure 6. Variation of bromine species during the oxidizing of Br^- by the EAP process. Reaction conditions: pH = 7.0, $[Br^-]_0$ = 1.0 mg/L, $[PDS]_0$ = 5 mM, $[NaClO_4]$ = 700 mg/L and I = 20 mA/cm^2, T = 30 ± 2 °C.

Fig. 6 shows the monitoring of the concentration of inorganic bromine during the EAP process. During the EAP reaction, the concentration of Br^- decreased continuously, and the formation of $HOBr/OBr^-$ and BrO_3^- was found in the solution. After formation in the early stage of the reaction, the concentration of $HOBr/OBr^-$ remained relatively stable, and the concentration of BrO_3^- continued to increase during the reaction.

By calculating the total molar concentrations of Br^-, $HOBr/OBr^-$ and BrO_3^- in the solution, it was found that the TIBr remained substantially constant during the EAP process. It could be inferred that, similar to the formation of BrO_3^- by only OH• or $SO_4^{\bullet-}$, in the EAP process, Br^- could be oxidized by active substances, such as OH•, $SO_4^{\bullet-}$ and Br•, generating BrO_3^- via $HOBr/OBr^-$ [11]. The unstable intermediate forms, such as Br_2^-, BrO•, and BrO_2^-, should also be formed during the reaction, but they did not show concentration accumulation. It is confirmed in the literature [21] that in the pH range related to water treatment, the intermediate form of bromine is mainly HOBr/OBr, and its concentration is at least 5 orders of magnitude higher than that of other active bromine species. Different from other types of PDS activation processes, the simultaneous cathodic reduction existing in the EAP process could also change the concentration distribution of bromine by-products. The high-valent inorganic bromine compounds that diffuse to the cathode, such as BrO_3^- and $HOBr/OBr^-$, can also accept electrons at the cathode and undergo a stepwise reduction to produce low-valent inorganic bromine products [17]. Therefore, the concentrations of bromine compounds detected during the EAP process are the result of the multiple effects of forward oxidation and reverse reduction. In the previous AOP process [22], the UV/H_2O_2 process is also a redox process. Under the condition of excessive H_2O_2, OH• is generated. OH• oxidizes Br^- to HOBr, and then HOBr is reduced back to Br^- by H_2O_2. This process can adequately inhibit the formation of the disinfection by-product BrO_3^-, but excessive H_2O_2 easily causes secondary pollution, which is always a defect that cannot be ignored. Therefore, from the perspective of suppressing by-products, the electroactivated PDS system can improve the oxidation efficiency while using cathode reduction to non-toxically suppress the generation of by-products.

According to previous research, when organic substances coexist in solution, such as the widely existing NOM, HOBr and Br· may enter the molecular structure of the brominated by-products through addition or substitution effects and play a key role in the transformation from inorganic to organic. The brominated by-products may also be mineralized by oxidants produced in the EAP process, causing organic bromine to be converted into inorganic compounds again. A possible mechanism of BrO_3^- formation and transformation of bromine by-products in the EAP process is summarized as follows.

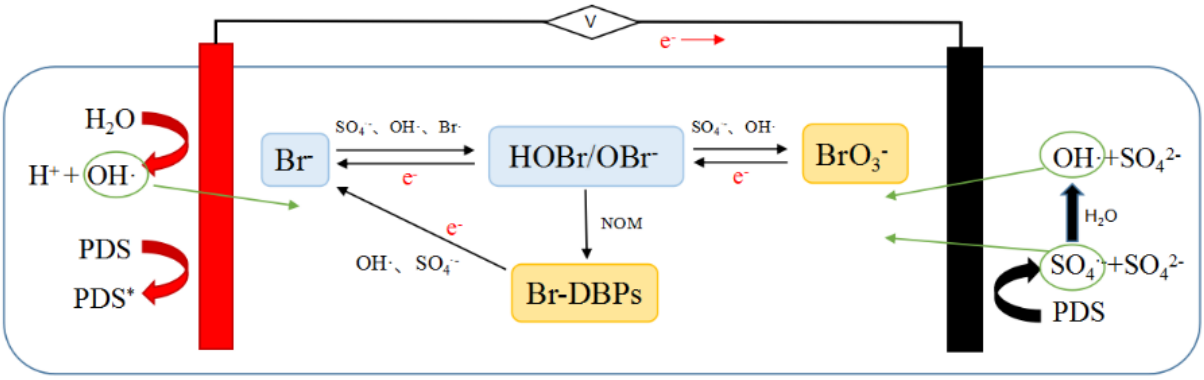

Figure 7. Possible mechanism of BrO_3^- formation and transformation of bromine by-products in the EAP process

