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# Improving *Microcystis aeruginosa* removal efficiency through enhanced sonosensitivity of nitrogen-doped nanodiamonds

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#### ABSTRACT

Traditional methods for algae removal in drinking water treatment, such as coagulation and sedimentation, face challenges due to the negative charge on algae cells' surfaces, resulting in ineffective removal. Ultrasonic cavitation has shown promise in enhancing coagulation performance by disrupting extracellular polymer structures and improving cyanobacteria removal through various mechanisms like shear force and free radical reactions. However, the short lifespan and limited mass transfer distance of free radicals in conventional ultrasonic treatment lead to high energy consumption, limiting widespread application. To overcome these limitations and enhance energy efficiency, advanced carbon-based materials were developed and tested. Nitrogendoped functional groups on nanodiamond surfaces were found to boost sonosensitivity by increasing the production of reactive oxygen species at the sonosensitizer-water interface. Utilizing low-power ultrasound (0.12 W/ mL) in combination with N-ND treatment for 5 min, removal rates of Microcystis aeruginosa cells in water exceeded 90 %, with enhanced removal of algal organic matters and microcystins in water. Visualization through confocal microscopy highlighted the role of positively charged nitrogen-doped nanodiamonds in aggregating algae cells. The synergy between cell capturing and catalysis of N-ND indicates that efficient mass transfer of free radicals from the sonosensitizer's surface to the microalgae's surface is critical for promoting cyanobacteria floc formation. This study underscores the potential of employing a low-intensity ultrasound and N-ND system in effectively improving algae removal in water treatment processes.

#### 1. Introduction

In light of the frequent occurrence of cyanobacteria blooms in water sources, the development of safe and efficient water treatment technologies for removing cyanobacteria has become an urgent scientific and technological imperative in the realm of drinking water treatment. Current methods like chemical pre-oxidation, coagulation, and sedimentation face challenges in maintaining water quality and operational efficiency [1–3]. The hydrophilic nature and negative charge of cyanobacteria's extracellular polymer hinder effective coagulation, leading to poor algae removal. Chemical pre-oxidation, involving chlorine, ozone, or permanganate, can disrupt extracellular polymer structures, but precise dosing is complex, risking algae cell rupture and algal organic matters release [4–6]. Collaboration between photocatalysis and nanomaterials can oxidize cyanobacteria using free radicals, preserving cell integrity. However, limited light penetration and shortlived free radicals pose challenges, hindering effective diffusion in water [7]. Addressing the regulation of oxidation reactions using free radicals to disrupt cyanobacteria structures, enhance coagulation, and manage organic matter release is crucial for ensuring safe drinking water through pre-oxidation and algae removal.

Ultrasonic algae removal technology utilizes ultrasound energy to effectively control algae, offering advantages over photocatalysis as it is unaffected by water turbidity. A number of studies have demonstrated the efficacy of ultrasonic removal/inactivation in combating harmful algae [8–11] and microcystins [12]. Rupture of gas vacuoles is proposed as a mechanism for ultrasonic algae removal [13]. A study by Peng et al. revealed varying removal rates of cyanobacteria at 20 kHz (0.038 W/ mL, ultrasonic probe), 740 kHz (0.113 W/mL, ultrasonic bath), and 1120 kHz (0.108 W/mL, ultrasonic bath) frequencies after 15 min of

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ultrasonic treatment – approximately 10.5 %, 9.5 %, and 35.4 %, respectively [14]. Moreover, another investigation documented a substantial cyanobacteria inactivation rate exceeding 85 % following ultrasonic treatment at 20 kHz and 0.403 W/mL for 30 min [15]. These findings underscore the promising potential of ultrasonic algae removal technology in effectively addressing cyanobacteria and enhancing water quality through targeted and efficient treatment methods.

Ultrasonic-enhanced coagulation has demonstrated efficacy in algae cell removal. Research by Zhang et al. [16] revealed a substantial increase in the coagulation removal rate of cyanobacteria cells from 35 % to 67 % within a brief timeframe (5 s) through ultrasonic pretreatment (150 kHz, 0.03 W/mL). Li et al. [17] highlighted that high-frequency ultrasonic pretreatment at 740 kHz and 0.02 W/mL results in minimal protein leakage and free radical generation over a 5-minute period. Liu et al. [18] observed that a short duration of less than 30 s of low-frequency ultrasonic pretreatment at 40 kHz and 1.0 W/mL significantly enhances coagulation performance. Ultrasonic treatment at specific frequencies and power levels has shown significant cyanobacteria inactivation rates, reinforcing the potential of ultrasonic algae removal technology in enhancing water quality effectively.

Recent studies have revealed the significant synergistic role of carbon-based nanomaterials in sonodynamic catalysis [19–23]. These nanomaterials exhibit exceptional sonodynamic therapy properties that facilitate the generation of free radicals, thereby boosting cell inactivation efficiency. Nonetheless, the precise catalytic mechanisms of these sonosensitizers warrant further investigation. Moreover, it should be noted that while research highlighting the removal of inactivated cyanobacteria using light/nano-materials is prevalent, there is a notable scarcity of studies on the removal of algae cells through the combination of ultrasound and novel nanomaterials.

Nanodiamonds (ND), a novel carbon nanomaterial, possess commendable attributes such as small size, extensive specific surface area, and robust electrical conductivity. These attributes render ND easily modifiable with various reagents, providing ample active sites for efficient adsorption processes. Consequently, ND is regarded as a highly promising material for environmental treatment [24–26]. The presence of graphene ND enables high catalytic activity in peroxide oxidation reactions, highlighting its potential for efficient sonochemical catalysis. Additionally, the inherent stability of nanodiamond ensures remarkable robustness and safety, especially in biological settings. These favorable characteristics position ND as a leading candidate material for investigating the catalytic mechanisms of sonosensitizers, emphasizing its crucial role in advancing the comprehension of nanomaterial-assisted sonodynamic reactions. If the unique properties of nanodiamonds, such as improved enhanced catalytic activity offer significant advantages over conventional materials in large-scale applications, the higher production costs may be justifiable.

