The Oxidation Mechanism of Aniline by Ozone Water and Ozone Micro-nano Bubble Water and Its Influencing Factors

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The oxidation mechanism of aniline by ozone water and ozone micro-nano bubble water and its influencing factors

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Abstract

Aniline is a kind of refractory contaminant that is difficult to be degraded by microorganisms. Ozone is a green and efficient reagent to oxidize aniline, while the ozone oxidation efficiency is restricted by the low ozone mass transfer rate. Micro-nano bubble ozonation has been developed as a new method to significantly improve the ozone utilization rate, while the characteristics of ozone micro-nano bubble when compared with dissolved ozone is not clear. The paper carried out batch experiments to research the oxidation effect of aniline by ozone water (OW) and ozone micro-nano bubble water (OMNBW), and found that the degradation rate of aniline by OMNBW was 2.8~5.9% higher than that by OW. The increase of pH had a negative effect on the degradation of aniline by OW and OMNBW. SO_4^{2-}, Cl^-, HCO_3^- and Mg^{2+} could inhibit the degradation efficiency by 0.04%, 0.99%, 0.44% and 10.4% for OW, while the ratios were 1.1%, 6.4%, 4.1% and 1.5% for OMNBW. The addition of humic acid and fulvic acid could decrease the oxidation rate of aniline by 35% and 49% for OW, while the ratios were 41% and 62% for OMNBW. Through quenching experiment, it was found that the direct oxidation by ozone molecules and the indirect oxidation by superoxide radicals were main pathways for aniline oxidation by OW and OMNBW. This work provided a practical guide for the application of OMNBW in wastewater and groundwater treatment process.

Keywords: aniline, ozone micro-nano bubble water, oxidation, pH, ion, pathway

1. Introduction

Aniline is an important chemical material and widely used in dyes, pesticides, explosive materials, pharmaceuticals and other industries (Huang et al. 2017, Zhou et al. 2014). Aniline is used to synthesize pesticides, chemical brighteners, dyes, etc. It is also a common by-product of petroleum, papermaking and coal industry (Zabihi-Mobarakeh and Nezamzadeh-Ejhieh 2015). Aniline is mutagenic, teratogenic and carcinogenic, and has been listed as one of 129 priority-controlled pollutants by the U.S. Environmental Protection Agency (USEPA) (Trautwein et al. 2015). In addition, aniline is difficult to degrade and easy to maintain high toxicity even at low concentrations (Orge et al. 2017). Therefore, it is necessary to develop water treatment technologies to degrade aniline in order to meet the relative standards.

The remediation technology of polluted water included physical adsorption, biological process and chemical oxidation. However, for wastewater containing complex components, the efficiency of physical adsorption was very limited (Liu et al. 2009). For relatively persistent pollutants such as aniline, biological methods were inefficient and usually spent more time than chemical methods (Ikehata et al. 2008). Chemical oxidation was one of the most commonly used methods for water treatment by different reagents, such as Fenton reagent, potassium permanganate, persulfate and ozone. However, the oxidation efficiency of Fenton process was highly dependent on pH and was easily affected by the various substances in actual water, such as chloride and bicarbonate (Neyens and Baeyens 2003). In addition, hydrogen peroxide was unstable with a short half-life (Clarizia et al. 2017). Persulfate must be activated before it could be used for water treatment, but both catalyst and sulfate would produce a large number of by-products, resulting in secondary pollution (Hou et al. 2012). Chemical oxidation by permanganate would produce MnO_2, which might also lead to secondary pollution (Li and Schwartz 2005).

Compared with other treatment technologies, ozone had been widely applied in

the treatment of drinking water and reclaimed water (Miao et al. 2015, Shen et al. 2008), because it produced fewer secondary pollutants than other oxidants. When ozone was applied to oxidize contaminants in water, ozone gas was often injected directly by gas sparger at the designed place. In this situation, the oxidation effect could only be significant in its impact radius, which was near the injection point (Mccray and Falta 1996, Yao et al. 2020). Some studies combine ozone with surfactants to extend the impact range, such as sodium dodecyl benzene sulfonate (Kim et al. 2004), while the addition of surfactants would also cause secondary pollution.