3.2. Effects of operating conditions on BrO_3^- formation

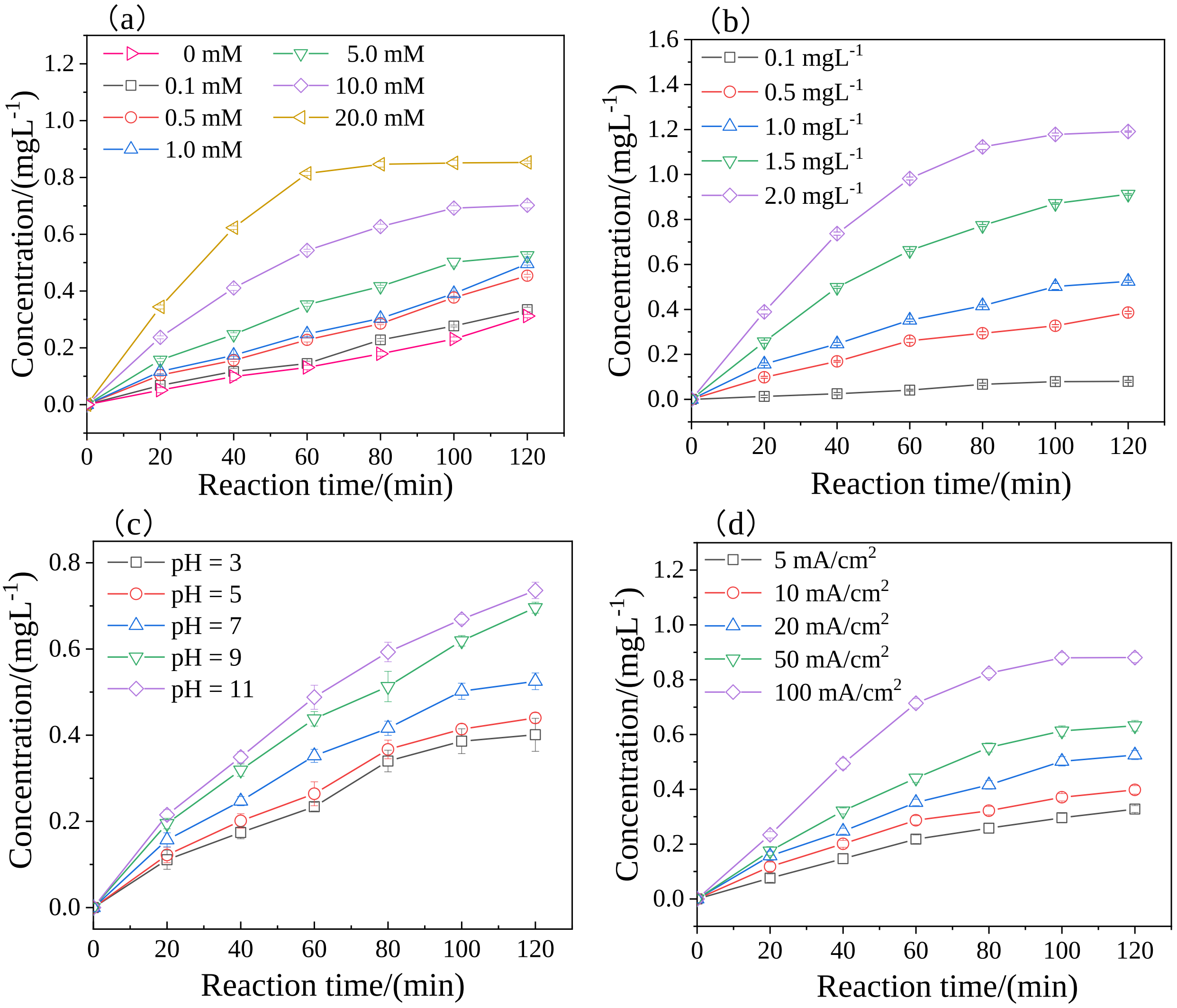

Figure 8. Effects of PDS dose (a), initial Br^- concentration (b), initial pH (c) and current density (d) on bromate formation in the EAP process. Reaction conditions: (a) pH = 7.0, $[Br]_0$ = 1.0 mg/L and I = 20 mA/cm^2; (b) pH = 7.0, [PDS] = 5 mM and I = 20 mA/cm^2; (c) $[Br^-]_0$ = 1.0 mg/L, [PDS] = 5 mM and I = 20 mA/cm^2; (d) pH = 7.0, $[Br^-]_0$ = 1.0 mg/L and [PDS] = 5 mM, T = 30 ±2 °C.

