



A novel one-step wet denitrification method by hydrodynamic cavitation and chlorine dioxide

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ARTICLE INFO

Editor: Luigi Rizzo

Keywords:

Hydrodynamic cavitation
Chlorine dioxide
Wet denitrification
Ship exhaust

ABSTRACT

Ships have brought substantial economic benefits, and meanwhile, they release exhaust gases, including plenty of nitrogen oxides (NO_x). Increasingly stringent air pollutant emission standards (e.g., MARPOL) for ships have been established at home and abroad to reduce the pollution of NO_x . In this paper, a promising technology for removing NO_x from ship exhaust by hydrodynamic cavitation (HC) and chlorine dioxide (ClO_2) was proposed. The mechanism of HC promoting denitrification was discussed. The various influencing factors of the HC enhancing ClO_2 circulation denitrification, such as the pressure difference (ΔP) between the inlet and outlet of the HC reactor, solution temperature (10.0–55.0 °C), NO initial concentration (500–1000 ppm), gas flow rate (1.0–1.6 L/min), solution pH (3.00–11.00), and ClO_2 concentration (0.001–0.100 mmol/L) on denitrification effect were studied in the experiments, in which the optimal conditions were established. On the basis of the results of HC enhancing ClO_2 circulation denitrification, HC enhancing ClO_2 non-circulation denitrification experiments were carried out. The results showed that the NO and NO_x removal efficiencies reached 93% and 90%. We also measured the final anions in solutions after denitrification by ion chromatography and discussed the reaction pathways.

1. Introduction

The continuous growth of world seaborne trade makes rapid growth in the global fleet. As of 30th October 2019, there were 96,295 ships with more than 100 gross tons worldwide. Ships bring substantial economic benefits [1]. Nevertheless, they also cause severe air pollution problems [2]. The exhaust gas from ships contains pollution sources such as particulate matter (PM), sulfur oxides (SO_x), and NO_x , which have adverse effects on the atmospheric environment and human health [3–7]. In response to ship pollution, increasingly stringent air pollutant emission standards (e.g., MARPOL) for ships have been established at home and abroad [8]. Scholars have studied many emission reduction technologies for the above reasons, finding that removing SO_x and PM from ship exhaust is easy, but it is challenging to remove NO_x . Denitrification is the key to the integrated treatment of ship exhaust.

Currently, there are many methods to reduce NO_x emission from ships, such as selective catalytic reduction (SCR) [9–11], exhaust gas recirculation (EGR) [12–14], and wet denitrification [15,16]. The

denitrification rate of the SCR system reached 80%–95% [17]. However, due to the burning of low-quality fuels, the particles in ship exhaust are more likely to pollute the catalyst, causing catalyst poisoning, which is not conducive to the SCR system's operation. Moreover, the SCR system using urea or ammonia has an excellent practical effect on land, but considering the reality of the ship, putting a large amount of urea or ammonia in the living area harms the crew's life, which is another complex problem in the application of this technology on board. The EGR system can satisfy the Tier III standard for NO_x emissions from ships, but it will lead to cylinder liner wear and increase exhaust products (e.g., PM and CO) [18]. The EGR system also has significant changes to the original engine structure, making it challenging to apply on existing ships in service.

The SCR and EGR only remove NO_x in exhaust emissions; however, wet denitrification technology can simultaneously remove various pollutants in the exhaust gas [18], which attracts the attention of researchers. SO_x and PM can be effectively removed by wet denitrification, while NO, which accounts for over 90% of NO_x in ship exhaust, is hard to dissolve

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in water [19], which brings challenges to wet denitrification [20–22]. For meeting the challenges, multi-step wet denitrification technology is investigated. Anette et al. [23] first used gaseous ClO_2 to oxidize NO to NO_2 , then absorbed NO_2 with Na_2SO_3 and Na_2CO_3 solution, and the removal efficiency of NO_x reached more than 90%. Although the denitrification efficiency of the multi-step wet denitrification technology is high, the multi-step wet denitrification system is complicated and occupies an ample space, which does not apply to the ship with limited space. For solving the complexity of the wet denitrification process, one-step wet denitrification technology is investigated. In 2020, Xiao et al. [24] proposed a micro-nano bubble (MNB) oxidation-absorption process based on sodium humate for simultaneous desulfurization and denitrification. MNBs are tiny bubbles less than 50 μm in diameter [6,7,25], which increases the gas-liquid contact area. The collapse of MNBs can produce hydroxyl radicals ($\bullet\text{OH}$) to further facilitate the removal of NO [24,26]. The results showed that the removal efficiency of NO could reach more than 91.1%. Biological treatment is a new method for the removal of NO_x . Mao et al. [27] proposed a method by biological trickling filter for the removal of NO and SO_2 . The results showed that the highest NO_x removal efficiency was 60.2%. Biological treatment by nitrifier-enriched-activated-sludge (NAS) technology is expected to improve NO_x removal efficiency. Sepehri et al. [28,29] proposed and proved that the enrichment of nitrifying bacteria could be achieved in NAS. They also found that a Chlorella vulgaris and NAS consortium could enhance nutrient removal and reduce metabolite generation [30]. Jin et al. [21] and Deshwal et al. [31] dissolved ClO_2 gas in water to directly remove NO_x in a bubbling reactor, and the NO_x removal efficiency was 66–72%. Furthermore, Deshwal et al. [32] used acidic NaClO_2 solution to remove NO_x from the simulated flue gas. Their results showed that ClO_2 , an intermediate product, participated in the oxidation and absorption of NO_x under acidic conditions, and the highest denitrification rate reached 81%. The one-step wet denitrification system is simple, but it is not easy to achieve a denitrification efficiency exceeding 90%. Research on a one-step denitrification system with small space occupation and high denitrification efficiency is a hot topic in ship air pollution control.