Bubbles with a diameter between 200 nm and 10 μm are usually called micro-nano bubbles (MNBs) (Agarwal et al. 2011). MNBs solutions might be a feasible option for the continuous introduction of gaseous oxidizing agents to contaminated water. Ozone micro-nano bubble water (OMNBW) was formed by the release of pressurized ozonated water. Compared with water containing ozone (OW), the small radius of MNBs made it more stable in water (Shangguan et al. 2018). In addition, MNBs had large specific surface area and high interior gas pressure, which was related to the high mass transfer rate of ozone from the gas phase to the liquid phase as well as the high gas dissolution capability (Ikeura et al. 2011, Li et al. 2013, Takahashi et al. 2015). When MNBs shrunk in water, charged ions quickly concentrated and enriched on a very narrow bubble interface, so MNBs had higher zeta potential (Takahashi et al. 2007). MNBs also had stronger migration ability, which had the potential ability to overcome the heterogeneity in porous media (Choi et al. 2008). OMNBW had been proven to be an effective oxidant for the oxidation of various organic pollutants, such as polycyclic aromatic hydrocarbons, chlorinated hydrocarbons and dyes (Hu and Xia 2018, Zhang et al. 2019). However, the oxidation mechanism of OMNBW and the influence of raw water quality was still not clear, which impeded the application of OMNBW in practical engineering.

This paper compared the oxidation efficiency and pathway of aniline by OMNBW and OW, since the formation of MNBs in this study was through the release of pressurized water. The effect of different water quality conditions, such as aniline

concentration, pH, inorganic ions and dissolved organic matter (DOM), were all studied in this paper. In addition, the oxidation mechanisms of aniline by OW and OMNBW were analyzed through quenching experiment. This paper could help guide the application of OMNBW in wastewater and groundwater treatment engineering.

2. Materials and methods

2.1 Chemicals and reagents

The chemicals used in the experiment, sodium sulfate (purity ≥ 99%), sodium chloride (purity ≥ 99.5%), sodium thiosulfate ($Na_2S_2O_3$) (purity ≥ 97%) were of analytical grade supplied by Shanghai Lingfeng Chemical Reagent Co. Ltd. Magnesium sulphate (purity ≥ 99%) was of analytical grade supplied by Xilong Scientific Co. Ltd. Tert-butyl alcohol (TBA) (purity ≥ 99%) was of analytical grade supplied by China National Pharmaceutical Group Co. Ltd. Sodium bicarbonate (purity≥99%), indigo disulfonate (purity ≥ 99%), *p*-benzoquinone (*p*-BQ) (purity ≥ 98%), fulvic acid (FA, purity ≥ 85%), furfuryl alcohol (purity ≥ 98%), humic acid (HA, purity ≥ 90%) were of analytical grade supplied by Shanghai Macklin Biochemical Co. Ltd.

2.2 Production of OMNBW and OW

OMNBW was created by a continuous OMNBW generation apparatus (HG-WNF-1, Hangzhou Guiguan Company, China). Ozone was generated from air in the ozone generator. As shown in Fig. 1, the simulated tap water and the air containing ozone were fed into the saturator at the flow rate of 360 mL/min and 140 mL/min, respectively. The ozonized water was pressurized to 300 kPa in the air saturator, and it was then released into the liquid storage tank with the volume of 12.5 L through the release head. The water in the liquid storage tank was controlled at 10 ℃ through ice bath. Stable dissolved ozone concentration at 1.36 mg/L could be obtained by aerating for about 5 min in the liquid storage tank.

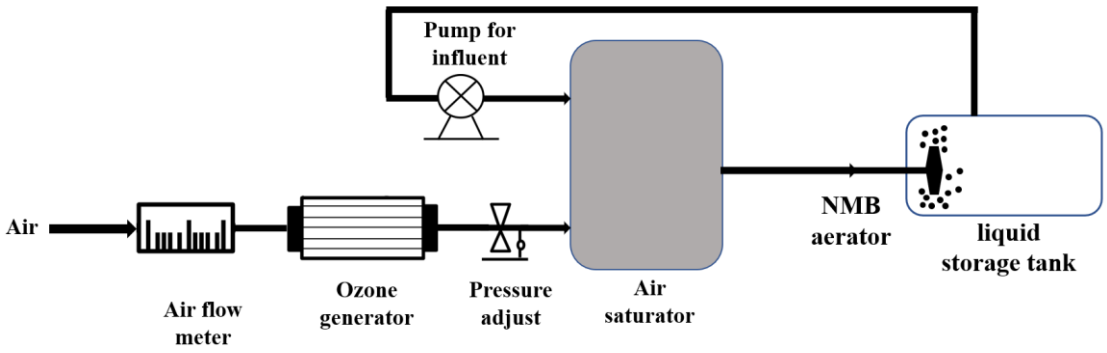

Fig. 1. Schematic diagram of OMNBW generation apparatus

OW was produced by bubbling air containing ozone into water in a cylinder with its volume of 1 L through a microporous diffuser, in which ozonized air was produced by an ozone generator (FL-803A, China). Ice was also added in water before aeration to control its temperature at 10 ºC. The aeration process kept for about 3 min to reach the stable ozone concentration at 1.36 mg/L.

