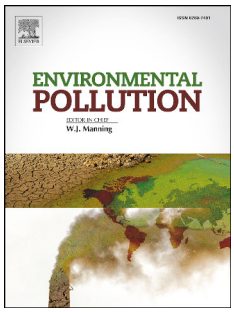
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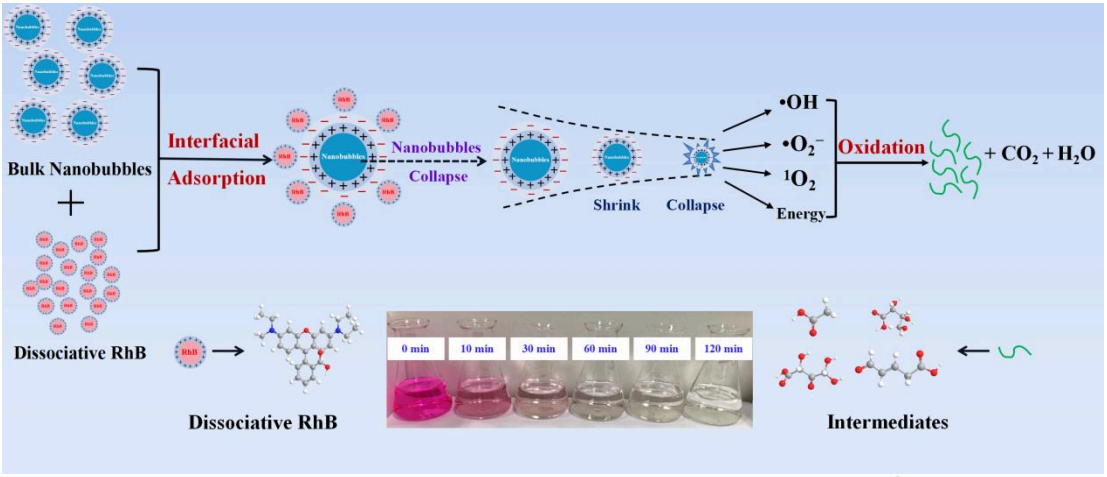
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# Exploring a chemical input free advanced oxidation process based on nanobubble technology to treat organic micropollutants

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## Abstract

Advanced oxidation processes (AOPs) are increasingly applied in water and wastewater treatment, but their energy consumption and chemical use may hinder their further implementation in a changing world. This study investigated the feasibility and mechanisms involved in a chemical-free nanobubble-based AOP for treating organic micropollutants in both synthetic and real water matrices. The removal efficiency of the model micropollutant Rhodamine B (RhB) by oxygen nanobubble AOP (98%) was significantly higher than for air (73%) and nitrogen nanobubbles (69%). The treatment performance was not significantly affected by pH (3-10) and the presence of ions ($Ca^{2+}$, $Mg^{2+}$, $HCO_3^-$, and $Cl^-$). Although a higher initial concentration of RhB (10 mg/L) led to a slower treatment process when compared to lower initial concentrations (0.1 and 1 mg/L), the final removal performance reached a similar level (~98%) between 100 and 500 mins. The coexistence of organic matter (humic acid, HA) resulted in a much lower reduction (70%) in the RhB removal rate. Both qualitative and quantitative analysis of reactive oxygen species (ROSs) using fluorescent probe, electron spin resonance, and quenching experiments demonstrated that the contributions of ROSs in RhB



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degradation followed the order: hydroxyl radical (•OH)> superoxide radical ($•O_2^-$)> singlet oxygen ($^1O_2$). The cascade degradation reactions for RhB were identified which involve N-de-ethylation, hydroxylation, chromophore cleavage, opening-ring and final mineralisation processes. Moreover, the treatment of real water samples spiked with RhB, including natural lake water and secondary effluent from a sewage works, still showed considerable removals of the dye (75.3%-90.8%), supporting its practical feasibility. Overall, the results benefit future research and application of chemical free nanobubble-based AOP for water and wastewater treatment.

**Keywords:** Micro/nanobubble technology, green technology, reactive oxygen species, organic micropollutant, water and wastewater treatment

## 1. Introduction

Numerous persistent micropollutants resulting from farming practices, industrial and household effluents have been identified in rivers and lakes globally (Devi et al., 2013; Xia et al., 2023). These micropollutants can pose significant risks to human health and ecological safety, even at trace concentrations (Murtaza et al., 2023; Yang et al., 2022). Advanced oxidation processes (AOPs), such as ozonation (van Gijn et al., 2022), photocatalysis (Zeng et al., 2022), and Fenton's reactions (Zhang et al., 2022) have been successful in removing organic micropollutants during water and wastewater treatment. However, those processes usually require significant energy consumption and the use of hazardous chemicals such as ozone, peroxide, and/or UV light. Moreover, unwanted by-products (e.g. Fenton sludge) may be generated and lead to increased operational costs (Muthusami et al., 2021). To mitigate the environmental impact of conventional AOPs, there is an urgent need to develop sustainable, cost-effective, and chemical-free alternatives.

Nanobubbles are gas cavities in the aqueous phase with diameters smaller than 1000 nm that possess unique physicochemical properties when compared to conventional bubbles. These properties include a long lifespan, high specific surface area, low buoyancy, aggregated gas density, and a negative surface charge (Lyu et al., 2019; Wang et al., 2020). As a result, nanobubbles have been employed in diverse fields, such as medicine delivery (Hernandez et al.,

2019), crop yield enhancement (Wu et al., 2019), food processing (Thi Phan et al., 2020), and environmental remediation (Hu and Xia, 2018; Wang et al., 2018). In water and wastewater treatment, nanobubble technology has demonstrated superior performance in improving biological and physiochemical treatment processes, leading to better removal of nutrients (Lyu et al., 2023; Zhang et al., 2021), taste and odour compounds (Soyluoglu et al., 2022), organic micropollutants (Fan et al., 2021a), and control of biofouling (Fan et al., 2021b). The current concepts of using nanobubble technology in AOPs has been mainly through the incorporation of nanobubbles with other AOPs to intensify the overall treatment performance. For instance, the removal efficiencies of oxytetracycline (Wang et al., 2020) and bacterial spores (Fan et al., 2021b) were significantly increased by adopting nanobubbles in photocatalytic processes. Similarly, adding nanobubbles in $H_2O_2$ based reaction processes improved the production of ROSs and enhanced the degradation of a fabric dye (Bui and Han, 2020). Previous studies to date have concluded that nanobubbles can reduce chemical usage and energy consumption in AOPs based on the premise of achieving an equivalent treatment performance. These applications align with a view that the generation of ROSs from nanobubbles can occur under external stimulations, such as through metal catalysis and UV light stimulations from incorporated AOPs. Nevertheless, recent studies have shown that ROSs can also be generated in solutions under ambient unstimulated conditions during the treatment process (Ji et al., 2020). Therefore, the extent to which the nanobubble technology can be used alone as a chemical-free AOP for water and wastewater treatment needs to be investigated.

In conventional AOPs, pH is an essential factor that influences the treatment performance. The efficacy of homogeneous Fenton reactions is usually higher under acidic conditions (Liu et al., 2021), thus, a chelating agent is sometimes used to regulate the system's pH level to enhance the degradation of the micropollutants (Ahmed et al., 2022). Regardless, the effects of pH on heterogeneous AOPs efficiency are determined by the properties of catalysts and the pollutants (Akpan and Hameed, 2009). Besides pH, other water quality parameters, such as ionic strength, hardness, alkalinity, and organic matter, can also reduce the oxidation potential of AOPs through quenching of the ROSs (Liao et al., 2001; Yu et al., 2021). Thus, it is crucial to assess the potential influencing factors on the proposed nanobubble-based AOP approach. While some

AOPs can generate ROSs for the destruction of parent micropollutant compounds, the ROSs may not be sufficient to entirely mineralise the molecules (Tran et al., 2021; Zeng et al., 2022). Moreover, many AOPs have been tested using only synthetic water samples, without validation treating real-world water matrices. Therefore, comprehending the degradation pathways of micropollutants and validating the process in actual water samples is an important step for evaluation of the effectiveness of the proposed nanobubble-based AOP approach.