HC is a hydrodynamic phenomenon that occurs when the liquid pressure suddenly drops below the vapor pressure and then increases. When the local pressure of the liquid drops suddenly, the molecules in the weak part of the liquid are pulled apart, forming cavities. The water will vaporize and enter the cavities since the pressure is below the saturated vapor pressure. When the pressure rises sharply, the cavities are compressed adiabatically, producing ultra-high temperature (1000–15000 K) and ultra-high pressure (10–500 MP) and eventually collapse [33–39]. When cavities collapse, microjets can be formed to enhance local mass transfer. The cavitation process can also cause hydrolysis, producing $\bullet\text{OH}$ [33,40,41]. Chemical reactions can be accelerated by the extreme chemical reaction environment created by cavitation [35,40,42,43]. Cavitation has been used in biofuel refining and wastewater treatment and achieved remarkable results. In addition, Oxidant ClO_2 is safe, environmentally friendly, low in cost [44], and has a robust oxidizing property [45,46], which is beneficial to the oxidation and absorption of NO_x . Therefore, a novel one-step wet denitrification method by HC enhancing ClO_2 is proposed in this paper. HC reactor can effectively improve wet denitrification efficiency and reduce the equipment footprint. The denitrification system mainly includes pumps, pipelines, and venturi injectors in practical applications. It takes up a small space suitable for ships with limited space.

We aim at the basic study of treatment theory and technology of removing NO_x by HC enhancing ClO_2 . Effects of the ΔP , solution temperature, NO initial concentration, gas flow rate, solution pH, and ClO_2 concentration on the denitrification effect were studied during the HC enhancing ClO_2 circulation denitrification experiments, in which the optimal experimental conditions were established. On the basis of the results of HC enhancing ClO_2 circulation denitrification, HC enhancing ClO_2 non-circulation denitrification experiments were carried out. We also

measured the final anions in solutions after denitrification by ion chromatography and discussed the reaction pathways.

2. Experimental section

2.1. Experimental materials

The experimental setup included a gas feeding system, an HC reactor unit, and a flue gas analysis system (Fig. 1). The gas feeding system consisted of NO (1000×10^{-6} mol/mol and 3000×10^{-6} mol/mol, balance with N_2), N_2 (purity $\geq 99.999\%$), and mass flow controllers (MFC, Beijing Sevenstar Electronics Co., Ltd) controlling the gas flow rate, and a mixing chamber. The HC reactor unit mainly consisted of a constant temperature water bath keeping the solution temperature constant, 12.0 L of high purity ClO_2 solution (ClO_2 , 11.12 mmol/L, purity $\geq 99.99\%$, Guangzhou ZLDL Materials Technology Co., Ltd, Guangdong, China.) and pure water (18.2 M $\Omega\cdot\text{cm}$ at 25.0 °C) in the thermostat bath tank as denitrification solution, a venturi injector (model 384, Mazzei Injector Company, LLC, Bakersfield, USA.) as the HC reactor, and an injection pump (model: LSP02–2B, Baoding Longer Precision Pump Co., Ltd.) as a continuous syringe. 1 mol/L H_2SO_4 solution and 1 mol/L NaOH solution were used to adjust the solution's initial pH value. The solution pH was measured by Mettler-Toledo s210 SevenCompact™ pH during experiments. The reaction samples were analyzed by Thermo Scientific DIONEX ICS-600 ion chromatography (Dionex Ionpac™ AS23). ClO_2 in samples was detected by a UV spectrophotometer (UV-1800, Shimadzu, Japan). A turbine flow transducer (LWGY-10, Jinhu Heshi Instrument Co., Ltd., China) was used for measuring the liquid flow rate. The phantom v2012 high-speed camera with 10,000 fps was used to take photographs of the bubbles at the HC reactor outlet. The flue gas analysis system included an electronic condenser and a gas analyzer (Gasboard-3000UV, Hubei Cubic-Ruiyi Instrument Co., Ltd.). The electronic condenser cooled the flue gas and removed moisture for weakening the corrosion of the gas analyzer. The gas analyzer measured the concentrations of NO, NO_2 , and NO_x .

2.2. Experimental procedures

Before each experiment, high-purity N_2 was used to empty the air in the pipeline. The denitrification solution in the constant temperature water bath was drawn by the pump, and the solution was driven to flow through the line. Whether the solution flowed through the HC reactor was controlled by adjusting valves i and j. The experiment system worked either in the circulation denitrification mode or non-circulation denitrification mode.

The device was in the circulation denitrification mode when valves c, d, e, g, h, j opened and valves a, b, f, i closed. The HC reactor inlet pressure (P_i) and outlet pressure (P_o) were adjusted by valves d and h. The liquid level of the first stage gas-liquid separator was controlled by valve g. When the denitrification solution quickly passed through the HC reactor, a suction pressure was generated, which sucked the mixed gas into the HC reactor, and then a large number of Gas-Filled-Bubbles would be formed in the HC reactor. The bubbles and denitrification solution flowed through the HC reactor and entered the first stage gas-liquid separator. The separated gas mixture passed through the second gas-liquid separator, the electronic condenser, and the gas analyzer in sequence. Simultaneously, the liquid flowed through valve e and then returned to the constant temperature water bath.

The HC enhancing ClO_2 non-circulation denitrification was an optimization of the HC enhancing ClO_2 circulation denitrification. During the non-circulation denitrification experiment, valves b, d, f, g, h, j opened, and valves e, i closed. Valves a, c controlled whether the gas passed through the HC reactor. The continuous syringe injected ClO_2 solution into the pipeline at a constant rate. The ClO_2 solution and the NO mixture were simultaneously sucked into the HC reactor and reacted. After the gas-liquid separation, the solution entered the beaker through valve f.