To enhance the effectiveness and sustainability of ultrasonic preoxidation for algae removal in drinking water treatment and facilitate algae coagulation using aluminum sulfate coagulant, we propose a novel approach that combines low-intensity ultrasound with a positively charged sonocatalyst to amplify free radical generation (Scheme 1). This innovative strategy aims to improve the transfer of short-lived free radicals to the surfaces of negatively charged algae cells, thereby optimizing pre-oxidation performance. Our research involves the characterization of advanced carbon-based materials to investigate their influence on sonosensitivity. Through the evaluation of nitrogen-doped nanodiamonds' ability to generate free radicals under varying ultrasonic intensities, we assess the efficiency of algae removal and its impact on water quality within the ultrasonic pre-oxidation system. The positively charged nature of nanodiamonds facilitates the transfer of free radicals, playing a vital role in promoting cyanobacteria floc formation. This study represents a potential towards developing a precise, efficient, and environmentally friendly ultrasonic pre-oxidation technology for algae removal in water treatment.

#### 2. Methods

#### 2.1. Characterization of nano-diamonds

The TEM spectrum was analyzed using the FEI Tecnai AI G2 F30s transmission electron microscope, operating at 300 kV produced by



Scheme 1. Diagram depicting the use of nitrogen-doped nanodiamonds to enhance algae removal efficiency in drinking water treatment via Improved Sonosensitivity.

American Fei Company. For sample preparation, a small amount of samples was dispersed in quantitative ethanol solution, followed by 5 min of ultrasonication, and then dropped onto a copper mesh (200/200 double square hole copper mesh) for testing. Analysis of the elements and valence states on the diamond surface was conducted using the ESCALAB 250Xi X-ray photoelectron spectrometer from Thermo Scientific Company, USA, with a scanning range of 0-1300 eV and peak positions calibrated to C1 s (284.6 eV). XRD patterns were analyzed using the AXS D8 ADVANCE polycrystalline X-ray diffractometer from Bruker AXS, Germany, with a scanning speed of 4°/min and a single sample scanning time of 20 min. The radiation source was the Cu target line ( $\lambda$ = 1.5418 Å) with a scanning range of 10-80°. Raman spectra were analyzed using the laser confocal Raman spectrometer from Renishaw in Via, UK. Oxygen vacancy analysis was conducted using the A300-10/12 paramagnetic resonance spectrometer from Bruker Company, Germany. Specific surface area and pore size analysis using the BET method utilized the Quadrasorb EVO from Anton Paar Company, USA.

# 2.2. Investigation of ultrasonic chemical reaction process for free radical generation

#### 2.2.1. Ultrasonic equipment

An 800 kHz ultrasonic device equipped with a disk-type transducer (HM800, Hanmei Co. Ltd., Taizhou, China) was employed to generate high-frequency ultrasound. The diameter of the ultrasonic disk is 1 cm. The ultrasonic intensity of each system was assessed through calorimetry. To measure free radical generation in the ultrasonic systems, potassium iodide dosimetry was utilized.

#### 2.2.2. Determination of $H_2O_2$ yield

To measure free radical generation in the ultrasonic systems, potassium iodide dosimetry was utilized. The initial concentration of potassium iodide is set at 1 mmol/L. In a 50 mL glass reactor, 1 mg of nanodiamond, 50 mL of KI solution, and 100  $\mu$ L of CCl<sub>4</sub> are mixed, and ultrasonic intensity is adjusted before placing an 800 kHz ultrasonic probe at the bottom of the beaker [27]. Ultrasound gel is applied between the probe and the beaker, followed by ultrasonic treatment for 0, 2, 5, 7, and 10 min. The amount of iodine produced is determined using ultraviolet–visible spectrophotometry at a wavelength of 354 nm through a standard curve of iodine solution. Each experiment is conducted in triplicate, with KI solution without nano-diamond serving as the control group.

#### 2.2.3. Rhodamine B degradation using high-frequency ultrasound

To delve deeper into the oxidation performance of the system, the efficiency of rhodamine B dye (RhB) removal was evaluated through high-frequency ultrasound both with and without a catalyst. The selection of Rhodamine B for the experiments was based on its common use as a fluorescent dye for detecting hydroxyl radicals. The initial concentration of the rhodamine B solution is 10 mg/L. In a 50 mL glass reactor, 1 mg of nano-diamond, 20 mL of rhodamine B solution, and 100  $\mu$ L of CCl<sub>4</sub> are combined. The beaker is immersed in an ultrasonic cleaning tank filled with water for varying durations of 0, 0.5, 1, 3, and 5 min, ensuring the liquid levels are consistent between the beaker and the tank. Using the standard curve of rhodamine B solution, the absorbance of rhodamine B is measured through ultraviolet–visible spectrophotometry at a wavelength of 554 nm. Each experiment is replicated three times, with a rhodamine B solution lacking nano-diamond serving as the control group.

#### 2.2.4. Free radical scavenger experiment

Tert-butanol (TBA) was chosen as a free radical scavenger agent, and different concentrations of TBA were added to the experimental system to explore the degradation mechanism of rhodamine B removal by ultrasound.

#### 2.2.5. Density Functional Theory (DFT) simulation

Density Functional Theory (DFT) simulation is used to investigate the adsorption energy of water (H<sub>2</sub>O) molecules adsorbed on the surface of ND and graphitized N-ND [23]. DFT calculations were conducted utilizing the Vienna Ab-initio Simulation Package (VASP) [28,29]. The exchange–correlation interactions were elucidated using the generalized gradient approximation (GGA) [30] with the Perdew–Burke–Ernzerhof (PBE) functional [31]. Spin-polarization was incorporated in all computations, along with a damped van der Waals correction utilizing Grimme's method to more accurately represent non-bonding interactions [32]. The plane wave cut-off energies were established at 500 eV, and the residual force and energy convergence criteria during atom relaxation were set at 0.005 eV Å<sup>-1</sup> and  $10^{-5}$  eV, respectively.