To explore the feasibility of nanobubble-based chemical input free AOP for water and wastewater treatment, the degradation of the target model compound Rhodamine B (RhB) was investigated in both synthetic and real water matrices. The impacts on the treatment performance by potential influencing factors, including initial RhB concentration (0.1-10 mg/L), pH (3-10), existing ions ($Ca^{2+}$, $Mg^{2+}$, $HCO_3^-$, and $Cl^-$), and organic matter (humic acid - HA), were assessed. The generation and contribution of different ROSs on RhB degradation were qualitatively and quantitatively analysed using fluorescent probe, electron spin resonance, and quenching experiments. Moreover, the primary contributing ROS, hydroxyl radicals (•OH), were monitored and visualized through the three-dimensional excitation and emission matrix (EEM) fluorescence spectra. The intermediate by-products were identified to reveal the degradation pathways of RhB. Finally, the perspectives of extrapolating the current findings to other applications and future research needs were discussed.

## 2. Materials and Methods

### 2.1 Nanobubble preparation and characterisation

Nanobubbles were generated using a commercial nanobubble generator (Shanghai Zhongchen Digital Technology Equipment Co., Ltd., Shanghai, China) with a power of 0.25 kW. The concentration, mean size, and size distribution of the nanobubbles were detected using a nanoparticle tracking analysis system (Nanosight NTA NS500, Malvern Instrument Co., Ltd. UK). The zeta potential of the nanobubbles was determined using a Zetasizer Nano ZS (90Plus PALS, Malvern Instrument Co., Ltd. UK). Dissolved oxygen (DO) was measured using a DO probe (JPBJ-608, INESA Scientific Instrument Co., Ltd. China).

### 2.2 Initial degradation experiments

RhB, as the target organic micropollutant, was spiked into a reaction tank filled with 8 L of deionised (DI) water, resulting in initial concentrations of 0.1, 1 and 10 mg/L. The degradation processes occurred in a homogeneous system, where bulk nanobubbles were continuously generated and introduced into the RhB solutions throughout the reaction duration. The reaction was conducted in a sealed stainless tank to avoid external energy input and photodegradation on RhB solutions during degradation (**Fig. S1**). Water samples were collected at intervals during the experiment, and the concentration of RhB was determined using a UV spectrophotometer (Varian Cary 60, Agilent Technologies Co., Ltd. USA). The total organic carbon (TOC) of the solutions was measured by a TOC analyzer (Multi N/C 3100, Analytik Jena AG Co., Ltd. German). The details about used chemicals and degradation experiments are provided in the supplementary material (**Text S1 and S2**).

### 2.3 Influencing factors on the effectiveness of the nanobubble-based AOP

Separated experiments were conducted to evaluate the impact of pH, existing ions, and organic matter on the degradation of RhB using nanobubble-based AOP treatment. HCl and NaOH were used to adjust the initial pH values from 3 to 10 before treatment. Moreover, NaCl, $NaHCO_3$, $CaCl_2$, $MgCl_2$, and humic acid (HA), were used to obtain different levels of ironic strength, alkalinity, hardness, and organic matter in the initial solution. The same sampling and analysis procedures used in the initial degradation experiment were followed.

### 2.4 Micropollutant removal mechanisms and degradation pathways

The contributions of different ROSs on the degradation of RhB were examined through a series of quenching experiments. The generation of •OH was further qualitatively detected by electron spin resonance (ESR) (EMXplus, X-band, Brucker Analytical Instruments Co., Ltd. German). In addition, a fluorescent probe method was employed to monitor the generation of •OH with time via three-dimensional emission matrix fluorescence (EEM) spectra. The production of the •OH in the experimental system was quantitatively measured from the calibration curve (Soyluoglu et al., 2021; Fang et al., 1996). Besides monitoring the changes in the parent compound of RhB, the degradation intermediates of RhB were identified by Ultra High Performance Liquid Chromatography (Ultimate 3000 UHPLC, Dinonex Co., Ltd, USA) with

Q Exactive mass spectra (MS, Thermo Fisher Scientific Co., Ltd, USA). The degradation pathway of RhB was then proposed based on those intermediates. Details regarding the setup of the UHPLC and fluorescent probe method are provided in the supplementary material (**Text S3 and S4**).

### 2.5 Further validations using real water matrices.

To validate the proposed nanobubble-based AOP, experiments were further conducted using four different water matrices, including i) deionized water; ii) tap water; iii) natural lake water collected from Yanqi Lake in Beijing (which serves as an important source of drinking water), and iv) secondary effluent from Bishui Wastewater Treatment Plant in Beijing. RhB was spiked at a concentration of 1 mg/L into those water samples. The experimental setup and sampling were similar to the details provided previously for the initial degradation experiments.

## 3. Results and Discussion

### 3.1 Nanobubble size, distribution and longevity

Nanobubbles were generated using a hydrodynamic cavitation method, which was deemed the most efficient way to produce a large number of bulk nanobubbles suitable for water and wastewater treatment (Lyu et al., 2019). Before operating the bubble generator, the ultrapure water contained bubbles that had an average size > 1 μm, with fewer than $10^5$ particles/mL in the nanoscale range (**Fig. 1a**). After 10 minutes operation of the generator, nanobubbles with an average size of 192±15 nm and a concentration of $4.2\times10^7$ particles/mL were produced (**Fig. 1b**). After turning off the generator, the stabilisation of the nanobubbles was monitored for 72 hrs. The average size of nanobubbles slightly increased with time and reached 232±14 nm after 72 h (**Fig. 1c-f**), likely from the fusion of nanobubbles (Wang et al., 2020). This was consistent with a small drop in bubble concentration between the beginning and end of the time period ($4.2\times10^7$ to $3.8\times10^7$ particles/mL, **Fig. 1f**). The results indicated that nanobubbles possessed significant longevity in water, which was in accordance with previous studies that have reported that nanobubbles can exist in water for several weeks and even months (Soyluoglu et al., 2021; Wang et al., 2020). The gas inside nanobubbles may exist as an aggregation and the diffusion of the gas into the nanobubbles is likely to be slow and take place over a long period of time.

Notably, nanobubble collapse would be accelerated during the treatment process by external stimulus from the presence of organic pollutants and/or under anaerobic conditions (Ji et al., 2020). The unique characteristics of longevity and strengthened gas utilisation efficiency provide nanobubbles with the potential to significantly enhance water and wastewater treatment.

**Fig. 1. is here.**

### 3.2 Screening test of different nanobubble treatments for micropollutant removal

Previous studies have reported that oxygen aeration through common diffusers can increase the photocatalytic removal of RhB, which was attributed to the enhancement of •OH generation (Lee et al., 2013). In this study, without the assistance of other AOP technologies, the conventional oxygen aeration treatment could only obtain approximately 19% removal of RhB after 120 mins for an initial concentration of 1 mg/L (**Fig. 2a**). However, under the same conditions, nearly complete removal (98%) of RhB was achieved in the oxygen nanobubble treatment group. It may be due to the rapidly increased charge density of the surface electric double-layer on nanobubbles during the continuous shrinkage process (Agarwal et al., 2011). Thus, immense energy can instantaneously be released when nanobubbles collapse and form extremely high localised temperature and pressure conditions. This can be sufficient to break the O-H bond of water molecules and induce generation of ROSs (Agarwal et al., 2011). The generated ROSs contributed to the oxidisation of RhB compounds in this study, similar to the degradation process in other AOPs.