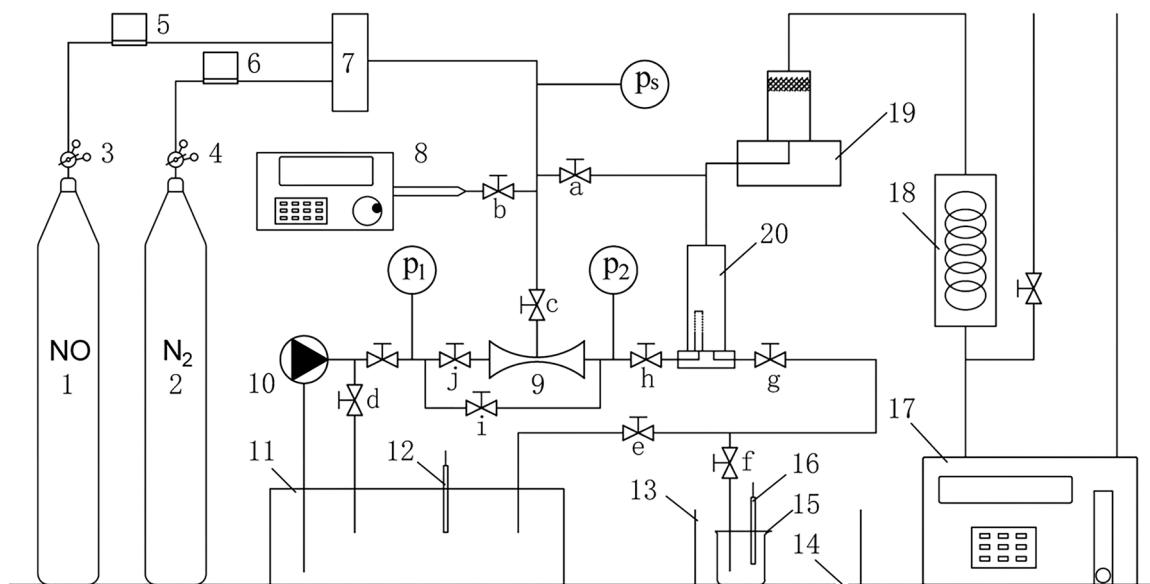


Fig. 1. Schematic diagram of experimental system: (1–2) gas cylinders; (3–4) reduced valves; (5–6) mass flow controllers; (7) gas mixer; (8) continuous syringe; (9) HC reactor; (10) pump; (11) constant temperature water bath; (12, 16) pH meter; (13) water tank; (14) drain hole; (15) beaker; (17) gas analyzer; (18) electronic condenser; (19) second stage gas-liquid separator; and (a–j) block valves.

When the solution overflowed in the beaker, it entered the water tank and then flowed through the drain hole to the waste collection point. The samples were sampled through valve f, and the gases were analyzed by the gas analyzer.

2.3. Data analysis

When the NO mixture flowed through the HC reactor, the NO reacted with the ClO₂ and was removed. The NO removal efficiency is calculated as follows:

$$\eta_{\text{NO}} = (C_{\text{NO}(b)} - C_{\text{NO}(a)}) / C_{\text{NO}(b)} \times 100\% \quad (1)$$

Where $\eta_{\text{NO}}(\%)$ is the NO removal efficiency. $C_{\text{NO}(b)}$ (ppm) and $C_{\text{NO}(a)}$ (ppm) are the NO concentrations before and after denitrification.

The NO_x removal efficiency is calculated as follows:

$$\eta_{\text{NO}_x} = (C_{\text{NO}_x(b)} - C_{\text{NO}_x(a)}) / C_{\text{NO}_x(b)} \times 100\% \quad (2)$$

Where $\eta_{\text{NO}_x}(\%)$ is the NO_x removal efficiency. $C_{\text{NO}_x(b)}$ (ppm) and $C_{\text{NO}_x(a)}$ (ppm) are the NO_x concentrations before and after denitrification,

3. Results and discussion

3.1. The mechanism of HC promoting denitrification

3.1.1. The gas-liquid mass transfer was facilitated by the HC reactor

Fig. 2 displayed photographs of bubbles in the first stage gas-liquid separator. The photographs were taken under the same conditions, except for the presence or absence of the HC reactor. The diameters of individual bubbles with and without the HC reactor were about 4 mm and 23 mm. The volume of a single bubble was about 190 times lower due to the presence of the HC reactor. Therefore, the HC reactor could

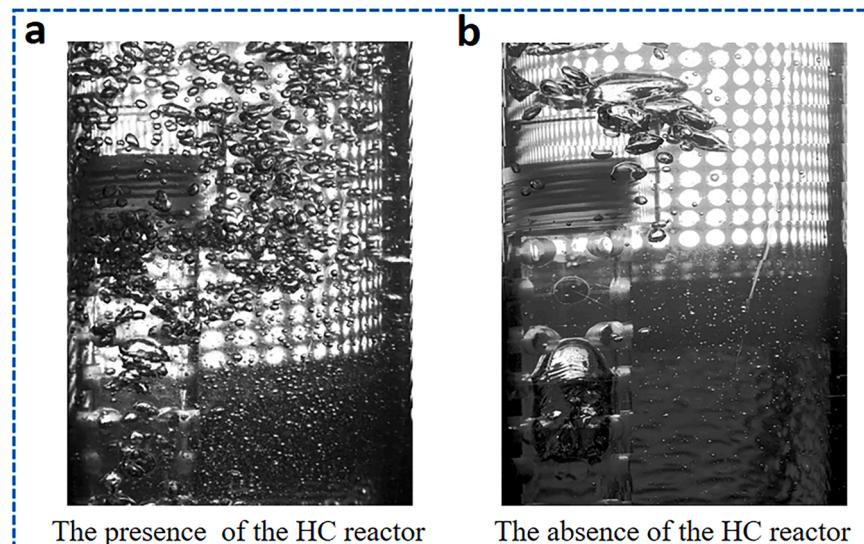
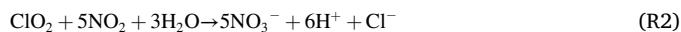
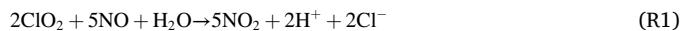
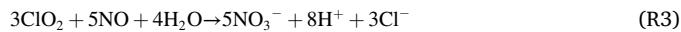


Fig. 2. a. Photograph of bubbles in the first stage gas-liquid separator for the solution passing through the HC reactor. b. Photograph of bubbles in the first stage gas-liquid separator for the solution not passing through the HC reactor.

increase the gas-liquid contact area, improving gas-liquid mass transfer. The micro-jets generated by cavitation also enhanced the gas-liquid mass transfer, which further promoted the oxidation of NO_x by the robust oxidant ClO_2 . ClO_2 oxidized NO to NO_2 , then NO_2 was oxidized to nitrate (NO_3^-), as shown in (R1) and (R2) [31].