The adsorption energy (Ead) is given by the equation:

$$E_{ad} = E_{surf+H_2O} - E_{H_2O} - E_{surf}$$
<sup>(1)</sup>

Here,  $E_{surf+H_2O}$  represents the total energy of the material adsorbed with  $H_2O$ ,  $E_{H_2O}$  stands for the total energy of  $H_2O$ , and  $E_{surf}$  denotes the total energy of the material.

#### 2.3. Ultrasonic algae removal experiment

#### 2.3.1. Selection of algae species and determination of biomass

*Microcystis aeruginosa*, sourced from the freshwater algae bank of the Chinese Academy of Sciences under the designation FACHB-905, was utilized in the experiment. The algae were cultured in a light incubator (model: GZP-300C) at a temperature of 25 °C using BG11 medium. Prior to the experiment, the algae culture in the logarithmic growth phase underwent centrifugation at 3500 rpm, followed by suspension in sterilized distilled water for subsequent use. The concentration of *Microcystis* cells is measured by haemocytometer (details were provided in supplementary material), and the removal rate in the experiment is calculated by the formula below:

Removal rate = 
$$(C_0 - C_1)/C_0 \times 100 \%$$
 (2)

Where:

 $C_0$  represents the initial number of algae cells before the reaction,  $C_1$  represents the number of algae cells after the reaction.

#### 2.3.2. Ultrasonic treatment of algae cells

The initial concentration of *Microcystis aeruginosa* solution was  $1.5 \times 10^6$  cells/L. In a 50 mL glass reactor, 1 mg of nano-diamond and 20 mL of *Microcystis aeruginosa* solution were combined. The beaker was immersed in an ultrasonic cleaning tank filled with water for treatment durations of 0, 0.5, 1, 2, 5, 7, and 10 min. The cell number of algae post-treatment were determined using haemocytometer. Each experiment was conducted three times, with the algae solution without nano-diamond serving as the control group.

#### 2.3.3. Cell observation

To examine the surface characteristics of *Microcystis* cells, a combination of settled cells and catalysts was observed using confocal microscopy (LSM 880, Carl Zeiss, Germany). Images of the *Microcystis* cells in their unoxidized state were captured, and the formations resulting from the interaction between cells and carbon catalysts post-oxidation and sedimentation were documented as *Microcystis* flocs. For cell supernatant, approximately 50,000 cells were sorted using flow cytometry (BD FACS Canto II, Becton Dickinson, Franklin Lakes, USA). The Invitrogen L10316 LIVE/DEAD BacLight bacterial viability kit (Fisher Scientific, USA) was utilized to assess the proportions of intact/viable (Syto-9 stained) and damaged/non-viable (Propidium iodide stained) cells within the sample. Green fluorescence emitted from the SYTO-9 stained samples under excitation from an argon laser (488 nm) was captured through a 550 nm bandpass filter, while red fluorescence from Propidium iodide was detected through a 610 nm bandpass filter.

#### 2.3.4. Coagulation experiment

After ultrasonic treatment, the reaction container was transferred to a blender at room temperature for further experimentation. A measured amount of aluminum sulfate flocculant was added to achieve a concentration of 6 mg/L. The *Microcystis* solution was initially vigorously stirred using a magnetic stirrer at 200 rpm for 2.5 min for thorough mixing. Subsequently, the stirring speed was reduced to 40 rpm for 10 min, followed by a 30-minute settling period. The supernatant sample extracted from 2 cm below the surface was carefully separated from the floc to assess the concentration of algae cells, COD, and microcystin content.

#### 2.3.5. Water quality analysis

The water samples were analyzed using a Chemical Oxygen Demand (COD) detection kit (COD detection reagents, Suijing Environmental Protection Technology Co., Ltd., Henan, China) and a water quality detector (SG-JL600, Suijing Environmental Protection Technology Co., Ltd., Henan, China) to indirectly assess cell integrity and the release of intracellular organic matter. The COD content in the water sample reflects these aspects, and the determination method follows the instructions provided in the kit. The microcystin content is determined using the Beacon Microcystin Plate kit and the 318-MC microplate analyzer. This measurement indirectly reflects cell integrity and the release of intracellular microcystins (MCs) based on the content of dissolved MCs in the water samples.

#### 3. Results and discussion

#### 3.1. N-ND

The XPS spectra of both ND and N-ND (see Fig. 1) indicate the presence of C, N, and O elements. In the C1s spectrum (Fig. 1), the functional groups observed at 284.4 eV and 285.9 eV correspond to

C=C and C-C bonds [33]. It is evident that the surface C content of ND is lower than that of N-ND, with a higher proportion of C-C functional groups in ND, while C=C groups predominate in N-ND. The study reveals that C=C content is even less than that of C-C. Examining the O1s spectrum (Fig. 1), two main peaks are discernible, denoted primarily as quinone or pyrone at 530.1 eV, and as carbonyl group (C=O) at 531.9 eV [34]. Interestingly, the O element content on the surface of N-ND is lower than that of ND, possibly due to the transformation of some carbonyl groups into other oxygen-containing substances during hightemperature annealing. Within the N1s spectrum (Fig. 1), XPS analysis demonstrates an increase in nitrogen content from 1.78 % in ND to 2.55 % in N-ND, suggesting successful addition of some N elements to the ND surface following melamine decomposition at high temperatures. The N1s spectrum can be deconvoluted into three sub-peaks representing distinct chemical bond states. Notably, the peak at a binding energy of 398.3 eV corresponds to pyridine nitrogen, while the peak at 399.2 eV represents lactam or cyanonitrogen, associated with N atoms combining with sp<sup>3</sup>-coordinated C atoms [35]. The 400 eV peak corresponds to graphite nitrogen, attributed to substituted N atoms (N-sp<sup>2</sup>C bond) combining with  $sp^2$ -coordinated C atoms in  $sp^2$  graphite configuration, positioned at a higher binding energy of 402.5 eV [36]. The presence of graphite nitrogen peak in the N1s spectrum of N-ND supports the presence of a graphitized shell on the N-ND surface, aligning with the findings of our previous work involving XRD and TEM analyses [37].