**Fig. 2. is here.**

Besides oxygen nanobubbles, other gases-filled nanobubbles, such as air and nitrogen, can also generate ROSs and have previously been shown to follow the order reactivity of oxygen > air > nitrogen (Ahmed et al., 2018). The current findings support that view for the degradation of RhB by nanobubbles, which decreased the degradation rate in the order of oxygen (98%), air (73%), and nitrogen (68%) nanobubbles (**Fig. 2a**). The pseudo-first-order kinetics model described the degradation reactions in all groups ($R^2$>0.90) and the reaction rate constants (k) for each group also exhibited the same trend as for the degradation rates (**Fig. 2b**, **Table S1**). This result was consistent with previous studies that investigated the effects of different gas-filled nanobubbles on the degradation of taste and odour compounds (Soyluoglu et al., 2022)

and phenol (Li et al., 2009) from water.

### 3.3 Removal mechanisms and degradation pathways for the micropollutant

#### *3.3.1 ROSs-based degradation mechanism*

Understanding the removal mechanisms of RhB by oxygen nanobubble AOP is crucial to direct future technology development and implementation. Quenching experiments were conducted to ascertain the contribution of individual reactive species, including •OH, $•O_2^-$, and $^1O_2$, during the degradation process. The removal rate of RhB decreased from 98% to 46%, 56%, and 68% when the •OH, $•O_2^-$, and $^1O_2$ were quenched, respectively (**Fig. 3a**, **Table S2**). The results supported the view that •OH, $•O_2^-$, and $^1O_2$ coexisted in the nanobubble solution (Liu et al., 2016), and all ROSs could contribute to the degradation of RhB. Moreover, based on the quenching experiments, the contribution of different ROSs to RhB degradation by oxygen nanobubbles followed the order of •OH > $•O_2^-$ > $^1O_2$ (**Fig. 3a**). Previous studies have also indicated that •OH was the most important oxidant in the oxygen nanobubble system for the degradation of oxytetracycline (Wang et al., 2020) and phenol (Li et al., 2009). To further verify the primary role of •OH in the degradation process, the ESR technique was employed to qualitatively detect the generated •OH. The results show that when 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was chosen as the spin-trap reagent, there was no significant signal corresponding to •OH in the DI water (**Fig. 3b**). However, an ESR spectrum of DMPO-•OH, containing four peaks with intensity ratios of 1:2:2:1 was detected in the oxygen nanobubble water, indicating the generation of •OH radical.

**Fig. 3. is here.**

Further evidence to demonstrate the formation of •OH radical in the nanobubble system was from the three-dimensional EEM spectra using disodium terephthalate (TP) as a fluorescence probe. A significant peak at the excitation wavelength of 315 nm and an emission wavelength of 425 nm was gradually formed from 0 to 120 min with an increase in the fluorescent intensity (**Fig. 4a-e**). Compared with the nanobubble water without the fluorescence probe, there were no peaks at the targeted fluorescent area on the EEM spectra (**Fig. S2a-e**). This suggested that the fluorescent adduct, 2-hydroxyterephthalate (TPOH), was formed by the hydroxylation reaction between the added TP and the •OH generated in the nanobubble system (Fang et al.,

1996). Furthermore, the •OH radical yield was also quantitatively calculated based on the calibration curves of TPOH (**Fig. S3**) (Soyluoglu et al., 2021; Fang et al., 1996). The results showed that approximately 38.23 nM •OH was generated in the oxygen nanobubble water after stable operation (**Fig. 4f**). The value was slightly higher than those (11-25.71 nM) reported in other nanobubble studies (Soyluoglu et al., 2021 and 2022), which may be attributed to the higher nanobubble concentration and smaller bubble size observed in this study. Although the generated •OH concentration was approximately two magnitudes lower than that in conventional AOPs, such as photocatalysis, Fenton, and Fenton-like reactions (0.9-11 μM) (Baba et al., 2015; Shen et al., 2022; Zhong et al., 2014), this study demonstrated that oxygen nanobubbles could achieve significant RhB removal efficiency without the need for external chemical inputs. The efficient utilisation of •OH in the present system was explained by the strong affinity between RhB and the nanobubble surface which facilitated the rapid use of the generated radicals for degradation. The production of $\bullet O_2^-$ and $^1O_2$ were not detected by both the electron spin resonance (**Fig. 3b**) and fluorescent probe (**Fig. 4f**) methods. This may have been due to the low concentration of these two ROSs generated, which fell below the detection limits, a result consistent with previous studies (Jia et al., 2023; Takahashi et al., 2021). Regardless, the results confirmed the important role of •OH radicals in degrading RhB in oxygen nanobubble treatment processes.

**Fig. 4. is here.**

It has previously been determined that the second order rate constant of RhB with •OH radical is $2.5\times10^{10}$ $M^{-1}s^{-1}$, a value several times higher than that seen for other common organic pollutants, like methylene blue ($3.8\times10^{9}$ $M^{-1}s^{-1}$), atrazine ($2.3\times10^{9}$ $M^{-1}s^{-1}$) and carbamazepine ($8.8\times10^{9}$ $M^{-1}s^{-1}$) (Grimme et al., 2010; Xie et al., 2022). This reaction rate is determined by the chemical structure and the intrinsic properties of the organic compounds. Thus, the combined factors of continuous generation of •OH in the circular reaction system and the high sensitivity of RhB with •OH mean that the oxygen nanobubbles are well placed to degrade RhB from aqueous solutions.

### *3.3.2 Degradation pathways of RhB*

For the purpose of understanding the degradation process of RhB, the variation in the absorption

spectra of degraded RhB in the wavelength range of 400-700 nm was examined (**Fig. 5a-c**). The typical absorption band at a wavelength of 554 nm was significantly diminished with the extension of the reaction time, which indicated the chromophore structure (conjugated xanthene ring) of the RhB was gradually destroyed by the oxidative attack from ROSs (Muthusami et al., 2021). In addition, the characteristic peak of RhB at 554 nm exhibited hypsochromic shifts during the reaction (**Fig. 5a-c**). Similar shifts were also observed in previous studies investigating RhB degradation by photocatalytic processes (He et al., 2009; Zeng et al., 2022). This hypsochromic shift illustrated that the degradation of RhB by oxygen nanobubbles is a chemical N-deethylation process, and a series of N-deethylated intermediates would be generated during the degradation (He et al., 2009).

The potential degradation pathways were speculated based on all of the detected intermediates (**Fig. S4** and **Table S3**). Specifically, there were two potential degradation pathways of RhB identified in this study. The first route was initiated by the N-deethylation process (**Fig. 5d**), where the ethyl group was progressively dissociated from RhB compounds (m/z=443) (Zhang et al., 2018). A series of N-deethylated products were detected in this process, including N, N-diethylrhodamine (DR) (m/z=416), N-ethyl-N-ethylrhodamine (EER) (m/z=388), N-ethyl rhodamine (ER) (m/z=361). Meanwhile, following attack by •OH, the hydroxylation product (m/z= 363) was also formed. Subsequently, amino, carboxyl, and benzoic acid were broken to form intermediates with m/z= 320, 272, and 196. Analogously, the second pathway started with a hydroxylation reaction (**Fig. 5d**). The upper component of the xanthene-containing conjugated structure and lower parts of the benzoic acid of RhB are connected by a single bond, which is easy to break (Wu et al., 2022a). Thus, the benzoic acid component and the ethyl group of RhB were attacked and replaced by •OH to form a series of hydroxylation intermediates (m/z= 371, 340, 323, and 227). After those intermediates were generated via the two pathways, the conjugated chromophore structure was broken to form products with smaller molecular weights (m/z= 121, 139, 179, and 181). Afterwards, these products were gradually dissociated into simple organic acids or alcohols via a ring-opening reaction (m/z= 60, 114, 136, and 149). Finally, the low molecular weight organic compounds were further mineralized to $CO_2$ and $H_2O$ to realize complete degradation.