The overall chemical reaction equation for the NO removal could be written as:



3.1.2. Gas phase mass transfer was enhanced by the HC reactor

The structure of the HC reactor was shown in the [Supplemental Information](#) section, [Fig. 1S](#). When the liquid flowed into the constricted section of the reactor, the liquid flow rate increased, so the kinetic energy of the liquid increased. The pressure energy of the liquid decreased according to the principle of energy conservation. Under low pressure, ClO_2 and H_2O molecules volatilized and existed in Gas-Filled-Bubbles. When the fluid passed through the expansion section of the HC reactor, the fluid pressure increased, and the bubbles were compressed and became smaller, promoting intermolecular collisions and improving gas phase mass transfer.

3.1.3. Influence of $\bullet\text{OH}$ generated by the HC reactor on denitration

Cavitation could cause the pyrolysis of water molecules to generate $\bullet\text{OH}$, according to R4 [47–51].



NO_x might react with $\bullet\text{OH}$, ultimately transforming to nitrite (NO_2^-) and NO_3^- , as shown in R5-R8 [52].



The result of pure water denitrification using an HC reactor was shown in the [Supplemental Information](#) section, [Fig. S2](#). It could be found from [Fig. S2](#) that the NO_x removal efficiency dropped quickly from 41.0% (70 s) to 31.9% (75 s) in 5 s, which indicated that $\bullet\text{OH}$ had no significant effect on NO_x removal in this work. The reason might be that the low solubility of NO made it difficult for $\bullet\text{OH}$ to contact NO molecules, which made R5 and R6 difficult to occur. Therefore, the improvement of the mass transfer process might be the main reason for the HC reactor to improve the denitrification effect of ClO_2 .

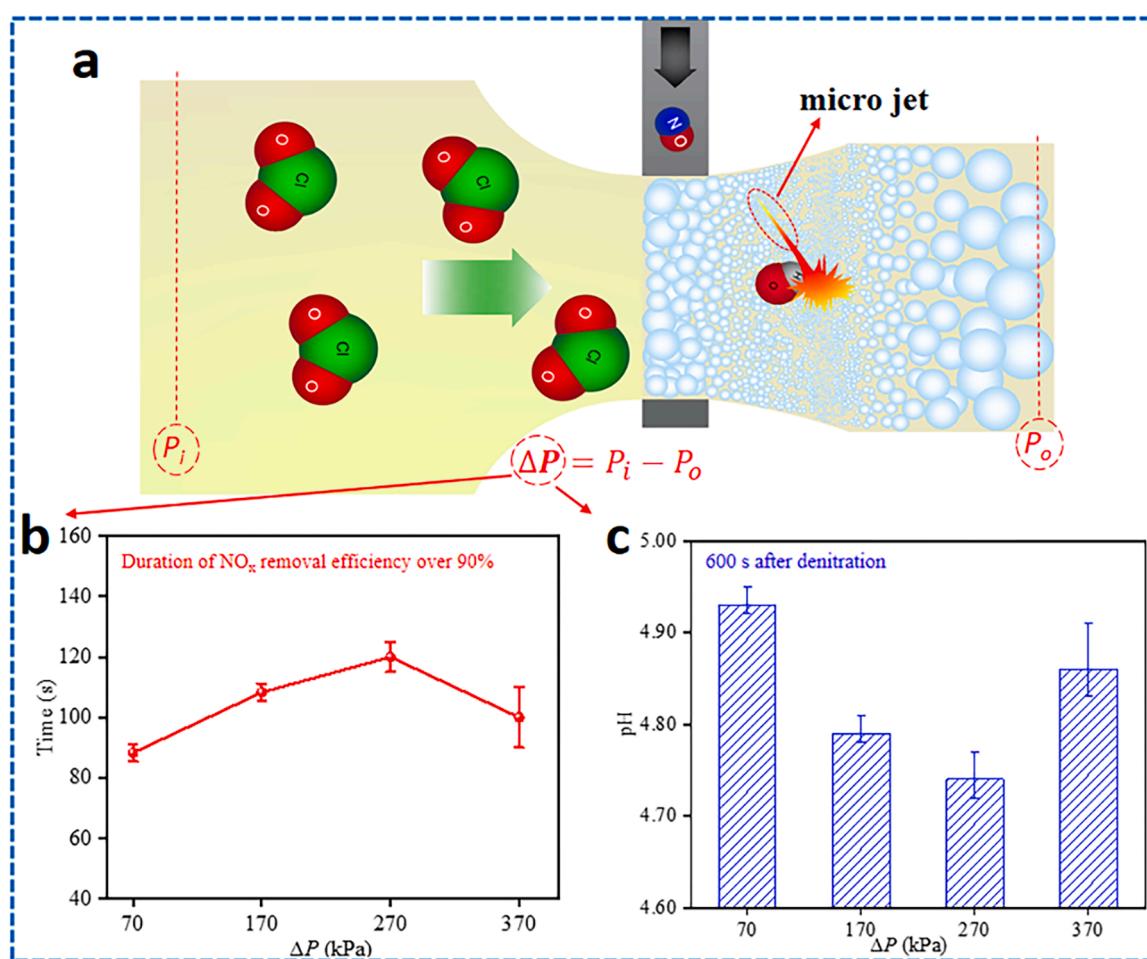


Fig. 3. Effect of the ΔP on NO_x removal. (Conditions: gas flow rate = 1.0 L/min, NO initial concentration 1000 ppm, ClO_2 concentration 0.01 mmol/L, solution temperature 25.0 °C.) a. Denitrification mechanism of HC enhancing ClO_2 . b. Variations of the duration for η_{NO_x} over 90% with ΔP . c. Variations of solution pH after 600 s denitrification with ΔP .