2.3 Aniline oxidation experiment

When the aniline oxidation experiment by OMNBW and OW was carried out, 140 mL aniline solution with the temperature of 10 ºC and a rotator were added in a conical flask of 280 mL before the addition of OMNBW, and the conical flask was placed on a magnetic stirrer with the rotating speed of 200 rpm. 140 mL OMNBW or OW were scooped from the liquid storage tank or cylinder and quickly poured into the conical flask. Then the flask was quickly sealed by the rubber stopper. The rubber stopper had two holes, in which one hole was connected with a syringe with its volume of 100 mL to balance the pressure, and the other hole was connected with the sampling port. 10 mL water in the flask was sampled each time by gastight syringe at various time intervals up to 5 min. The obtained water sample was quenched by adding 1 mL $Na_2S_2O_3$ solution with its concentration of 0.1 M, and then it was filtered by the 0.22 μm membrane for detection.

The influence of pH on the degradation of aniline by ozonation was investigated by adding H_2SO_4 or NaOH solution with its concentration of 0.01 M to adjust pH between 5.0 and 9.0. When the effect of ions was considered, 250 mg/L SO_4^{2-}

(Na_2SO_4), 200 mg/L HCO_3^- ($NaHCO_3$), 250 mg/L Cl^- (NaCl) or 450 mg/L Mg^{2+} ($MgSO_4$) was mixed with aniline solution individually before the oxidation process. When the effect of dissolved organic matter was considered, humic acid (HA) or fulvic acid (FA) with its concentration of 50 mg/L was added to the aniline solution. The mixed solution was stirred evenly by the magnetic stirrer before the oxidation experiment.

In the quenching experiments, sodium thiosulfate, TBA or *p*-BQ was first mixed with aniline solution individually, and the mixed solution was stirred evenly. The molar ratios of sodium thiosulfate, TBA and *p*-BQ to aniline were 1330:1, 1256:1 and 860:1 respectively in order to completely quench the objective reaction. The decomposition kinetics of ozone in OMNBW and OW were also carried out in this paper. In this experiment, OMNBW or OW with its volume of 280 mL was added directly into the same conical flask, and then the solution was sampled by gastight syringe at various time intervals up to 40 min. Unless specified, all experiments were carried out when the initial aniline concentration was 1 mg/L, temperature was 10 ℃, pH was 8.0 and stirring speed was 200 rpm. All experiments were conducted in duplicate.

2.4 Analytical methods

The ozone concentration of OMNBW and OW was monitored using the indigo method (Wang et al. 2019). Briefly, 1 mL indigo solution with its concentration of 1.25 mM and 10 mL sample solution was mixed in a glass colorimetric tube. The absorption measurements for the indigo method were performed at the wavelength of 610 nm on a spectrophotometer (SG1000, China).

The aniline concentration was measured by high performance liquid chromatography (HPLC) (Waters e2695, USA) with a C18 column (4.6×150 mm, 5 μm). The mobile phase was an aqueous mixture (40% methanol and 60% water) at a flow rate of 1 mL/min. The injection volume was 10 μL, and the liquid sample was measured at the wavelength of 233 nm.

3. Results and discussion

3.1 The kinetics of ozone self-decomposition

The pseudo first-order kinetic model could be used to show the difference of self-decomposition rate between OMNBW and OW as Eq. (1).

$$\frac{dC}{dt} = -k_1 C \tag{1}$$

where C was the dissolved ozone concentration (mg/L), k_1 was the first-order decomposition coefficient (s^{-1}), t was the reaction time (s). Eq. (1) could be integrated to obtain the following equation:

$$\ln \frac{C_t}{C_0} = -k_1 t \tag{2}$$

where C_t was the dissolved ozone concentration at time t (mg/L), C_0 was the initial dissolved ozone concentration (mg/L). The decomposition of ozone in OMNBW and OW systems was shown in Fig. 2.