**Fig. 5. is here.**

### 3.4 Influencing factors on micropollutant degradation

#### *3.4.1 Effect of initial concentrations and the degree of mineralisation*

Following the screening test, the oxygen nanobubble treatment approach for the removal of RhB was further studied. For initial concentrations of RhB of 0.1, 1, and 10 mg/L, oxygen nanobubble treatment could achieve >97% removal in all groups in 90, 120, and 480 min's reaction time, respectively (**Fig. 2c**). The analysis of the kinetics demonstrated that the RhB degradation process fitted with the pseudo-first-order model ($R^2$>0.90), with the removal rate constant for RhB decreasing from 0.036 $min^{-1}$ at 0.1 mg/L to 0.006 $min^{-1}$ at 10 mg/L (**Fig. S5**, **Table S4**). The results showed that the initial concentration affected the degradation rate of RhB by the oxygen nanobubble treatment, a result consistent with the photocatalysis treatment of RhB (Madima et al., 2022). At a high initial concentration of RhB, the degradation intermediates (by-products) may compete for the consumption of ROSs with the parent RhB compound, leading to a slower reaction rate (Geng and Thagard, 2013). Alternatively, the intermediates with lower molecular weight may diffuse into the nanobubbles, changing the condition of the bubble structure (and therefore likely bubble collapse) (Wang et al., 2008), which in turn suppresses the generation of ROSs. Nevertheless, further investigation and/or direct characterisation is needed to confirm these assumptions.

Compared with the removal of RhB by other AOPs, oxygen nanobubble treatment could reach equivalent removal efficiency (>97%) (**Table S4**) (Yu et al., 2021; Zhang et al., 2022). Under the same initial concentration of 1 mg/L, the reaction rate constant of oxygen nanobubble AOP was twice as high as the Fenton-like reactions. However, at an initial concentration of 10 mg/L, the reaction rate constant of the Fenton-like reaction was 2.6 times higher than that of oxygen nanobubbles (**Table S4**). This was mainly caused by the 80 times higher reaction volumes of the oxygen nanobubbles than for the Fenton-like reactions listed in the **Table S4**, which led to the 2.6~8.0 times longer reaction time. Furthermore, previous studies on RhB removal have typically only assessed the removal efficiency of the parent compound rather than an evaluation of the mineralisation of RhB. In this study, approximately 40%-50% of TOC removal was achieved in all treatment groups for different initial concentrations of RhB using treatment by

oxygen nanobubble (**Fig. 2d**). The results demonstrated that the oxygen nanobubble AOP could not only decolour the RhB-contaminated water, but also provide a significant degree of mineralisation of RhB. However, optimisation of the operation strategies for the complete degradation of RhB still needs to be studied.

### *3.4.2 Effect of pH and charge neutralization*

The pH of industry effluent varies, which in turn could affect the treatment performance of AOPs (Liu et al., 2021). Therefore, treatment of 1 mg/L RhB by oxygen nanobubbles was carried out at different pH levels (3-10) to assess the effects of the pH on the degradation process. Some small differences in RhB removal were identified at different pH, however, the final removal rates of RhB in all groups reached 95%±3% and did not exhibit a clear distinction between pH (**Fig. 6a**). The reaction rate constants of all groups fluctuated between 0.023~0.029 $min^{-1}$, without showing a significant difference (**Table S5**). A previous study also found that the pH of solutions did not significantly affect the removal of geosmin and 2-methylisoborneol by oxygen nanobubbles in the pH range of 3-10 (Soyluoglu et al., 2022). Thus, it is evident that oxygen nanobubble technology can play a significant role in degrading RhB from water across a wide range of pH.

**Fig. 6. is here.**

Part of the stable removal of RhB under different pH conditions may have been due to the characteristics of the negatively charged nanobubbles, which had a negative zeta potential across pH 3-10, decreasing from -3.63 to -22.89 mV from the lowest to highest pH (**Fig. 6b**). The negatively charged surface of the oxygen nanobubbles in this pH range was also observed in other studies (Fan et al., 2021b; Wang et al., 2020). In an acidic solution, excess $H^+$ may attract to the surface of the nanobubbles and increase the zeta potential values, which explains why the bubbles were less negative at low pH. RhB is a typical non-volatile cationic dye, indicating that RhB typically exists in cationic form when in water (Geng and Thagard, 2013). Therefore, the positively charged RhB will adsorb onto the negatively charged oxygen nanobubbles at the bubble-water interface. The •OH radical and shock waves are generated at the gas-liquid interface when bubbles collapse (Agarwal et al., 2011) and contribute directly to the RhB degradation. As a result, after the reactions, the zeta potentials of nanobubbles were

increased from 2 to 7 mV in each group and reached -1.16 to -16.95 mV (**Fig. 6b**). This hypothesis was verified by previous studies showing that the degradation reactions of most non-volatile compounds occur not in the interior of the bubbles but at the bubble-solution interface and in the bulk solution (Hua and Hoffmann, 1996). Thus, it could be inferred that the removal of RhB by oxygen nanobubbles is an interfacial adsorption enhanced ROSs oxidation process.

### *3.4.3 Effect of background ions and organic matter*

The presence of various background components in water, such as ionic strength, hardness, and alkalinity, pose significant challenges for ROS-based AOPs in degrading organic micropollutants from water or wastewater (Liao et al., 2001; Yu et al., 2021). Previous studies have also highlighted the impact of foreign ions on the stability of nanobubbles (Soyluoglu et al., 2022). However, the current findings demonstrate that oxygen nanobubbles can achieve favourable removal efficiency of RhB (exceeding 92%) in the presence of 300 mg/L of background ions, including $Ca^{2+}$, $Mg^{2+}$, $HCO_3^-$, and $Cl^-$ (**Fig. 6c**). There was no statistical difference ($p > 0.05$) in RhB removal rates for systems with and without background ions, suggesting that they have negligible impact on the degradation by oxygen nanobubbles. Due to electrical attraction, the non-volatile cationic dye becomes localised at the bubble-water interface where degradation reactions typically occur (Hua and Hoffmann, 1996). Therefore, the •OH radicals and shock waves generated at the nanobubble-water interface during bubbles collapse (Agarwal et al., 2011) can be directly utilised for RhB degradation, with minimal interference from other existing components. However, a slight decrease in the removal rate was observed, and it followed the order of DI water (97.59%) > $CaCl_2$ (96.25%) > $MgCl_2$ (95.58%) > $NaHCO_3$ (93.22%) > NaCl (92.91%) (**Fig. 6c**). The degradation kinetics in all groups was as good fit to the pseudo-first-order kinetic model, with the degradation constant decreasing from 0.028 $min^{-1}$ in DI water to 0.020 $min^{-1}$ in the presence of $NaHCO_3$ and NaCl (**Fig. S6**). The reduction in degradation efficiency of RhB may be attributed to the scavenging effects of the coexisting ions on •OH radical (Devi et al., 2013; Grebel et al., 2010), which inhibit the oxidation capacity of the nanobubbles. It is generally agreed that organic matter can significantly challenge AOP processes used in water treatment. In this study, the presence of 10 mg/L humic acid (HA) resulted in a significant reduction (70%) in the RhB removal rate during

the oxygen nanobubble AOP treatment (**Fig. 6c**). Amphiphilic HA macromolecules can reduce the concentration of bulk nanobubbles and increase their overall surface potential through hydrophobic interactions or adhesion (Soyluoglu et al., 2021; Sugano et al., 2017), thereby significantly affecting the oxidation potential of oxygen nanobubbles.