3.2.1 Effect of applied PDS dose

PDS is the precursor of $SO_4^{\bullet-}$ in the EAP process, and the dose of PDS is also an important parameter used to regulate the oxidation performance in practical applications. Fig. 8(a) describes the effect of PDS dose (0-20 mM) on BrO_3^- formation in the EAP process. Regardless of whether PDS was added, the concentration of BrO_3^- in solution increased gradually during the reaction, and the generation rate of BrO_3^- increased with increasing PDS dose. When PDS was not added, after 120 min of electrolysis, the concentration of BrO_3^- formed by the electrochemical-only process was only 0.312 mg/L. Upon increasing the PDS dose from 0.1 mM to 20 mM, the production of BrO_3^- was 0.335 mg/L, 0.454 mg/L, 0.496 mg/L, 0.525 mg/L, 0.702 mg/L and 0.853 mg/L. When the PDS dose was less than

1 mM, the generation rate of BrO_3^- increased slightly; when the dose was higher than 1 mM, the generation of BrO_3^- was accelerated significantly. In the UV/persulfate process, where sulfate radicals are the main active substances [12], the lag phase observed under low persulfate conditions occurs because sufficient $SO_4^{\bullet-}$ exposure is required to convert bromide to bromic acid salt, and no bromate is formed when the $SO_4^{\bullet-}$ exposure is insufficient. In the EAP process, no similar lag phase was observed. This is because in addition to $SO_4^{\bullet-}$, the process also has electrogenerated OH•, and there is no phenomenon of insufficient free radical exposure.

An increase in the PDS dose increases the yield of $SO_4^{\bullet-}$ in the EAP process, thereby increasing the total amount of free radical oxidants that could oxidize Br^- in the solution so that the final concentrations of BrO_3^- were increased gradually. However, PDS itself can also react with $SO_4^{\bullet-}$ and OH• in the process (Eqs. 5 and 6) [23]. Therefore, with an increase in the amount of PDS, PDS will play a greater competitive role for active species, which will reduce the oxidation efficiency, and the rate of BrO_3^- generation will gradually decrease.

$$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow S_2O_8^{\bullet-} + SO_4^{2-} \qquad (k = 6.1 \times 10^5\ M^{-1}s^{-1}) \qquad (5)$$

$$OH\bullet + S_2O_8^{2-} \rightarrow S_2O_8^{\bullet-} \qquad (k = 1.2 \times 10^7\ M^{-1}s^{-1}) \qquad (6)$$

3.2.2 Effect of initial Br^- concentration

Generally, the concentration of Br^- in natural water is in the range of 0.01 to 1 mg/L. When the Br^- concentration is less than 0.02 mg/L, Br^- will not be converted to BrO_3^-; however, when the concentration exceeds 0.1 mg/L, the formation of BrO_3^- should be substantial [24]. The effects of different initial Br^- concentrations (0.1-2.0 mg/L) on BrO_3^- formation are shown in Fig. 8(b).

When $[Br]_0$ was 0.1 mg/L, the BrO_3^- concentration in the solution was 0.08 mg/L after 120 min of EAP treatment. BrO_3^- production increased with increasing initial Br^- concentration from 0.1 mg/L to 2.0 mg/L. When the amount of active species in the EAP process remains stable, the increase in the Br^- concentration in the reaction substrate will promote the generation rate of BrO_3^-. In the same reaction time, the higher the initial Br^- concentration is, the stronger the formation potential of high-valent bromine inorganic by-products may be. This is consistent with the conclusion mentioned in the literature [25] that a higher bromide concentration will increase the chance of the active material reacting with bromide ions at or near the anode surface. Therefore, when the EAP process is adopted to treat bromide-containing water, it is necessary to pay more attention to the initial concentration of Br^-; it is necessary to reduce the concentration level of Br^- in the raw water to control the formation of BrO_3^-.