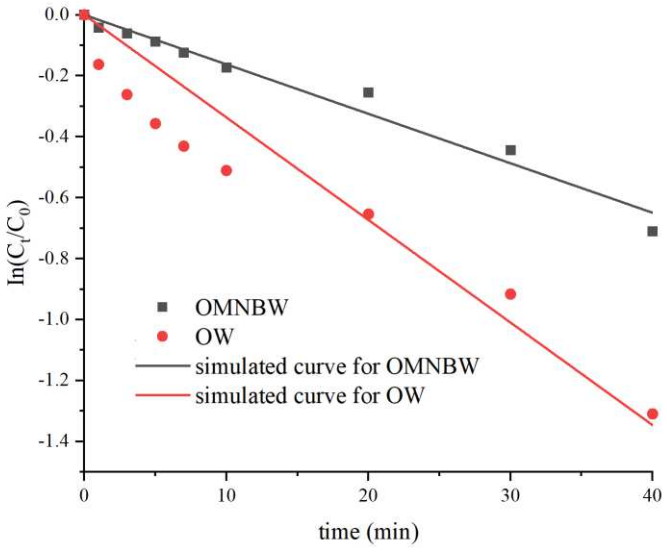

Fig. 2. Ozone self-decomposition curve in OMNBW and OW

The k_1 value for OMNBW and OW were 0.016 min^{-1} and 0.033 min^{-1} respectively, which showed that the self-decomposition of ozone in OMNBW was much slower than that in OW. Previous studies showed that the half-life of ozone in the gas phase was about twice longer than that in the liquid phase (Derco et al. 2021). When pressurized

water containing ozone was released into the tank, a large fraction of ozone in OMNBW still existed in the gas phase, and then gradually dissolved in water with the disappearance of bubbles (Fujioka et al. 2021), which led to a longer half-life of ozone in OMNBW. The slow release of ozone from gas phase to the liquid phase induced a slower but longer reaction rate between ozone and target contaminants.

3.2 The aniline oxidation kinetics by OMNBW and OW

The reaction of ozone and organic substance in aqueous media could be described by the direct molecular reaction by ozone molecules and indirect reaction by hydroxyl radicals (•OH) (Hamdi El Najjar et al. 2013). Fig. 3 showed that both OMNBW and OW could oxidize aniline within 30 s, which could be deemed as an instantaneous reaction. Turhan and Uzman (2010) found that when aniline was oxidized by ozone in a bubble column, it was completely degraded within 30 min. Aeration by air bubbles containing ozone required the accumulation of ozone in water, while the direct oxidation by OW could obtain a very high ozone concentration at the start of reaction, which led to the instantaneous degradation of aniline within 30 s in this study.

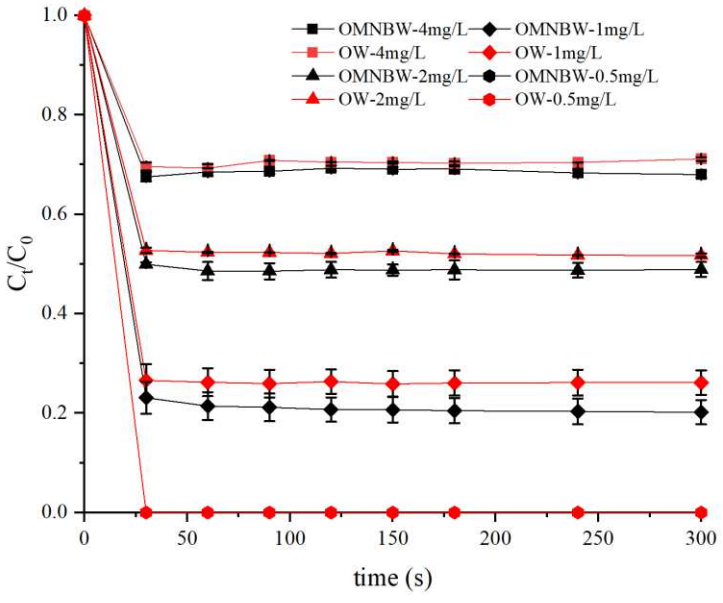

Fig. 3. Degradation of aniline by OW and OMNBW with different initial aniline concentrations

When the initial aniline concentration was 0.5 mg/L, aniline was completely

degraded within 30 s by both OMNBW and OW. When the initial aniline concentration was 1 mg/L, the degradation rate of aniline by OMNBW reached 79.8% in 5 min, which was 5.9% higher than that by OW. When the initial aniline concentrations were 2 mg/L and 4 mg/L, the degradation rate by OMNBW were 51.1% and 32%, which were 2.8% and 3.1% higher than that by OW respectively. The results showed that although aniline could react with ozone molecules directly, the removal rate of aniline by OMNBW was still higher than that by OW when the dissolved ozone concentration was the same. Previous studies showed that MNBs would release a large amount of •OH in the process of annihilation (Liu et al. 2016). At the same time, MNBs had small size and large specific surface area (Agarwal et al. 2011). Therefore, MNBs could adsorb more contaminants and increase the oxidation rate, which finally induced a higher removal rate of aniline in this study.