Overall, the summary mechanism of RhB degradation by the proposed oxygen nanobubble AOP follows a successive set of distinct phases (**Fig. 7**). In the homogeneous aqueous system, due to the electrical neutralization, the RhB in the cationic form is adsorbed on the liquid-bubble interface by the negatively charged oxygen nanobubbles. Then, the bulk oxygen nanobubbles continuously shrink and eventually collapse to emit significant energy and produce ROSs (•OH, $•O_2^-$, and $^1O_2$). The high redox potential of ROSs, in particular •OH, makes them effectively oxidise RhB. RhB degradation starts from the chemical N-deethylation process, and a series of N-deethylated intermediates are then generated, which can then lead to complete mineralisation of RhB.

**Fig. 7. is here.**

### 3.5 Validation test in real water samples and engineering implications.

To further test the practical feasibility of nanobubble technology-based AOP, experiments on the degradation of RhB were conducted in DI water, tap water, lake water, and secondary effluent for sewage works. **Table 1** summarises the selected water quality parameters of the three real waters. The levels of nitrogen and phosphorus nutrients in secondary effluent were 1.6-2.7 and 1.7-5.0 times higher than the lake water and tap water, respectively. The COD and turbidity also exhibited a similar trend, following the order: secondary effluent > lake water > tap water. The presence of existing inorganic and organic compounds were hypothesised to make the target pollutant more challenging to remove due to the effects of radical quenching and competition reactions (Liao et al., 2001; Soyluoglu et al., 2022). The degradation performance of RhB in tap water (92.18%) and lake water (90.78%) was slightly lower than that seen for DI water (97.59%) (**Fig. 6d**). Moreover, even though the composition of secondary effluent was more complex, the removal efficiency of RhB was still able to 75.32% (**Fig. 6d**). The reduction in the removal rate for RhB was due to the competitions between coexisting organic matter in the real waters with RhB compounds on the available ROSs (Soyluoglu et al.,

406 2022). The differences in the COD levels in the three waters support this point (**Table 1**). After
407 oxygen nanobubbles treatment, the COD levels exhibited significant decreases of 43%-51% in
408 three water matrices, as a result of the degradation of RhB and other organic matters. In addition,
409 the ammonia and total nitrogen decreased by approximately 15 and 10%, respectively (**Table**
410 **1**), a result consistent with that seen elsewhere (Wu et al., 2022b). Based on the above results,
411 the oxygen nanobubble-based AOP has been demonstrated to be a feasible option for RhB
412 removal in real waters.

413 **Table 1 is here.**

414 Due to the generation of highly ROSs, AOPs have become an effective approach for
415 degradation of organic pollutants with complex macromolecular structures. This study
416 demonstrated a novel and functionally effective AOP technology using oxygen nanobubbles
417 that did not produce additional solid wastes, or require application of other additional chemicals.
418 Oxygen nanobubbles achieved equivalent removal and mineralization effects on RhB as seen
419 for conventional AOPs through interfacial adsorption-enhanced ROSs oxidation processes.
420 Compared with RhB, other more refractory organic pollutants are more difficult to oxidize,
421 leading to relatively low removal rates when treated by individual nanobubbles. For example,
422 the stable ring structure of geosmin and 2-methylisoborneol results in <40% removal of these
423 compounds when treated by oxygen nanobubble (Soyluoglu et al., 2022). For these refractory
424 organic pollutants, an integrated approach that combines nanobubble technology with other
425 AOPs may need to be deployed. For example, with the assistance of oxygen nanobubbles, the
426 photodegradation efficiency of oxytetracycline was improved from 28% to 60% (Wang et al.,
427 2020). In addition, the proposed oxygen nanobubble technology can not only improve the
428 efficiency of conventional AOPs in degrading organic pollutants but has also been identified as
429 a means to reduce energy demand and chemical usage in these processes. Although the energy
430 and chemical input for nanobubble generation is expected to be much lower than for other AOP
431 approaches, the cost-benefit analysis and life cycle assessment of the proposed approach should
432 be carried out in scaled-up studies. In summary, this study has presented a green technology
433 using oxygen nanobubbles as an AOP that provides great promise to effectively remove organic
434 micropollutants from water.

## 4. Conclusion

This study has demonstrated that oxygen nanobubble induced AOP can act as an effective and chemical free additive technology for treating organic micropollutants in both synthetic and real water matrices. The removal efficiency of the model micropollutant RhB treated with oxygen nanobubbles were significantly higher than those treated with air and nitrogen nanobubbles. The initial RhB concentrations (0.1-10 mg/L), pH (3-10), and existing ions ($Ca^{2+}$, $Mg^{2+}$, $HCO_3^-$, and $Cl^-$) exhibited negligible effects on ultimate RhB removals by oxygen nanobubble AOP. However, the RhB removal rate was reduced to 70% in the presence of organic matter (HA). The electrical neutralization between oxygen nanobubbles and RhB compounds further enhanced the ROSs oxidation on RhB. The •OH was certified as the primary ROS that contributed to RhB degradation through qualitative and quantitative measurement. The potential degradation pathway of RhB involved the processes of N-deethylation, hydroxylation, chromophore cleavage, ring-opening and final mineralization. Moreover, the practical feasibility of nanobubble-based AOP was further validated from the considerable RhB removals (75.3%-90.8%) when treating real water samples, including natural lake water and secondary treated wastewater effluent. This work provides a new insight into water and wastewater treatment through an innovative and chemical free oxygen nanobubble based AOP.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Author contributions**

**Bangguo Wang:** Investigation, Methodology, Software, Validation, Writing – original draft. **Lijing Wang:** Conceptualization, Investigation, Supervision, Writing – review & editing, Funding acquisition. **Tao Lyu:** Conceptualization, Data verification, Writing – review & editing. **Wenxi Cen:** Formal analysis, Writing – original draft. **Yang Zhang:** Resources, Supervision. **Kaili Zhang:** Resources, Project administration. **Yuanxun Zhang, Yinghui Han and Lei Wang:** Experimental method guidance, Data verification. **Peter Jarvis, Gang Pan and Wei Fan:** Writing – review & editing, Language polishing.