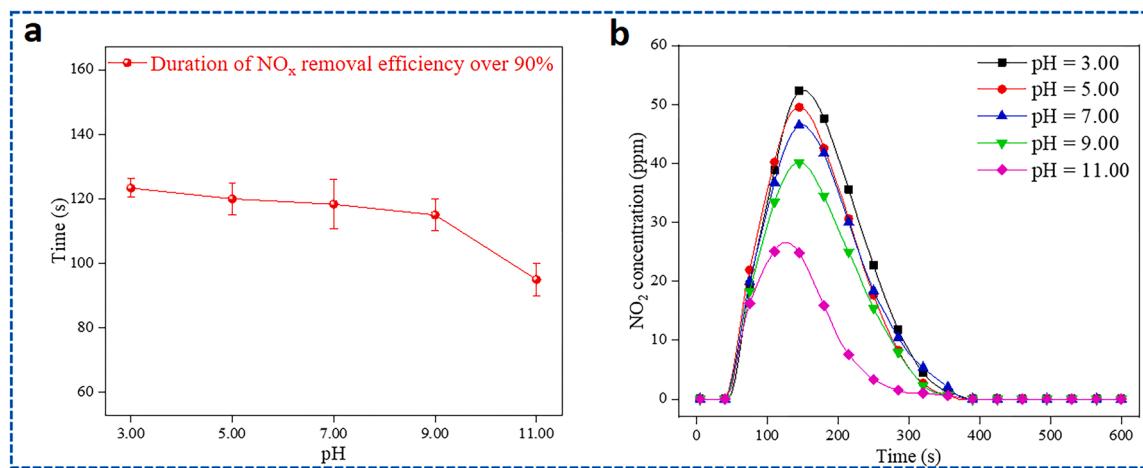


Fig. 5. Effect of initial solution pH on denitration. a. Variations of the duration for η_{NO_x} over 90% with solution pH. b. Variations of NO₂ concentration with time under different initial solution pHs.

molecules or ions in the solution are affected by the reaction temperature [19]. The effect of reaction temperature on NO_x removal was studied experimentally by varying solution temperature from 10.0 °C to 55.0 °C as shown in Fig. 6. From Fig. 6a, the duration for η_{NO_x} over 90% had a change of increasing at first and then dropping with the rise of solution temperature. The maximum value of the duration for η_{NO_x} over 90% was achieved at 25.0 °C. For this, there were two reasons. On the one hand, The increase in solution temperature will accelerate the diffusion rate of NO and ClO₂ molecules, causing an increase in the chemical reaction rates[51]. Meanwhile, p_v increased as the solution temperature increased. Thereby C_v was down. These promoted the denitration effect. On the other hand, the elevated temperature increased the escape rate of ClO₂ gas. Meanwhile, An increase in temperature would reduce the solubility of NO and NO₂ in aqueous solution [16,19,32]. These inhibited the denitration effect.

Fig. 6b displayed the effect of reaction temperature on the solution pH after 600 s denitration. The denitration solution's initial pH value was about 5.70 in this series of experiments. The solution pH after 600 s denitration was 4.79, 4.74, 4.80, and 4.90. The lowest pH after 600 s denitration was obtained at 25.0 °C. Higher denitration efficiency has lower pH, according to (R3). Thus, 25.0 °C was the optimum solution temperature for HC enhancing ClO₂ circulation denitration from 10.0 °C to 55.0 °C.

3.5. Effect of NO initial concentration on NO_x removal

The effect of NO initial concentration on denitration during the HC enhancing ClO₂ circulation denitration experiments was shown in Fig. 7. Fig. 7a showed that with the increase of the NO initial concentration, the duration of the NO concentration being 0 ppm gradually decreased. In other words, the higher NO initial concentration led to a shorter duration for η_{NO_x} over 90% (Fig. 7b). The NO concentration gradually increased to the near initial NO concentration due to the rapid consumption of ClO₂. The curves of NO and NO_x concentrations versus time did not overlap (Fig. 7a) because a small amount of NO₂ was produced in the denitration process (Fig. 7c).

Fig. 7d showed the solution pH after 600 s denitration at different NO initial concentrations. The pH of the solution was determined by the amount of NO_x absorbed. The greater the amount of NO_x absorption, the lower the pH. The NO_x absorption was affected by the NO initial concentration and the duration for η_{NO_x} over 90%. The longer the duration of the high denitration rate and the higher the initial NO concentration, the more NO_x absorption. Results showed that with the increase of NO initial concentration, the solution pH after 600 s denitration showed a decreasing trend, which was also because the lower initial concentration of NO took longer to consume ClO₂ dose in the solution, which caused more ClO₂ to overflow. However, when the NO initial concentration increased from 1000 ppm to 1250 ppm, the pH values were almost