3.3 Influence of pH

It could be observed from Fig. 4 that the degradation rate of aniline by OMNBW or OW both decreased significantly with the increase of pH. Theoretically, during the oxidation process of organic substances by ozone, alkaline conditions would be beneficial to the degradation of contaminants than acidic conditions, because alkaline environment would produce more •OH that would oxidize contaminants without selectivity (Remucal et al. 2020). In addition, a higher pH would also increase the lifetime of MNBs, because MNBs became more negative and had stronger repulsive force (Hamamoto et al. 2018). However, the higher pH during ozonation would also lead to the instability of ozone molecules (Derco et al. 2021), which further resulted in the quick decrease of aqueous ozone concentration.

In alkaline environment, molecular ozone would easily decompose to •OH, which had a very short survival time with the half-life of 10^{-3} μs (Mei et al. 2019). If it did not contact pollutants for the first time, •OH would die out and may reduce the ozone utilization rate. Therefore, the aniline oxidation rate by OW decreased from 83.3% to 69.3% when pH increased from 5 to 9. However, MNBs would produce much •OH in

the process of annihilation (Liu et al. 2016), which could degrade aniline effectively. In addition, the surface of MNBs were negative charged, and MNBs had small size and large specific surface area (Agarwal et al. 2011), which could effectively adsorb pollutants. Therefore, the degradation rate of aniline by OMNBW when pH was 9 was only 1.3% lower than that when pH was 8 (Fig. 4b), which indicated that the oxidation of aniline by OMNBW was less affected by the solution pH when compared with OW.

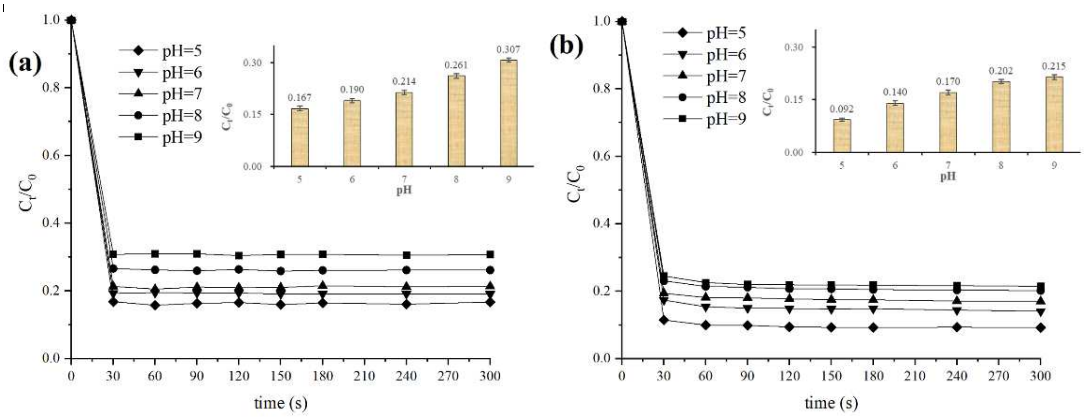

Fig. 4. Influence of pH on aniline degradation (a: OW; b: OMNBW)

3.4 Influence of inorganic ions

Different anions had different influence on ozone oxidation effect (Ji et al. 2018). In this paper, the influence of common ions on the degradation of aniline by OMNBW and OW was investigated, which included SO_4^{2-}, Cl^-, HCO_3^- and Mg^{2+} that were representative ions in the raw water (Santafé-Moros and Gozálvez-Zafrilla 2010). As shown in Fig. 5a, SO_4^{2-}, Cl^- and HCO_3^- only reduced the degradation efficiency by 0.04%, 0.99% and 0.42% respectively for OW, which was related to the direct oxidation of aniline by molecular ozone. For OMNBW, SO_4^{2-} inhibited the degradation rate of aniline by 1.1%, but Cl^- and HCO_3^- inhibited the degradation rate by 6.4% and 4.1% respectively, which showed that these three anions had a relatively significant influence on the oxidation of aniline by OMNBW. According to previous studies, HCO_3^- and Cl^- were well-known free radical inhibitors and had been widely used for •OH scavenging (Clarizia et al. 2017, Liu et al. 2013). Therefore, the inhibition of Cl^- and HCO_3^- on OMNBW might be through the inhibition of free radical pathway. However, OW did not form as much •OH as OMNBW (Liu et al. 2016), so the inhibition by HCO_3^- and

Cl^- were not significant for OW.