In Fig. 2, the specific surface area ( $S_{BET}$ ) value of ND is measured at 230.0 m<sup>2</sup>g<sup>-1</sup>, while that of N-ND is recorded at 367.6 m<sup>2</sup> g<sup>-1</sup>. The increased specific surface area of N-ND offers a larger contact area for pollutants. For sonosensitizers, the enhanced surface area provides more active sites, consequently improving sonosensitivity. Referring to Fig. 2b, the adsorption–desorption isotherms of both ND and N-ND exhibit characteristics of type IV, and the pore size distribution is evident from Fig. 2c. Micropores are predominant in both ND and N-ND, with N-ND exhibiting a slightly smaller average pore size compared to



Fig. 1. XPS spectrum of ND and N-ND a) full spectrum; B-d) C1s, O1s, N1s.



Fig. 2. Characteristics of ND and N-ND. (a) S<sub>BET</sub>; (b) Nitrogen adsorption-adsorption isotherms; (c) pore size distribution plots; (d) EPR spectra; (e) Raman; (f) Zeta of ND and N-ND.

ND. In the EPR oxygen vacancy analysis (Fig. 2d), a distinct peak is observed in the spectra of both ND and N-ND, indicating the presence of prominent oxygen vacancies in both materials, aligning with the findings from the O 1 s XPS spectra. The abundance of oxygen vacancies (OVs) may facilitate electron capture (e<sup>-</sup>) and enhance the exposure of active sites on the surface of sonosensitizers [38].

The Raman spectrum, depicted in Fig. 2e, indicates features of the nano-diamond materials. The spectrum of ND reveals a Raman peak at 1325 cm<sup>-1</sup>, characteristic of nano-diamonds with sp<sup>3</sup> structure. In contrast, for the untreated nano-diamond (N-ND), two distinct peaks are observed. This occurrence can be attributed to the phase transition experienced by nano-diamonds from diamond to graphite during high-temperature vacuum annealing. The first broad peak, appearing at approximately 1360 cm<sup>-1</sup> (referred to as the D peak), results from sp<sup>2</sup> ring motions. The second peak, located at 1580 cm<sup>-1</sup> (known as the G peak), showcases graphite-like characteristics, indicating the formation of a graphite structure post-annealing at 1000°C [39]. Zeta potential

data, detailed in Fig. 2f, highlights the potential values of -29 mV and 34.6 mV for ND and N-ND, respectively. The negative zeta potential observed in untreated powder stems from the coverage of most diamond surfaces by oxygen-containing groups, such as carboxyl, carbonyl, alcohol, and ether, which are generated during nano-diamond production and acid purification processes. The negatively charged potential is attributed to the dissociation of these carboxyl groups (COOH) and carbonyl groups (C=O) on the diamond particle surfaces [40]. Conversely, N-ND, following high-temperature annealing, exhibits a positive zeta potential, possibly due to the emergence of a graphite shell (sp<sup>2</sup>) and certain nitrogen-containing functional groups on the N-ND surface [41].

In the material characterization section, we employed XPS, BET, Raman spectroscopy, oxygen vacancy analysis, and Zeta potential measurements to analyze and characterize ND and N-ND. Through comparison, it was observed that the prepared N-ND, in comparison to unmodified ND, not only exhibits a higher presence of N elements on the material surface but also undergoes hybridization with sp<sup>2</sup>, resulting in the formation of a graphitized shell. Post-modification, the N-ND material displayed a larger specific surface area, the generation of oxygen vacancies, acquired a positive charge, and exhibited functional groups such as Pyridinic N and graphitic N. These attributes are expected to contribute to the exceptional catalytic performance of N-ND.

#### 3.2. Sonochemical performance

To demonstrate the sonosensitivity of N-ND, we conducted  $H_2O_2$  productivity testing. Fig. 3a-b illustrates the results of  $H_2O_2$  production in a KI solution when combined with N-ND under ultrasonic treatment. At an ultrasonic intensity of 0.12 W/mL, the N-ND ultrasonic system generated twice the amount of  $H_2O_2$  compared to pure ultrasound (Fig. 1a). When the ultrasonic intensity was increased to 1.17 W/mL, the production of  $H_2O_2$  by the N-ND ultrasonic system was three times higher than that of pure ultrasound (Fig. 1b).

The change in radius of a single cavitation bubble under different ultrasound intensities was simulated (Fig. 3c-d). The simulations that were performed following a previous work [27]. The results revealed that the variation in cavitation bubble radius intensified with increasing ultrasound intensity. The increased cavitation intensity in a single cavitation bubble could facilitate the generation and mass transfer of free radicals. Moreover, a higher concentration of N-ND resulted in a greater quantity of produced  $H_2O_2$  (Fig. 3a-b). This could be explained by a previous work, we observed that N-ND may act as gas nuclei in ultrasonic cavitation, enhancing cavitation intensity [37]. The result confirmed that N-ND could enhance the  $H_2O_2$  generation from ultrasonic cavitation.

Additionally, in temperature experiments (Fig.S1) we found that within the temperature range of 15–45 °C, higher temperatures

correlated with increased  $H_2O_2$  production. Notably, at an ultrasonic intensity of 0.12 W/mL, the  $H_2O_2$  production levels at 15 °C and 25 °C were similar, possibly due to the limited number of cavitation bubbles at lower ultrasonic intensities, resulting in less temperature dependence. However, at an ultrasonic intensity of 1.17 W/mL, significant variations in  $H_2O_2$  production were observed between temperatures, signifying that as temperature rises, gas-core liquid surface tension and viscosity decrease, promoting cavitation occurrence. By integrating literature findings and experimental data, we assert that N-ND effectively enhances  $H_2O_2$  production under ultrasonic influence. Even at low ultrasonic intensities (0.12 W/mL), N-ND responds to ultrasound excitation to produce  $H_2O_2$ , confirming its sonosensitivity.