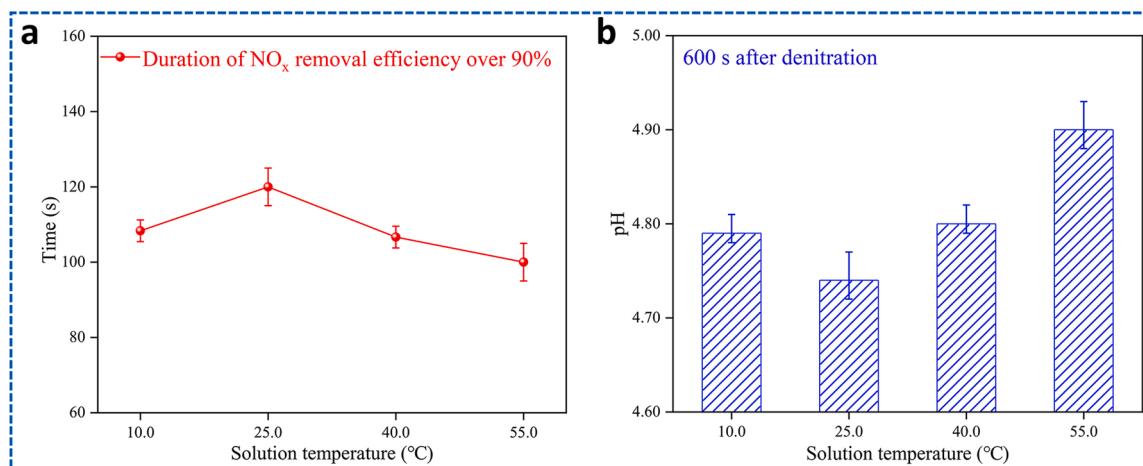


Fig. 6. Effect of solution temperature on denitration. (Conditions: gas flow rate 1.0 L/min, NO initial concentration 1000 ppm, ClO₂ concentration 0.01 mmol/L, ΔP 270 kPa) a. Variations of the duration for η_{NO_x} over 90% with solution temperature. b. Variations of solution pH after 600 s denitration with solution temperature.

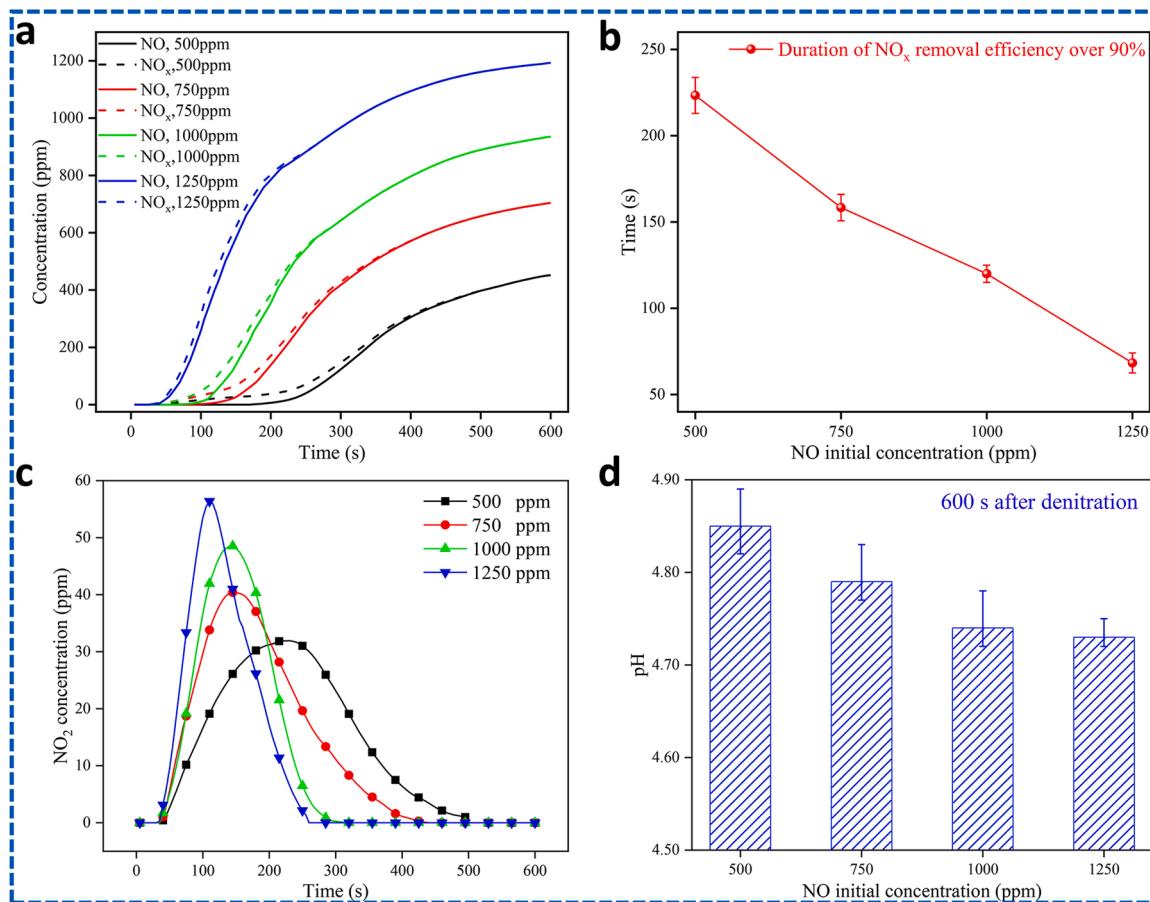


Fig. 7. Effect of NO initial concentration on denitration. (Conditions: gas flow rate 1.0 L/min, ClO₂ concentration 0.01 mmol/L, solution temperature 25.0 °C, ΔP 270 kPa) a. Variations of NO concentration and NO_x concentration with time under different NO initial concentrations. b. Variations of the duration for η_{NO_x} over 90% with NO initial concentration. c. Variations of NO₂ concentration with time under different NO initial concentrations. d. Variations of solution pH after 600 s denitration with NO initial concentration.

equal, which showed that the ClO₂ dose in the solution could be almost utilized when the NO initial concentration was 1000 ppm.