It could also be observed from Fig. 5 that Mg^{2+} inhibited the OW oxidation rate by 10.4%, but it only inhibited the OMNBW oxidation rate by 1.5%. The effects of Mg^{2+} on ozone oxidation pollutants were mainly divided into two aspects. Mg^{2+} could promote the production of •OH and had complexation with some ozonation intermediates such as carboxylic acids, so that these intermediates were easier to be oxidized (Sui et al. 2010). In addition, Mg^{2+} could promote the decomposition of ozone and inhibit the degradation efficiency of contaminant (Rischbieter et al. 2000, Sui et al. 2010), which was consistent with the aniline oxidation results by OW. However, Mg^{2+} has less inhibition on aniline degradation efficiency by OMNBW. It might be caused by the negatively charged bubbles that could preferentially adsorb Mg^{2+} (Agarwal et al. 2011), which reduced the catalytic effect of Mg^{2+} on dissolved ozone. In addition, bubbles also inhibited the direct contact between gas-phase ozone and Mg^{2+}, which prolonged the ozone lifetime at the same time.

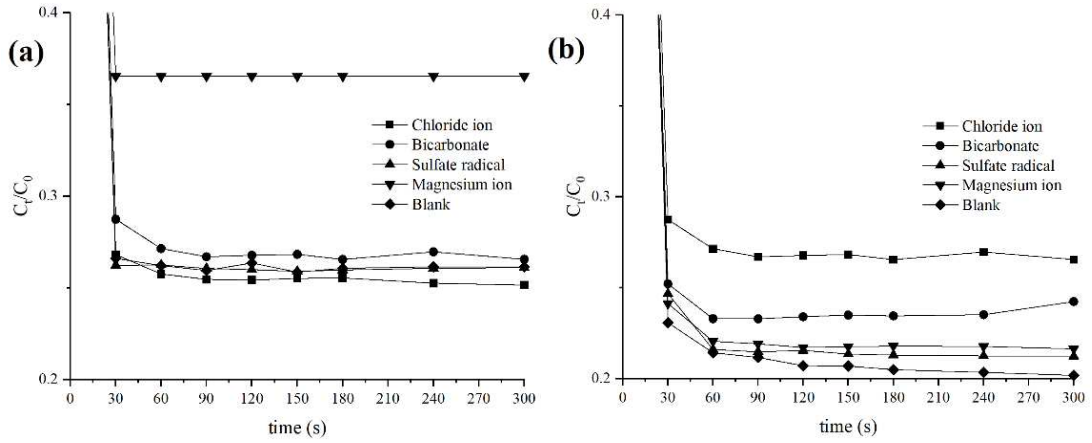

Fig. 5. Influence of different ions on aniline oxidation (a: OW; b: OMNBW)

3.5 Influence of DOM

The influence of HA and FA on aniline oxidation by OMNBW and OW was shown in Fig. 6, which showed that both HA and FA had great inhibition effects on the oxidation of aniline by OMNBW and OW. When HA was added in the solution, the degradation rate of aniline by OW and OMNBW decreased by 35% and 41%, while FA inhibited the aniline degradation rate by 49% and 62% respectively, indicating that FA

with small molecules would react with oxidants more easily (Wang et al. 2017). According to previous research, HA and FA could be oxidized by ozone, which competed with aniline and reduced the aniline oxidation rate as well (Wang et al. 2020). The ozone oxidation mechanism by OMNBW was mainly divided into the direct oxidation by molecular ozone dissolved in water and the "interface degradation" after pollutants were adsorbed on bubbles. DOM with a high concentration would be adsorbed by bubbles and covered the bubble surface, which competed for limited adsorption sites. Therefore, the existence of DOM would inhibit the oxidation of aniline by the competed adsorption and oxidation. It could be inferred that for OMNBW, the oxidation of contaminants was more relied on the molar concentration of contaminants rather than the chemical reaction rate. In OMNBW, contaminants were more easily degraded when they were adsorbed on bubble surface. Both the adsorption capacity of contaminants on bubble surface and the molar concentration of contaminants would affect the ozone oxidation rate, which improved the oxidation selectivity of ozone by OMNBW.