In recent years, theoretical and experimental studies have demonstrated that free radicals and electrons can be generated at the gas-liquid interface of droplets, with the generated electrons subsequently initiating the single-electron reduction process of other substrate molecules [42]. Motivated by these research, we have developed a hypothesis on how N-ND influences the chemical reaction at the gas-liquid interface of cavitation bubbles. During ultrasonic cavitation, •OH radicals (as per equation (3) are produced at the gas-liquid interface. These •OH groups can quickly recombine to generate  $H_2O_2$  (equation (4), featuring redox properties. It is worth noting that in many cases, •OH radicals and •H radicals lead to the production of H<sub>2</sub>O. However, when activated by acoustic cavitation-generated energy, N-ND may produce electrons and holes (as in equation (5)). The holes could react with  $H_2O$  to generate •OH. On the other hand, Zhang et al. proposed that electrons serve as carriers mediating redox reactions on water droplets, setting the stage for subsequent chemical reactions such as bond fracture and formation. In this regard, within the ultrasound field, with H<sub>2</sub>O<sub>2</sub> acting as a substrate, the reaction with electrons supplied by N-ND results in its decomposition into water and oxygen (equation (7). If oxygen is



Fig. 3. Ultrasonic effects. The factors affecting the production of  $H_2O_2$  by N-ND of two different intensities of ultrasonic radiation (a) 0.12 W/mL and (b) 1.17 W/mL; Bubble radius-time profile for a single bubble exposed to 800 kHz ultrasound at (c) 0.12 W/mL and (d) 1.17 W/mL.  $R_0$  is set as 5  $\mu$ m.

available, it can react with protons and electrons to produce  $H_2O_2$  (equation (8) [43]. In this way, the  $H_2O_2$  with oxidizing capability is being continuously produced. And through the thermodynamic action of ultrasonic cavitation,  $H_2O_2$  can generate highly oxidizing • OH (equation (9).

$$H_2O \rightarrow \bullet OH + \bullet H \text{ (sonolysis)}$$
 (3)

• 
$$OH + •OH \rightarrow H_2O_2$$
 (4)

$$N-ND \rightarrow N-ND^* + h^+ + e^-$$
(5)

$$H_2O+h^+ \rightarrow \bullet OH$$
 (6)

$$H_2O_2 + e^- \to H_2O + O_2$$
 (7)

$$O_2 + 2 e^- + H^+ \to H_2O_2$$
 (8)

$$H_2O_2 \rightarrow \bullet OH \text{ (sonolysis)}$$

In addition, when  $H_2O_2$  is used as a substrate and introduced into the system of N-ND and ultrasound at the specified ultrasonic intensities (Fig. S1e,f), the concentration of  $H_2O_2$  decreases. Based on experimental observations (a decrease in  $H_2O_2$  concentration) and the mechanisms outlined in literature [42], we posit that N-ND can furnish electrons for the chemical reactions mediated by acoustic cavitation within the sound field.

Furthermore, depicted in Figure S1 a-b, the pH level has minimal impact on the ultrasonic system when the sonosensitizer N-ND is introduced, with the treatment effect being comparable to that of pure ultrasound. This indicates that pH does not significantly affect the acoustic sensitivity of N-ND. In contrast, the conventional Fenton oxidation reaction is strongly pH-dependent, necessitating additional adjustment and potentially causing reactor corrosion. The N-ND&US system demonstrates the ability to effectively generate free radicals under neutral conditions, highlighting the advantage of this system.



(9)

Fig. 4. Effect of *tert*-butanol (TBA) concentration on degradation of Rhodamine B in different ultrasonic systems (a) 800 kHz (0.12 W/mL) ultrasound; (b) 800 kHz (1.17 W/mL) ultrasound; (c) 800 kHz (0.12 W/mL) ultrasonic + ND; (d) 800 kHz (1.17 W/mL) ultrasound + ND; (e) 800 kHz (0.12 W/mL) ultrasonic + N-ND; (f) 800 kHz (1.17 W/mL) ultrasonic + N-ND.

To further investigate the oxidation performance of the system, the

removal efficiency of rhodamine B dye (RhB) using high-frequency ultrasound with and without a catalyst was tested, as illustrated in Fig. 4. Comparing the two ultrasonic systems, it was noted that the removal rate of RhB increased with higher ultrasonic intensities. When the ultrasonic intensity was set at 1.17 W/mL, the addition of the N-ND catalyst enhanced the degradation efficiency when compared with the ultrasonic system using solely ultrasound and ND. In the presence or absence of the catalyst, the ultrasonic-assisted degradation process of RhB can be modelled using a pseudo-first-order kinetic model (Fig.S2). The apparent rate constant, as depicted by the slope of the fitting line, varies with different catalysts, with N-ND and 1.17 W/mL ultrasound displaying the highest sonochemical degradation rate constant and consequently achieving the highest degradation efficiency (99.8 %). This emphasizes that N-ND can enhance ultrasonic cavitation effects and increase the production of free radicals.

To determine the primary free radical involved in the degradation process, TBA solutions of varying concentrations were introduced into the degradation system. As observed in Fig. 4, the degradation rate of RhB and the final degradation rate in all three systems decreased as the TBA solution concentration increased, indicating that the primary free radical responsible for the degradation of RhB is the hydroxyl radical (•OH). Additionally, this confirms that the N-ND catalyst exhibits commendable sonocatalytic activity at various ultrasonic intensities.

In order to explore the types of free radicals produced by ultrasound and N-ND, EPR was tested, and the results are shown in Fig. 5. The signal of DMPO-OH (1:2:2:1) was obtained in each ultrasonic system, which confirmed that the free radicals were mainly hydroxyl radicals(•OH). This confirms our speculation about the sonocatalytic mechanism of N-ND (equation (1)–(4). It can be seen from the figure that the higher the ultrasonic intensity, the more obvious the free radical signal, probably because the stronger the ultrasonic intensity, the more free radicals are produced. And the N-ND ultrasonic system has more carbon free radical signals than other systems. Combined with the data of material characterization, we successfully introduced nitrogen functional groups, including pyridine, pyrrole, graphite nitrogen, into nano-carbon materials. These functional groups can effectively enhance the basicity of the catalyst [44,45]. These Lewis bases, which are rich in unpaired electrons, can break the hydrogen bond between  $H_2O$  molecules, better adsorb water molecules and reduce the reactivity of free water. The charge trends of  $H_2O$  adsorbed on the surface of ND and graphited N-ND were compared by DFT simulation (Fig. 5). It is generally believed that the more electrons gather in the bonding region between  $H_2O$  and surface functional groups, the more stable the adsorption of  $H_2O$  molecules. As can be seen from the Fig. 5a-b, when  $H_2O$  is adsorbed on the graphed N-ND surface, the electron aggregation is mostly Nd, so the ability of graphed N-ND to adsorb  $H_2O$  molecules is enhanced, which is beneficial to activate water molecules into hydroxyl radicals.