3.6. Effect of gas flow rate on NO_x removal

The influence of the NO gas flow rate on the denitration effect during

the HC enhancing ClO₂ circulation denitration experiment was studied. Fig. 8 showed the experimental results. Fig. 8a was the variation of the duration for η_{NO_x} over 90% with gas flow rate. The larger the gas flow rate was, the shorter the duration for η_{NO_x} over 90% took. Solution pH after 600 s denitration under different gas flow rates in Fig. 8b reflected very interesting results. Although a larger gas flow rate consumed ClO₂

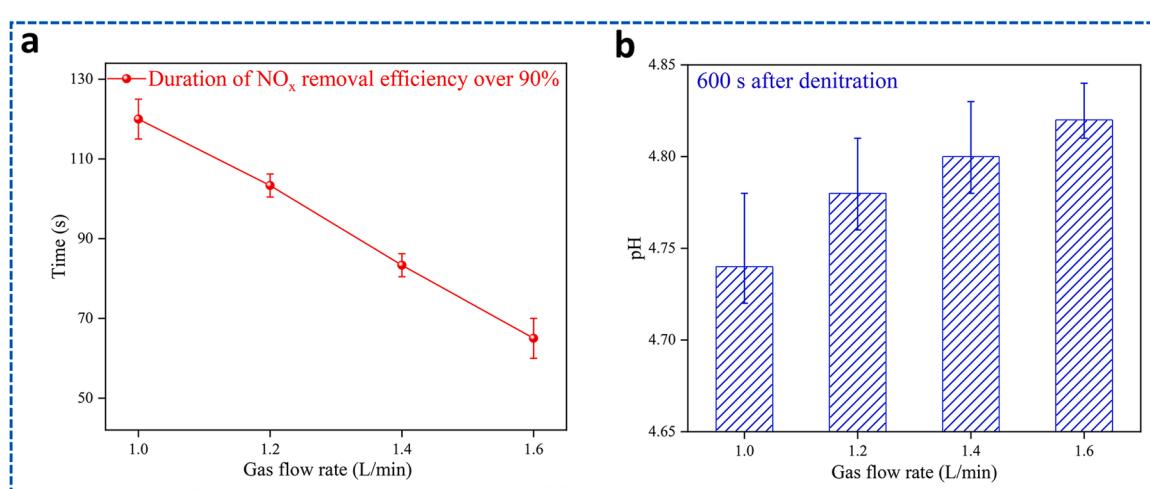


Fig. 8. Effect of gas flow rate on denitration. (Conditions: NO initial concentration 1000 ppm, ClO₂ concentration 0.01 mmol/L, solution temperature 25.0 °C, ΔP 270 kPa) a. Variations of the duration for η_{NO_x} over 90% with gas flow rate. b. Variations of solution pH after 600 s denitration with gas flow rate.

in the solution faster, the lowest pH was obtained when the gas flow rate was 1.0 L/min. It might be because the gas flow rate increased from 1.0 L/min to 1.6 L/min cavitation bubbles were more difficult to collapse, leading to the formation of cavity cloud, which reduced the cavitation intensity[58], resulting in more ClO₂ overflows (Table S1). Therefore, the optimal gas flow rate was 1.0 L/min under the experimental conditions.

3.7. Effect of initial ClO₂ concentration on denitration

Fig. 9 showed the effect of initial ClO₂ concentration on NO_x removal during the HC enhancing ClO₂ circulation denitration experiments. The increase in initial ClO₂ concentration improved the denitration effect. The higher the initial ClO₂ concentration was, the longer it took for the NO_x concentration to drop to about 0 (Fig. 9a); namely, the higher the concentration of ClO₂ was, the longer duration of η_{NO_x} over 90% took, as shown in Fig. 9b (Except for the duration of the initial ClO₂ concentration of 0.001 mmol/L). It could be found from Fig. 9b that the duration of pure water denitrification for η_{NO_x} over 90% was 40 s, which might be the reason for the experiment design, and the actual effective duration for η_{NO_x} over 90% was 0 s. The solution pH was measured continuously during the experiments, and the experimental results were confirmed by the variations of solution pH with time under different ClO₂ concentrations. The solution pH after 1800 s denitration remained about 5.91, 4.72, 4.41, 4.30, and 3.78 when the initial ClO₂ concentration was 0 mmol/L, 0.01 mmol/L, 0.02 mmol/L, 0.03 mmol/L, and 0.10 mmol/L (Fig. 9c).

There was still NO₂ in the gas after denitration, and the concentration of NO₂ increased with the initial ClO₂ concentration (Fig. 9d). The

escape property of ClO₂ could explain this. NO₂ was carried by the escape of ClO₂, and a higher ClO₂ escape rate was caused by a higher initial ClO₂ concentration, which led to a higher concentration of NO₂. Therefore, a lower initial ClO₂ concentration could reduce the production of NO₂ and the escape of ClO₂ (Table S2). However, the initial ClO₂ concentration should not be too low. A too low concentration would not achieve a high denitration effect. As shown in Fig. 9b, when ClO₂ concentration was 0.001 mmol/L, the actual effective duration for η_{NO_x} over 90% was 0 s, the same as that of ClO₂ concentration of 0 mmol/L. Therefore, under the premise of ensuring η_{NO_x} over 90%, the lowest possible ClO₂ concentration was the best choice. Within the scope of this experiment, 0.010 mmol/L was the best initial ClO₂ concentration.

3.8. Study on HC enhancing ClO₂ non-circulation denitration

During HC enhancing ClO₂ circulation denitration, a too-high initial concentration of ClO₂ led to too high NO₂ concentration after denitration. As shown in Fig. 9d, when the initial concentration of ClO₂ was 0.100 mmol/L, the highest concentration of NO₂ was 111 ppm. HC enhancing ClO₂ non-circulation denitration mode was designed to solve the problem.