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**Table 1**

Selected water quality parameters (including RhB) for real water samples before and after nanobubble-based AOP treatment.

| | Tap water | | Lake water | | Secondary effluent | |
|---|---|---|---|---|---|---|
| | Before treatment | After treatment | Before treatment | After treatment | Before treatment | After treatment |
| Total phosphorus (mg/L) | 0.14 | 0.13 | 0.29 | 0.30 | 0.48 | 0.46 |
| Labile phosphorus (mg/L) | 0.02 | 0.02 | 0.04 | 0.03 | 0.10 | 0.09 |
| Total nitrogen (mg/L) | 3.5 | 3.1 | 3.7 | 3.4 | 6.1 | 5.3 |
| Ammonia nitrogen (mg/L) | 0.31 | 0.26 | 0.43 | 0.37 | 0.86 | 0.74 |
| COD (mg/L) | 14.1 | 6.8 | 41.3 | 21.1 | 59.5 | 33.9 |
| Average particle diameter (μm) | <DL | <DL | 23.84 | 23.36 | 66.40 | 63.65 |
| Turbidity (NTU) | 0.12 | 0.09 | 1.59 | 1.36 | 17.92 | 16.22 |
| pH | 7.39 | 7.29 | 7.75 | 7.45 | 7.26 | 7.23 |
| RhB removal (%) | | 92.18% | | 90.78% | | 75.32% |

DL: detection limit

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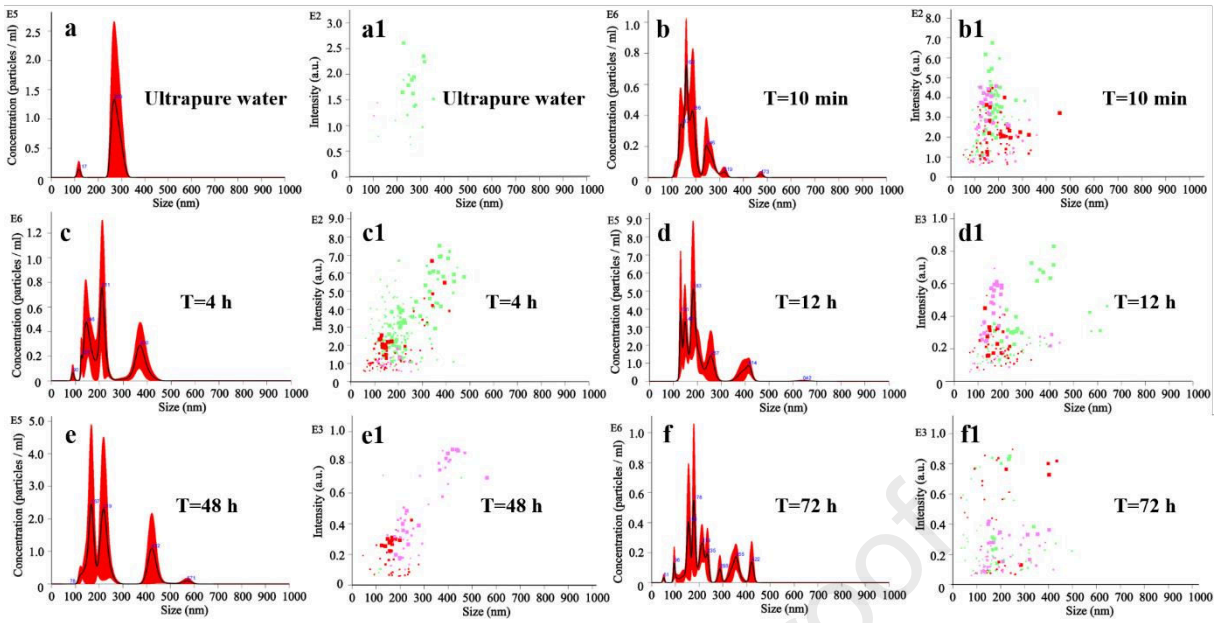



**Fig. 1.** The size and distribution of nanobubbles in ultrapure water (a) and the prepared nanobubble water at 10 min (b), 4h (c), 12h (d), 48h (e), and 72h (f). The operation time of the generation was 10 mins. Different colours in the intensity/size graphs (a1-f1) represent the results from three separate measurements.

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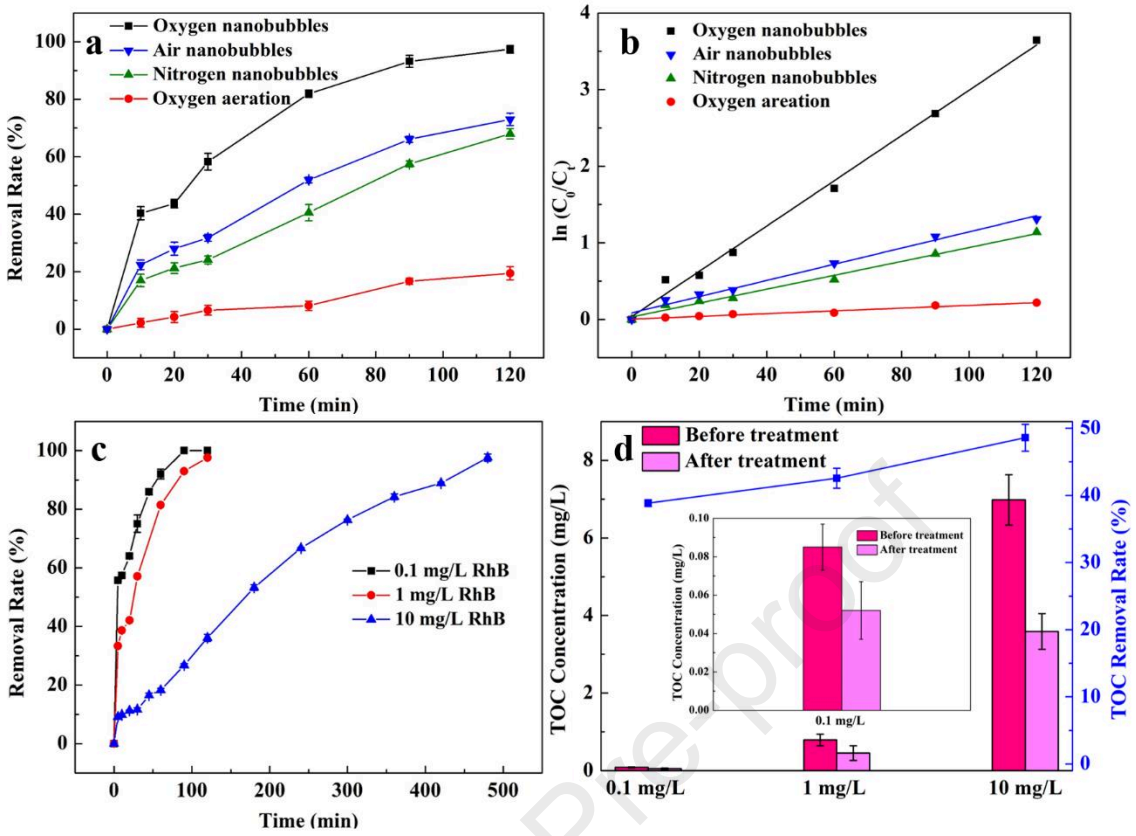



**Fig. 2.** The remove rates of RhB at an initial concentration of 1 mg/L for water treated by oxygen, air and nitrogen nanobubble, and conventional oxygen aeration process (a), as well as the fitted first-order kinetics model (b), the removal rate of RhB by oxygen nanobubble treatment for different RhB initial concentrations (c), the initial and final concentrations of TOC in all treatment groups (d).