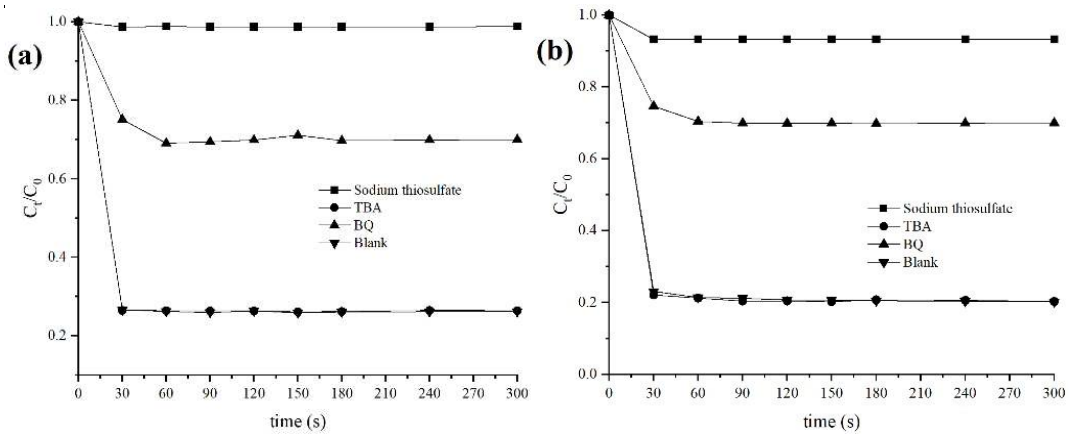

Fig. 6. Influence of DOM on aniline degradation (a: OW; b: OMNBW)

3.6 The oxidation pathways by free radicals

Previous data in Section 3.2 showed that at the same dissolved ozone concentration, OMNBW had a stronger removal rate of aniline than OW, which might be caused by the free radicals that was formed in OMNBW. TBA was very easy to react with •OH ($k_{TBA\text{-}\bullet OH} = 6.0\times10^{8}$ M^{-1} s^{-1}), but it hardly reacted with ozone ($k_{TBA\text{-}O3} = 3.0\times10^{-3}$ M^{-1} s^{-}

[1]) (Nawrocki 2013, Nawrocki and Kasprzyk-Hordern 2010). Therefore, TBA was applied to identify the existence of •OH in OMNBW and OW. Fig. 7 showed that the aniline oxidation rate by OW only decreased by 0.30% after the addition of TBA as scavenger, while the oxidation rate by OMNBW only decreased by 0.15%. It indicated that indirect pathway by •OH took a very small fraction in the aniline oxidation process. In addition, previous studies reported that TBA tended to disperse in aqueous solution and was not efficient in capturing radicals near bubble surface (Yao et al. 2020). Therefore, the reason for the low quenching effect in OMNBW might be the generation of •OH at the bubble surface rather than in the solution.

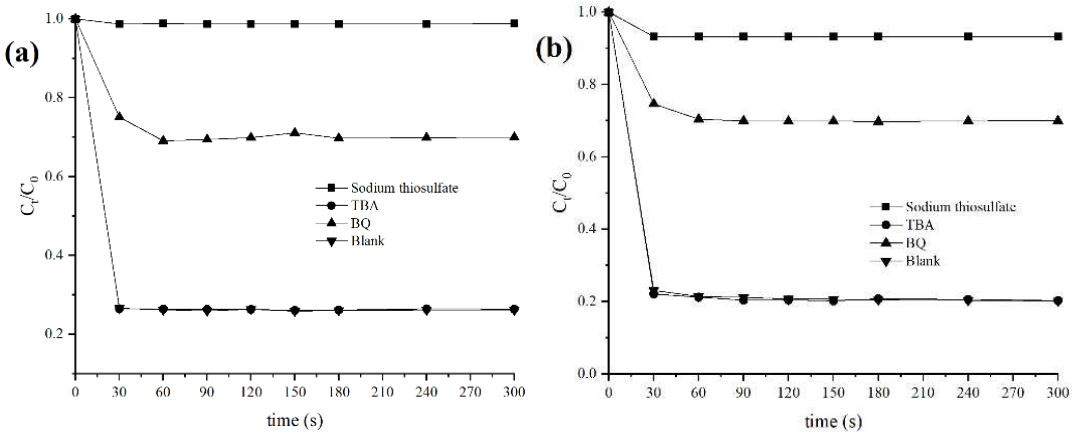

Fig. 7. Effect of free radical on aniline degradation (a: OW; b: OMNBW)

Ozone could initiate free radical chain reactions in water (Acero and Gunten 2001, Staehelin and Hoigne 1985). These free radical chain reactions played an important role in promoting the decomposition of ozone into various reactive oxygen species (e.g. • OH, $O_2^{\bullet-}$, $O_3^{\bullet-}$) (Guo et al. 2021). Ozone could react with water or hydroxyl ion to produce some primary •OH and HO_2• (Eqs. 3, 4), and these radicals could further react to form $O_2^{\bullet-}$ (Eq. 5). Once formed, $O_2^{\bullet-}$ could quickly react with ozone to form $O_3^{\bullet-}$(Eqs. 6, 7). There were increasing studies claiming that $O_2^{\bullet-}$ was the main reactive oxygen species (ROS) for the removal of ozone-resistant pollutants (Tan et al. 2017, Wang et al. 2016).