3.2.3 Effect of pH levels

Fig. 8(c) depicts the effects of initial pH on the formation of BrO_3^- during the EAP process. As the pH increased from approximately 3.0 to 11.0, after 120 min of reaction, the amount of BrO_3^- in the solution increased gradually from 0.401 mg/L to 0.736 mg/L. Overall, the acidic environment was beneficial to the inhibition of BrO_3^- formation in the EAP process.

The pH of the solution is one of the key factors affecting the distribution of $SO_4^{\bullet -}$ and OH• in the total active species in the EAP process. In an alkaline environment, an increase in OH^- promoted the formation of OH• on the BDD anode; additionally, the $SO_4^{\bullet -}$ generated by cathodic activation were converted into OH• (Eq. 4), whose reaction rate with Br^- (10^{10} $M^{-1}s^{-1}$) is approximately 2.85 times faster than that of $SO_4^{\bullet -}$ (3.5×10^9 $M^{-1}s^{-1}$). This may increase the oxidation rate of Br^- to BrO_3^- in the EAP process.

When the pH was strongly acidic, the $SO_4^{\bullet -}$ radicals generated by electrochemical activation were more likely to react with each other quickly to produce $S_2O_8^{2-}$ (Eq. 7) [23] and reduced the concentration of active radicals in the EAP process. At the same time, the reduction of BrO_3^- to Br^- on the surface of the cathode could be improved [26]; this is also one of the reasons for the lower formation of BrO_3^- under acidic conditions**.**

$$SO_4^{\bullet -} + SO_4^{\bullet -} \rightarrow S_2O_8^{2-} \qquad (k = 8.1 \times 10^8\ M^{-1}s^{-1},\ pH = 5.8) \quad (7)$$

In addition, it should be noted that the change in pH could affect the form of HOBr/OBr^-. It is generally believed that the reaction of HOBr molecules with organic matter is the key step in the conversion of inorganic bromine to organic bromine. Therefore, when the pH is lower than the dissociation constant of HOBr (p*K*a = 8.7 at 25 °C [27]), especially in the superacid range, more +1-valent bromine is present as the HOBr molecule, which might also increase the generation probability of brominated by-products with higher toxicity.

3.2.4 Effect of current density

In the EAP process, the electric current acts as the driving force for active substance formation. The current densities applied on the electrodes have a significant influence on the yield of active species, which also affects the formation of BrO_3^- by-products during the reaction. Fig. 8(d) depicts the effects of current density (5-100 mA/cm^2) on the amount of BrO_3^- produced in the EAP process. With increasing current density, the concentrations of BrO_3^- after 120 min of EAP treatment were 0.157 mg/L, 0.247 mg/L, 0.352 mg/L, 0.416 mg/L, 0.502 mg/L, and 0.525 mg/L.

Theoretically, the higher the current density applied, the more current passes through the electrode per unit area, and the more active species (including OH• on the anode and $SO_4^{\bullet -}$ on the cathode) are expected to be produced in the EAP process. Increasing the current density will be beneficial to the degradation of pollutants in water; however, higher oxidant production in the process also increases the formation probability of BrO_3^- by-products. In addition, there are studies [28] proving that when the current density is relatively high, bromate may continue to be oxidized to form perbromate. This is one of the reasons why the concentration of bromate is decreased after the current density increases to a certain degree. At the same time, the higher voltage caused by the higher current density will also make both the anodic and cathodic side reactions more intense. Therefore, in practical applications, the current efficiency of pollutant degradation and the amounts of by-products generated should be considered together to reasonably determine the applied current density.

3.3. Effect of coexisting NOM

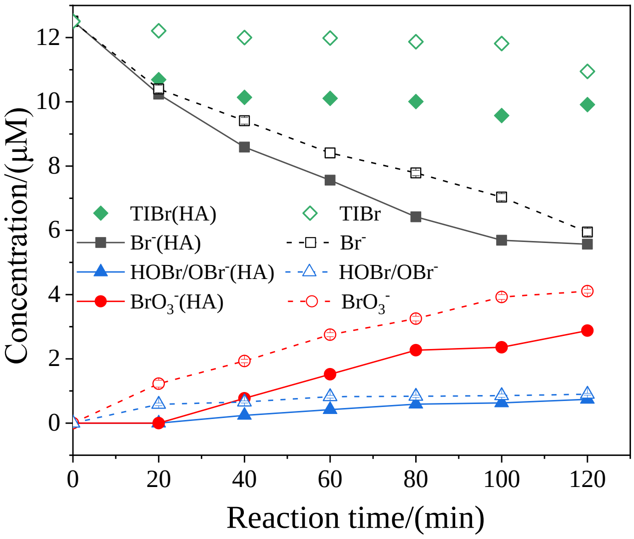

Figure 9. The variation in Br^-, $HOBr/OBr^-$, BrO_3^- and TIBr with time in the presence or absence of HA. Reaction conditions: pH=7, $[Br^-]_0$ = 1.0 mg/L, $[HA]_0$ = 3.0 mg/L (as TOC), [PDS] = 5 mM and I = 20 mA/cm^2, T = 30 ±2 °C.