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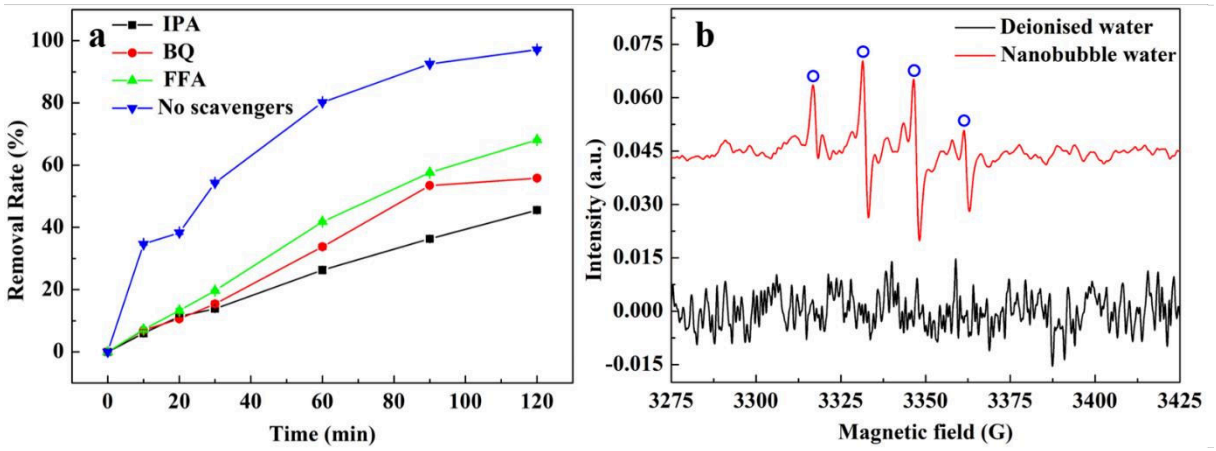



**Fig. 3.** Effect of scavengers on the degradation of RhB at an initial concentration of 1 mg/L (a), ESR evidence for •OH production from oxygen nanobubbles (b).

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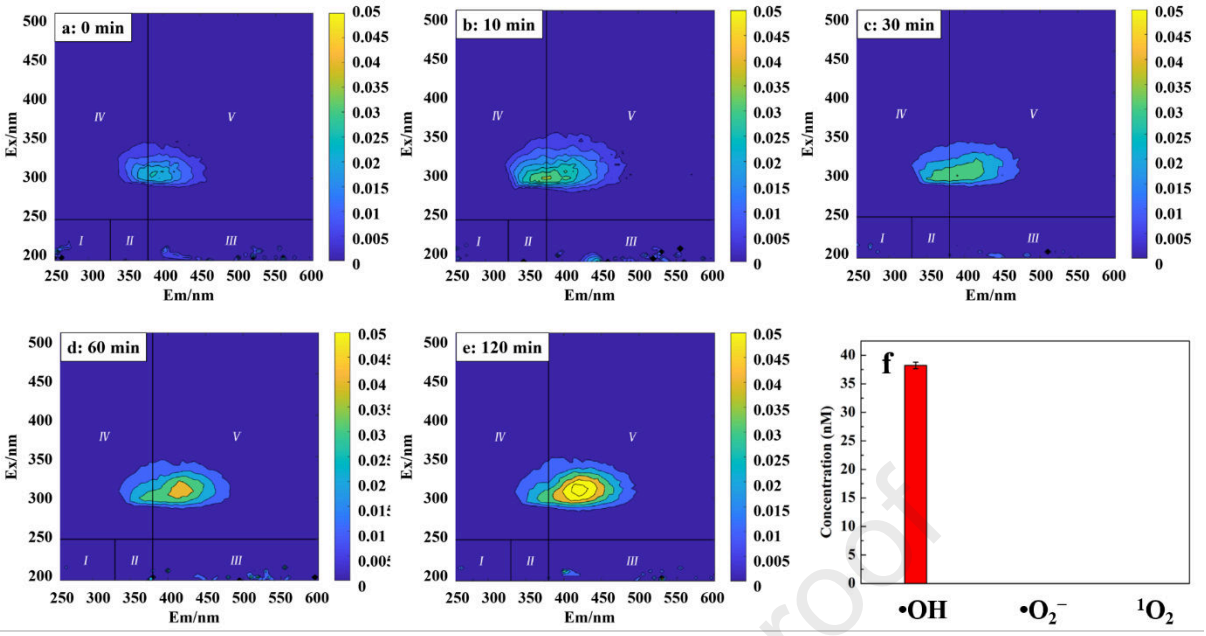



**Fig. 4.** Excitation and emission matrix (EEM) fluorescence spectra of oxygen nanobubble water in the presence of the fluorescent probe at different times (a-e) and the concentrations of ROSs generated in the experimental system (f).

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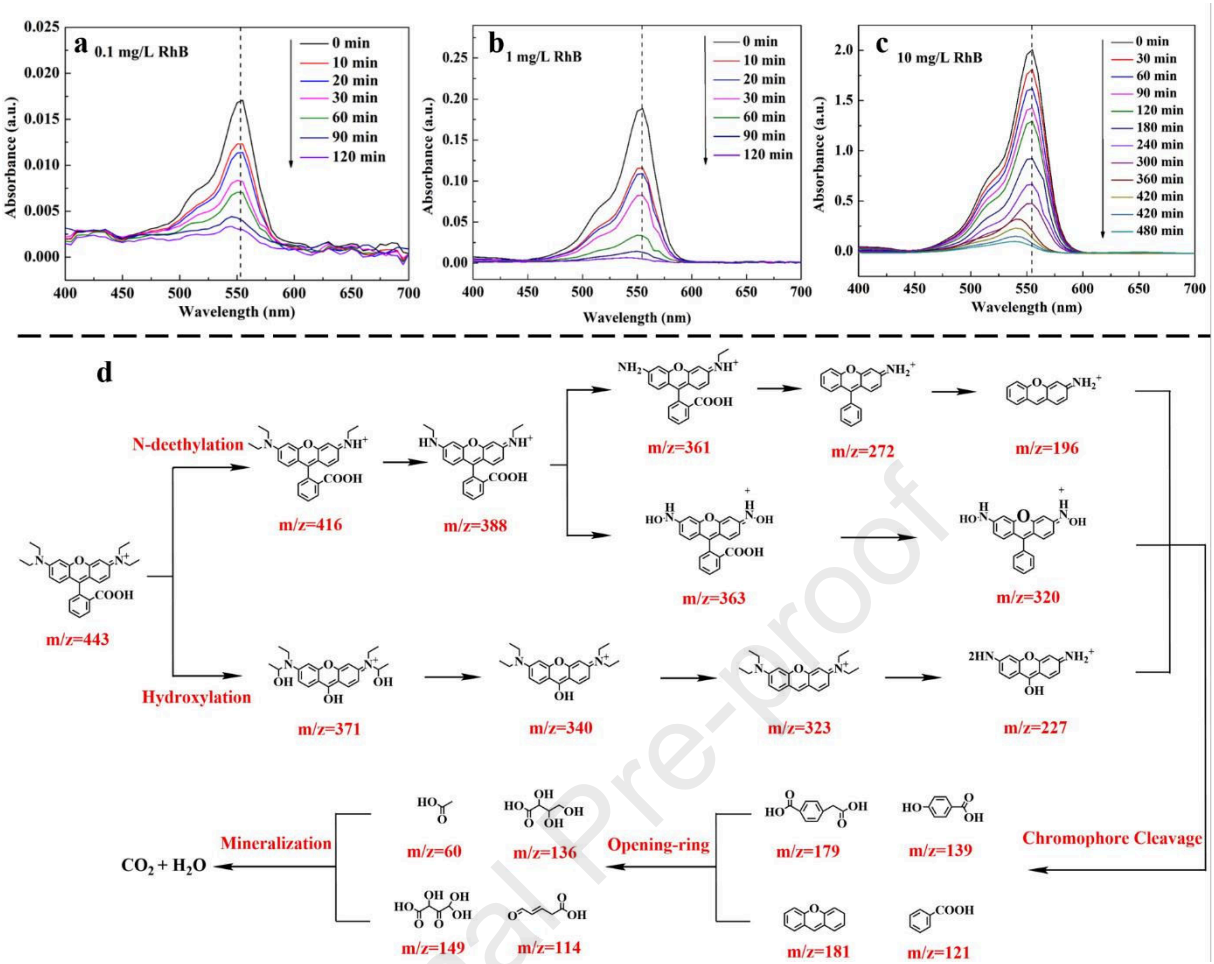



**Fig. 5.** UV-vis absorption spectral variations for RhB at different reaction times for initial dye concentrations of 0.1 (a), 1 (b), and 10 (c) mg/L; the potential degradation pathway of RhB by oxygen nanobubbles (d).