The combination of ultrasound and a sonosensitive agent represents a novel strategy for cell inactivation inspired by photodynamic therapy. In this integration, low-intensity ultrasound (US) is utilized to stimulate the electrons in the sonosensitizer, prompting them to transition from the valence band to the conduction band. The subsequent separation of electrons and holes leads to their individual reactions with water molecules, yielding hydroxyl radicals (•OH) with significant biological toxicity, ultimately inducing cell death. The therapeutic efficacy of Sonodynamic Therapy (SDT) heavily relies on the sonodynamic performance of the sonosensitizer. Inorganic semiconductor nanomaterials like titanium dioxide (TiO<sub>2</sub>) possess a wide bandgap structure and exhibit rapid recombination of electron-hole pairs, limiting their ability to generate sufficient Reactive Oxygen Species (ROS) for cell death. On the other hand, carbon-based nanomaterials can efficiently harness the energy from inertial cavitation and convert it into ROS, leading to the production of hydroxyl radicals (•OH) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) [20]. Previous studies have confirmed that pyrrole N and pyridine N present in N-doped graphene quantum dots serve as reaction sites during the sonochemical process [23]. Additionally, the p-n junction in quantum dots effectively suppresses electron-hole pair recombination, allowing excited holes to efficiently consume reducing organic compounds within the microenvironment. This process enhances oxidation efficiency, thereby promoting inactivation [19].



Fig. 5. Adsorption between  $H_2O$  and surface functional groups: (a) N-ND, (b) ND; (c) The EPR spectrum obtained by DMPO spin capture in different oxidation systems Conditions: pH=7.0, ND/N-ND 20 mg/L, 10  $\mu$ L/mL DMPO. In the DFT simulations, the charge distribution of  $H_2O$  adsorbed on the surfaces of ND, N-ND, and graphitized N-ND was compared using electron density difference maps in figures (d), (e), and (f). Yellow areas indicate electron-rich regions, whereas blue areas indicate electron-deficient regions.

In the absence of sonication, both ND and N-ND did not exhibit

significant effects on the removal of cyanobacterial cells (Fig.S3). The

variations in algae cell counts following different ultrasonic treatments

and the impact of ultrasonic treatment combined with flocculation are

depicted in Fig. 6. Regardless of the presence of a sonosensitizer, the

algae removal efficacy at an ultrasonic intensity of 1.17 W/mL surpasses

that at 0.12 W/mL, underscoring the positive correlation between ul-

trasonic intensity and algae removal efficiency-a trend well-

documented in other studies [46]. Compared to pure ultrasound and

Based on our experimental data and findings from literature, it is suggested that functional groups such as pyridine, pyrrole, and graphitic nitrogen play a crucial role in enhancing the basicity of the catalyst and disrupting the hydrogen bonds between water molecules. Consequently, graphitized N-ND exhibits superior water molecule adsorption capabilities and reduces the reactivity of free water molecules, resulting in the production of reactive oxygen species (ROS). The significantly enhanced sonochemical catalytic efficiency of N-ND compared to the control sample ND further supports the notion that the presence of lattice nitrogen atoms in graphitized N-ND is pivotal to its exceptional sonochemical catalytic performance.

# Preoxidation

## Preoxidation + coagulation

3.3. Algal removal





2

Time(min)

1

3

**Fig. 6.** The number of algal cells treated at 0 h under different ultrasonic conditions and the change of algal cell number after flocculation at 0.5 h (a) 800 kHz ultrasound; (b) 800 kHz ultrasonic + flocculation; (c) 800 kHz ultrasound + ND; (d) 800 kHz ultrasound + ND+flocculation; (e) 800 kHz ultrasound + N-ND; (f) 800 kHz ultrasound + N-ND+flocculation; (e) 800 kHz ultrasound + N-ND; (f) 800 kHz ultrasound + N-ND+flocculation; ND/N-ND concentration: 20 mg/L, flocculant concentration: 6 mg/L.

ultrasound with ND, the ultrasound & N-ND system notably enhanced algae removal capabilities. This enhancement can be attributed to the sonosensitive agent N-ND amplifying the cavitation effect and boosting the production of free radicals. Furthermore, upon the addition of a flocculant, the removal rate of the N-ND & ultrasound system exceeded 90 % within 5 min. This outcome indicates that the N-ND with low-intensity ultrasound system markedly enhances the flocculation effect, achieving a high degree of algae cell removal even with minimal flocculant usage. This not only demonstrates the efficacy of the system in reducing algae cells but also signifies the potential to lower the flocculant losage required [47].

In Fig. 7a, it is evident that *Microcystis aeruginosa* cells, with a diameter of 2–3  $\mu$ m, are uniformly suspended in the algae culture medium, showing no inclination for aggregation. In Fig. 7b and 7c, the application of ultrasound & N-ND treatment induces the aggregation of initially well-dispersed *Microcystis aeruginosa* cells. Notably, the algae cells exhibit no conspicuous damage or cracking; instead, a substantial flocculation precipitate forms around the algae cells. A comparison between Fig. 7b and Fig. 7c reveals that higher ultrasonic intensities result in a greater number of algae cells within the flocculating precipitate, forming larger flocs. This observation indicates that the 800 kHz (1.17 W/mL) ultrasound & N-ND system is capable of flocculating *Microcystis* cells while maintaining their structural integrity.