$$O_3 + H_20 \rightarrow 2HO_2^{\bullet} \quad (3)$$

$$O_3 + OH^- \rightarrow O_3 + \bullet OH \quad (4)$$

$HO_2^{\bullet} \rightleftharpoons H^+ + {}^{\bullet}O_2$ (5)

$O_2^{\bullet-} + O_3 \rightarrow O_2 + O_3^{\bullet-}$ (6)

$O_3^{\bullet-} \rightleftharpoons O_2 + O^{\bullet-}$ (7)

p-BQ was frequently used to trap superoxide radicals ($O_2^{\bullet-}$) with a rate constant of 9.0~9.8×10^8 M^{-1} s^{-1} (Burns et al. 2012), and *p*-BQ could also react with •OH with a rate constant of 1.2×10^9 M^{-1} s^{-1} (Burns et al. 2012). However, *p*-BQ hardly reacted with ozone ($k_{p\text{-BQ-O3}}$ = 2.5×10^3 $M^{-1}s^{-1}$) (Mvula and von Sonntag 2003). As the quenching experiment by TBA had proven that •OH could hardly play any role in the reaction, the effect of *p*-BQ on the aniline oxidation could be attributed to the effect of $O_2^{\bullet-}$. Fig. 7 showed that the degradation of aniline by OW was inhibited by 44% after the addition of *p*-BQ, while the inhibition rate increased to 50% for OMNBW, indicating that $O_2^{\bullet-}$ played important role in the aniline oxidation process. Compared with OW, OMNBW produced more $O_2^{\bullet-}$, which indicates that OMNBW could trigger more chain reactions in the degradation of aniline. In addition, when pH was neutral or alkaline, the indirect oxidation by $O_2^{\bullet-}$ was the main oxidation pathway (Beltran et al. 1994, Derco et al. 2021).

$Na_2S_2O_3$ could react with almost all oxidizing substances quickly because of its strong reducibility, so it was often used as an oxidant scavenger (Shen et al. 2008). Fig. 7 showed that the addition of excessive $Na_2S_2O_3$ almost eliminate the ability of OW to oxidize aniline. However, OMNBW could still oxidize aniline by 7.5%. If it was in homogeneous aqueous solution, excess $Na_2S_2O_3$ should be able to quickly remove all oxidative substances, which contradicted with the experimental result in this study. The probable reason might be that negatively charged $S_2O_3^{2-}$ could not be effectively adsorbed by negatively charged micro-nano bubbles (Li et al. 2014). On the contrary, bubbles could effectively adsorb positively charged aniline molecules, resulting in the

oxidation reaction of aniline by ozone at the bubble interface, which led to the aniline oxidation process.

4. Conclusion

In this paper, batch experiments were carried out to research the influence factors and oxidation mechanism of aniline oxidation by OW and OMNBW. Experimental results showed that the half-life of ozone in OMNBW was 106% larger than that of OW, which was caused by the prolonged life of ozone in the gas phase in OMNBW. A lower pH value would induce a higher oxidation efficiency of aniline for both OW and OMNBW, but the degradation efficiency of OMNBW reduced less than OW when pH rose from 8 to 9. SO_4^{2-}, Cl^- and HCO_3^- with their concentrations at 5~10 mM had almost no effect on OW, but they could reduce the oxidation rate by 1.1%, 6.4% and 4.1% for OMNBW respectively. For OW and OMNBW, Mg^{2+} could inhibit the aniline oxidation rate by 10.4% and 1.5%, respectively. For OW and OMNBW, the addition of HA could decrease the removal rate of aniline by 35% and 41%, while the ratios were 49% and 62% for FA. When OW acted as the oxidant, hydroxyl radical, superoxide radical and molecular ozone contributed 0.3%, 43.7% and 56.0% for aniline oxidation, while for OMNBW these ratios were 0.2%, 49.8% and 50.0% respectively. The addition of excessive sodium thiosulfate completely inhibited the oxidation of aniline by OW, but aniline was still oxidized by 7.5% in the OMNBW system, indicating the interfacial oxidation of aniline in bubble surface. This paper provided a strong support for the application of OMNBW in wastewater and groundwater treatment engineering.

Statements and Declarations

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Ethical approval

Not applicable

Competing interests

The authors have no relevant financial or non-financial interests to disclose.

Consent to participate

All participates agreed to participate in this study and signed the informed consents.

Consent to publish

All authors reviewed and approved the manuscript for publication.

Author contributions

ZX did the aniline oxidation experiment, and wrote the original draft of the paper. JS, YL and LL all offered valuable suggestions for the manuscript. DS helped form the experimental plan, guided the experiment, and offered valuable suggestions for the manuscript. SQ guided the experiment, revised the manuscript and obtained funding for the study.

Data availability

The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

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