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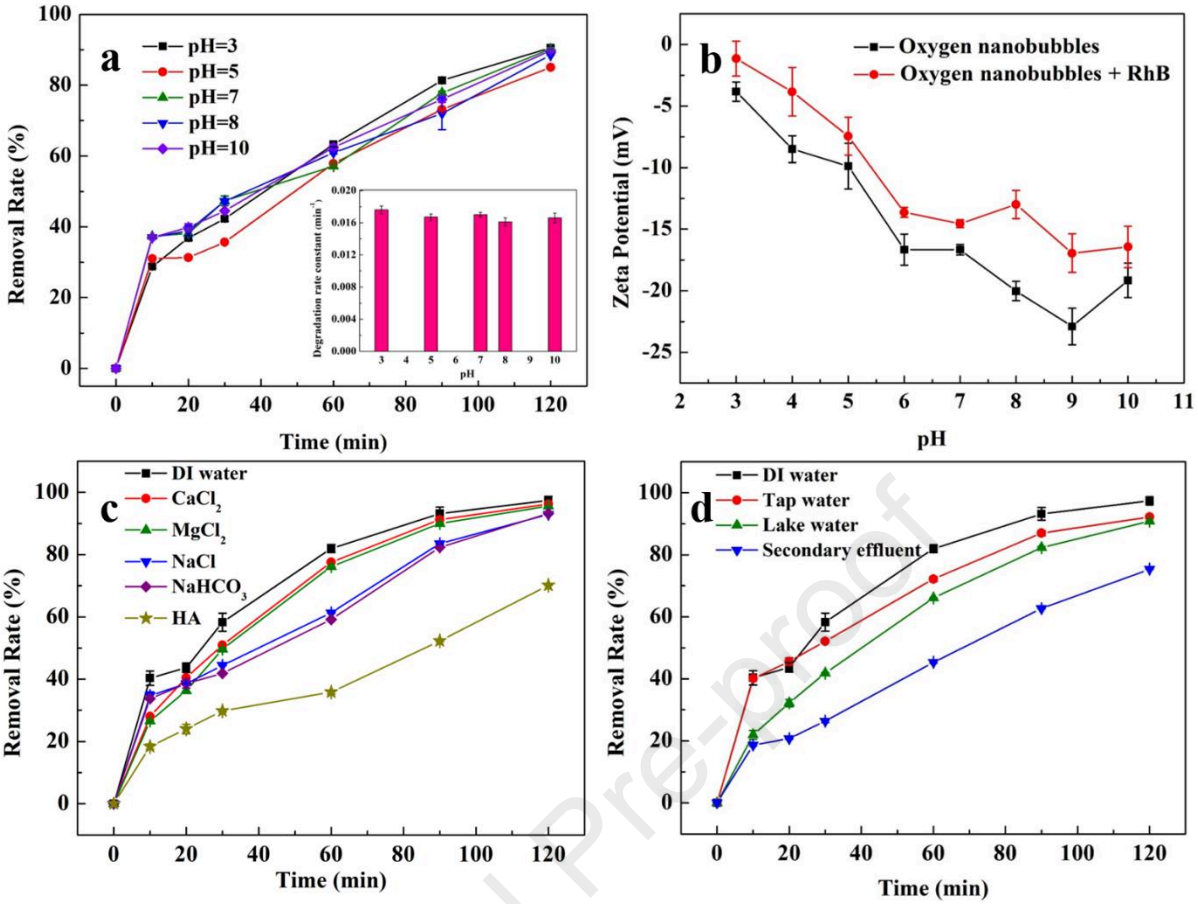



**Fig. 6.** The removal efficiencies of RhB at an initial concentration of 1 mg/L by oxygen nanobubble treatment under initial pH levels of 3-10 (a), the Zeta potential of oxygen nanobubbles before and after reacting with RhB (b), the removal efficiencies of RhB at an initial concentration of 1 mg/L in the presence of different background ions and organic matter (humic acid – HA) by oxygen nanobubble treatment (c) and removal in different real water samples by oxygen nanobubble treatment (d).

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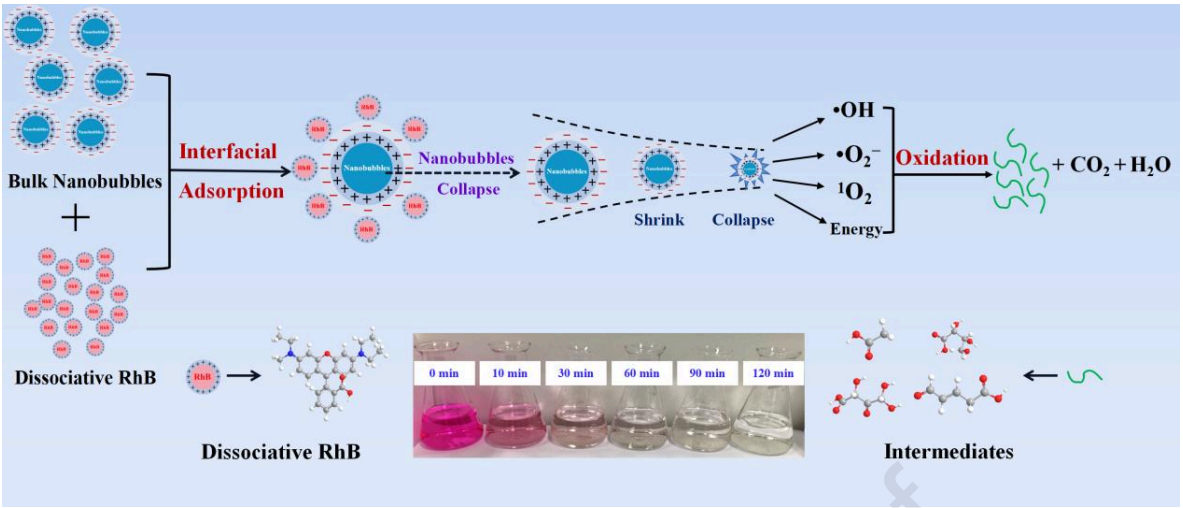



**Fig. 7.** The proposed mechanism of RhB degradation by oxygen nanobubbles.

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**Highlights**

- Nanobubble based advanced oxidation process was effective to remove micropollutant
- Hydroxyl radical dominate the degradation of model micropollutant Rhodamine B (RhB)
- Degradation occurred by electrical attraction and oxidation at bubble-dye interface
- The initial concentrations, pH, and existing ions negligibly affect RhB treatment
- Considerable RhB removals (75.3%-90.8%) were achieved in three real water matrices

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**Bangguo Wang:** Investigation, Methodology, Software, Validation, Writing – original draft. **Lijing Wang:** Conceptualization, Investigation, Supervision, Writing – review & editing, Funding acquisition. **Tao Lyu:** Conceptualization, Data verification, Writing – review & editing. **Wenxi Cen:** Formal analysis, Writing – original draft. **Yang Zhang:** Resources, Supervision. **Kaili Zhang:** Resources, Project administration. **Yuanxun Zhang, Yinghui Han and Lei Wang:** Experimental method guidance, Data verification. **Peter Jarvis, Gang Pan and Wei Fan:** Writing – review & editing, Language polishing.

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**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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# Exploring a chemical input free advanced oxidation process based on nanobubble technology to treat organic micropollutants

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