The half-life of free radicals in water is about  $10^{-6}-10^{-9}$  s, and the ultimate mass transfer distance under ideal conditions is only about 90 nm [7]. Given the transient nature of free radicals during the preoxidation of cyanobacteria, their short lifespan hinders efficient diffusion in water. We hypothesize that positively charged N-doped nanoparticles (N-ND) possess the ability to capture negatively charged algae cells. Upon excitation by acoustic cavitation, N-NDs could generate free radicals on the surface of algae cells. This process enables moderate preoxidation in close proximity, addressing challenges related to the brief lifespan of free radicals and constrained mass transfer distance.

Subsequently, the integrity of the cell membranes of suspended *Microcystis* subjected to various ultrasonic treatments was assessed, with the results illustrated in Fig. 8. Interestingly, at an ultrasonic frequency of 800 kHz and intensity of 0.12 W/mL, a higher proportion of algae cells exhibited increased permeability following pure ultrasonic treatment when the N-ND sonocatalytic agent was added. It was observed that the proportion of intact cells after ultrasonic treatment at 800 kHz (1.17 W/mL) is almost equal to that following treatment at 800 kHz (0.12 W/mL). Furthermore, the algae cell removal rate was higher under the former conditions.

Ultrasonic method has been applied in many reports to remove cyanobacteria cells in water, but the mechanism of removal usually involves the destruction of cyanobacteria cells, which may lead to the



Fig. 7. Morphology of algal cells and floc after treatment under confocal microscope (a) control group; (b) 800 kHz (0.12 W/mL) ultrasonic + N-ND; (c) 800 kHz (1.17 W/mL) ultrasonic + N-ND, ND/N-ND concentration: 20 mg/L.



Fig. 8. Permeability changes of Microcystis aeruginosa cells treated with different ultrasonic conditions.

release of microcystins and other algae organic substances [48]. However, maintaining the integrity of cells is very important to control the release of harmful cyanobacteria toxins. Therefore, the most ideal algae removal method is to remove intact algae cells without cracking them [49]. Compared with the previous ultrasonic algae removal work, in the combined pre-oxidation system of ultrasonic and N-ND, the *Microcystis* cells remain intact in water and sediments, which indicates that this new strategy of low intensity ultrasound + sonosensitive agent to remove *Microcystis* cells is relatively safe.

Common oxidants like hydrogen peroxide, permanganate, and ozone can oxidize cyanobacteria cells, disrupting their structure and function to eliminate them. However, excessive use of oxidants may lead to oxidation of other microorganisms and organic matter in water, resulting in the generation of secondary pollutants that impact water quality and ecosystem. Oxidant treatment can also produce by-products, affecting water safety. It is crucial to carefully control oxidant dosage and treatment time to minimize adverse effects on water quality.

On the other hand, ultrasound offers operational flexibility with precise control over frequency, amplitude, and treatment duration, preventing over-oxidation of algae cells. Ultrasound can penetrate water to target cyanobacteria cells without direct interference. Our study demonstrates that low-intensity ultrasound combined with sonocatalyst can selectively condition algae cell surfaces without damaging cell integrity. Furthermore, the interaction between positively charged nano-diamonds and negatively charged algae cells forms a network structure conducive to enhancing algae removal efficiency when integrated with traditional flocculants.

#### 3.4. Effects on water quality

Fig. 9 depicts the variations in UV<sub>254</sub>, Dissolved Organic Carbon (DOC), and microcystins post-flocculation treatment using different ultrasonic systems. The removal efficiency of natural humic macromolecules ( $UV_{254}$ ) and Chemical Oxygen Demand (COD) in water remains

consistently high, around 90 %, with high-frequency ultrasound, regardless of the presence of sonosensitizers, as evidenced in Fig. 9a-b. The underlying mechanism responsible for the efficient removal of organic matter in ultrasonic-assisted flocculation warrants further investigation. While some studies suggest that free radicals generated from ultrasonic cavitation degrade organic matter, others propose that damaged cells may absorb nutrients and regenerate post-ultrasonic treatment, leading to a decrease in organic matter content [16]. Moreover, the composition of the cell wall and surrounding substances of *Microcystis aeruginosa*, primarily comprised of peptidoglycan and protein with strong adsorption capabilities, plays a significant role in the removal of organic substances following ultrasound treatment [50].

Analyzing the presence of microcystins in the supernatant, as illustrated in Fig. 9(c), reveals that the ultrasound and N-ND system effectively removes microcystins. For the experiment on algal toxin removal, the calculation formula is as below:

Removal rate = (Microcystin concentration after treatment/Microcystin concentration in control group)  $\times$  100 % (10)

Specifically, the removal efficacy of the 800 kHz ultrasound + sonosensitive agent system surpasses that of ultrasound alone. Notably, in the 800 kHz (0.12 W/mL) ultrasound & N-ND system, the microcystin removal rate is 40 % higher than in pure ultrasound, while in the 800 kHz (1.17 W/mL) ultrasound & N-ND system, the removal rate is 50 % higher, indicating the beneficial impact of incorporating sonosensitizers on microcystin removal. For microcystins removal, since the sonication time was within 10 min, while algal toxins are relatively difficult to degrade, therefore, compared to the removal rates of UV<sub>254</sub> and COD, the degradation rate of algal toxins is relatively low. But the results show that the ultrasound & N-ND treatment system ensures that microcystins meet drinking water standards, safeguarding the safety of drinking water.



Fig. 9. Effects of 800 kHz ultrasound on algae organic matters under three treatment conditions (a)  $UV_{254}$  removal rate; (b) COD removal rate; (c) Microcystin removal rate, ND/N-ND concentration: 20 mg/L, flocculant concentration: 6 mg/L.