According to the proposed transformation mechanism of the bromine by-products (shown in Fig. 8), when the EAP process is used to treat micro-polluted bromide-containing water in which organic substances coexist, there is a possibility of producing brominated by-products. The presence of organic matter will affect the distribution of bromine inorganic by-products. Humic acid, a common organic matter in natural water, was mixed with synthetic bromide-containing water to simulate coexisting organic matter, and the change in the concentrations of the main inorganic bromine compounds in the presence of HA was investigated (Fig. 9).

Compared with the absence of HA, in the presence of HA, the Br^- concentration in the solution decreased faster during the EAP process, especially in the first 100 min; after 100 min, the decreasing rate of Br^- concentration became slower. After 120 min of EAP treatment, the Br^- concentration decreased to 0.437 mg/L (5.47 μM). With decreasing Br^-, the concentrations of $HOBr/OBr^-$ and BrO_3^- in the solution showed an increasing trend; at 120 min, the concentrations were 0.071 mg/L (0.74 μM) and 0.483 mg/L (3.78 μM), respectively. Both of these values are lower than those in the absence of HA (0.086 mg/L and 0.525 mg/L). As seen by analysing the sum of the molar concentrations of the three major inorganic bromine compounds, different from the stable TIBr in the absence of HA, the TIBr in the solution showed an apparent loss after 20 min of reaction, decreasing from 12.52 μM to 10.24 μM. This demonstrates that the reduced bromine may transfer to brominated by-products after being converted to Br· or HOBr and reacting with organics.

HA is a macromolecular organic compound with an aromatic structure and functional groups such as carboxyl, phenolic hydroxyl, carbonyl, quinone, and methoxy groups. It can easily react with free halogens, such as hypohalous acid and halogen free radicals, to generate halogenated by-products including trihalomethanes (THMs) and haloacetic acid (HAAs) [29,30]. Without adding chlorine to the synthetic solution in this study, four types of Br-THMs and Br-HAAs were detected during the EAP process (tribromomethane, TBM; bromoacetic acid, MBAA; dibromoacetic acid, DBAA;

tribromoacetic acid, TBAA) (not shown). It is noteworthy that the sum of Br-HAAs and Br-THMs in the solution decreased after 100 min of EAP treatment, and at this time, the Br^- decreasing rate decreased, and the TIBr concentration rebounded. This shows that after conversion from an inorganic state to an organic state, bromine could return to the transformation process of inorganic bromine via the unselective mineralization of by-products by the active substances in the EAP process. The results also basically verify the hypothesis shown in Fig. 8.

As a typical AOP method, when the EAP process is adopted to treat bromide-containing water, the co-existence of organics may reduce the formation of BrO_3^- by-products, but there is also the risk of generating more toxic brominated by-products.

4. CONCLUSIONS

In this study, an electrochemically activated persulfate process was constructed with a BDD anode and Ti cathode and was used to treat synthetic bromide-containing water. A possible mechanism of BrO_3^- formation and transformation of bromine by-products was discussed, and the effects of the operating conditions on BrO_3^- formation were investigated. The results suggest the following:

(1) In this EAP process, the oxidation of electrogenerated free radical substances and the reduction of the cathode are the major driving forces for the transformation of bromine. The main components of free radicals are the electrogenerated OH• on the BDD anode and $SO_4^{\bullet -}$ electroactivated on the cathode.

(2) In the EAP process, Br^- can be oxidized to BrO_3^- through the continuous stepwise reaction. When organic matter coexists in the solution, bromine can be converted into brominated by-products via the reaction of organics and HOBr or Br•.

(3) Increasing the PDS dose and current density could improve the oxidation efficiency of pollutants in the EAP process but could also increase the generation rate of BrO_3^- by-products. Acidic environments are beneficial for inhibiting the formation of BrO_3^- but might also increase the risk of the formation of brominated by-products.

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