#### 4. Discussion

The conventional coagulation-sedimentation process in drinking water treatment plants struggles to effectively remove algae due to the electronegativity of cyanobacteria particles and the negative charge groups in algae-derived organic matter, impacting coagulation efficiency and effluent quality [51]. Whereas pre-oxidation combined with

coagulation can enhance algae cell removal by reducing the inhibitory effect of negative organic substances on coagulants, the use of oxidants like chlorine, hydrogen peroxide, and ozone for pre-oxidation may damage algae cells, leading to the release of microcystins into water and the formation of carcinogenic disinfection by-products during subsequent chlorination. In terms of ensuring the safety of drinking water, acoustic cavitation can destroy the extracellular polymer structure and improve the coagulation performance of cyanobacteria by controlling the shear force, micro-jetting free radicals generated by it, thus improving the efficiency of coagulation and algae removal [50,52–56]. However, the half-life of free radicals in water is about  $10^{-6}$ - $10^{-9}$  s, and the ultimate mass transfer distance under ideal conditions is about 90 nm [7]. The life of free radicals is extremely short, which is not conducive to achieve effective diffusion in water. In order to remove algae by pre-oxidation, it is necessary to explore whether the free radical mass transfer process can be ensured, and can also effectively collide with algal extracellular polymers in a short mass transfer distance, and then oxidize and damage extracellular polymers.

To address the challenge of efficient algae removal while maintaining water safety, a novel pre-oxidation approach is proposed in this study. By combining low-intensity ultrasound with a positively charged sonocatalyst, the generation and mass transfer of free radicals on the surface of negatively charged algae cells are enhanced, optimizing oxidation energy efficiency. The results of material characterization and theoretical calculations confirmed that the use of positively charged N-ND, facilitates improved acoustic sensitivity by enhancing the interaction between functional groups and water molecules, thereby increasing free radical yield. This innovative treatment method involves ultrasound coupled with sonocatalst to induce cavitation bubbles [37] that mechanically vibrate, conditioning algae cell surfaces without compromising cell integrity. Moreover, the formation of a network structure between positively charged nano-diamond and negatively charged algae cells shortens the distance between free radicals and algae cell surfaces, enhancing free radical utilization for efficient flocculation and algae removal. Importantly, the application of ultrasound/nitrogen-doped nano-diamond shows no significant effects on water quality, affirming the safety and efficacy of this technology.

In the research process of ultrasonic algae removal, researchers found that high-intensity ultrasonic waves can produce high-energy ultrasound waves, which can damage the cell wall and cell membrane of algae and lead to the death of algae cells. However, in order to ensure the quality and safety of drinking water and not destroy the structure of microalgae, researchers tend to use low-intensity ultrasound to treat algae-containing water [50,52–54,57]. It has been reported that ultrasound can destroy the organic matter (S-AOM) adsorbed on the surface of algae cells, and make algae cells unstable, thus improving the efficiency of flocculation and algae removal. Our work provides a novel idea for how to ensure the generation and accumulation of free radicals in the process of random ultrasonic cavitation, and at the same time, to promote the generated free radicals to effectively collide with the target pollutant molecules in a short mass transfer distance, and then to remove organic substances by oxidation.

It is worth noting that in the ultrasound field, the strong interaction between Pyridinic N and graphitic N on the surface of nano-diamond contributes to the catalytic cracking of electron-hole pairs of N-ND and water molecules in the excited state, thus generating  $\cdot$ OH and H<sub>2</sub>O<sub>2</sub>. Compared with chlorine oxidants, the possibility of these ROS and algaederived organic products generating carcinogenic disinfection byproducts is reduced. The related degradation pathway and toxicology research will be carried out in the unexplored research work.

While some researchers may raise concerns about the cost of nanodiamonds, it is important to emphasize that the primary aim of this study is to highlight the role of carbon-based materials with sonosensitivity in safe algae removal processes. Moreover, previous research has demonstrated the capability of annealed nano-diamonds in facilitating Fenton-like oxidation and direct electron transfer mechanisms in carbon materials for persulfate activation [35,36]. Therefore, studying the catalytic performance of nanodiamonds is beneficial for establishing an efficient oxidation system for organic removal studies. In our work, we found that nitrogen-doped functional groups on graphene-based carbon materials can enhance ultrasonic cavitation by serving as electron-rich Lewis bases that promote the generation of reactive oxygen species (ROS). The integration of low-power ultrasound with a carbon-based sonocatalyst, such as N-doped nano-diamond, forms a network structure with algae cells to improve algae removal rates without compromising cell integrity. The future goal is to identify cost-effective and stable carbon-based sonocatalysts with similar properties of N-ND to enable a safe and efficient ultrasonic algae removal process.

#### 5. Conclusion

Ultrasonic algae removal plays a crucial role in ensuring the safety of drinking water by combatting the escalating prevalence of algal blooms stemming from water eutrophication. This method effectively enhances water quality without relying on additional chemicals, effectively conditioning the extracellular organic matter of cyanobacteria and laying the groundwork for subsequent treatments such as coagulation. In this study, a straightforward approach was employed to acquire N-ND as a sonosensitizer, showcasing remarkable catalytic performance in highfrequency, low-power ultrasonic treatment. The synergistic application of high-frequency ultrasound and N-ND achieved an impressive removal rate exceeding 90 % for Microcystis aeruginosa algae within a mere 5minute timeframe, simultaneously demonstrating efficient elimination of organic matter and microcystins from water. Detailed mechanistic investigations validated that N-ND actively facilitates the generation of reactive oxygen species, facilitating the conditioning of algae cells and enhancing coagulation for improved algae removal. The integration of low-power high-frequency ultrasound with a positively charged sonosensitizer not only optimizes free radical generation but also enhances oxidation efficiency. This study unveils a novel strategy for developing efficient catalysts and managing cyanobacterial blooms. Future research endeavors will focus on identifying cost-effective carbon-based sonosensitizers to further enhance the safety and efficiency of ultrasonic algae removal methods.

#### 6. Contribution statement

Xiaoge Wu designed the experiments and wrote the paper. This work was supported by her project funding. Su Yang conducted the experiments. Wenshu Li conducted the experiments and wrote the paper. JuanJuan Wang revised the paper. Matevz Dular supervised the experiments and revised the paper. Xiao Tan supervised the experiments and revised the paper.

#### CRediT authorship contribution statement

Xiaoge Wu: Writing – review & editing, Writing – original draft, Supervision. Su Yang: Writing – original draft, Data curation. Wenshu Li: Writing – original draft, Data curation. JuanJuan Wang: Resources, Project administration. Matevž Dular: Writing – review & editing. Xiao Tan: Writing – review & editing.

#### 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.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2024.106993.

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