3.8.1. The experiment of HC enhancing ClO₂ non-circulation denitration

Non-circulation denitration experiments were carried out at solution temperature 25.0 °C, ΔP 270 kPa, 11.12 mmol/L ClO₂ feeding at a rate of 4 ml/min, gas flow rate 1.0 L/min, and NO initial concentration 1000 ppm. As shown in Fig. 10a, the η_{NO} and η_{NO_x} first increased rapidly and then stabilized at about 93% and 90%, respectively. The variations of solution pH with time also reflected the results of the non-circulation

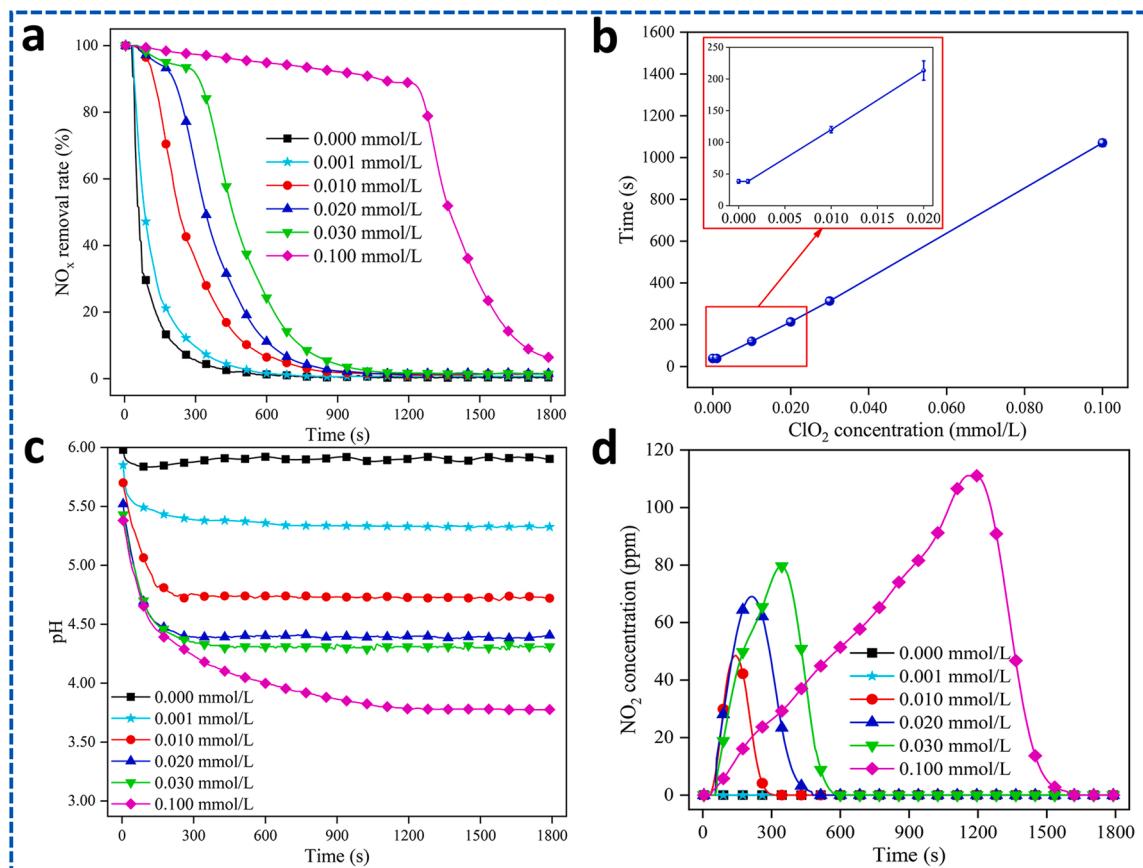


Fig. 9. Effect of initial ClO₂ concentration on denitration. (Conditions: gas flow rate 1.0 L/min, NO initial concentration 1000 ppm, solution temperature 25.0 °C, ΔP 270 kPa) a. Variations of η_{NO_x} with time under different ClO₂ concentrations. b. Variations of the duration for η_{NO_x} over 90% with ClO₂ concentration. c. Variations of solution pH with time under different ClO₂ concentrations. d. Variations of NO₂ concentration with time under different ClO₂ concentrations.

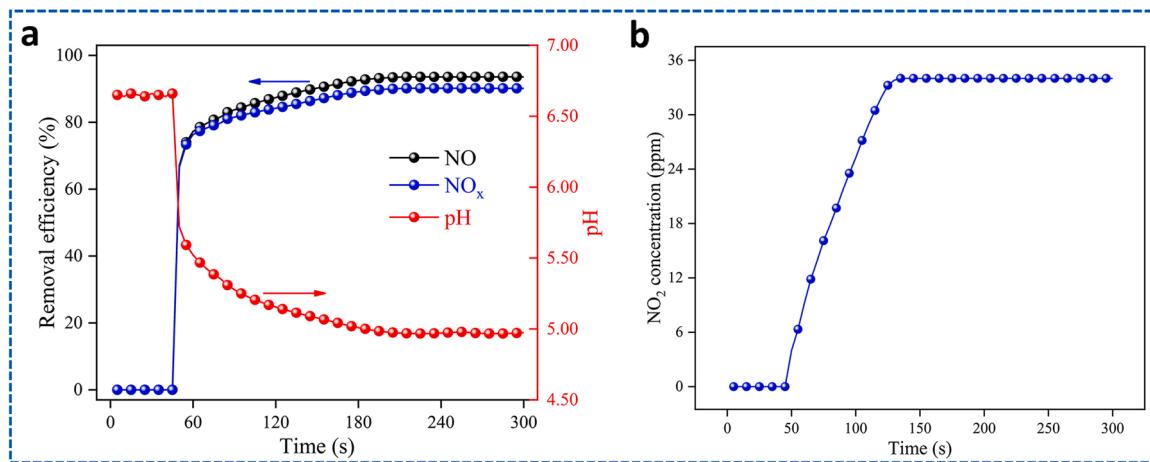


Fig. 10. Variations of removal efficiencies and solution pH with time, and NO₂ concentration with time. (Conditions: gas flow rate 1.0 L/min, NO initial concentration 1000 ppm, 11.12 mmol/L ClO₂ feeding at a rate of 4 ml/min, solution temperature 25.0 °C, ΔP 270 kPa.).

denitration. One reason for achieving stable and efficient denitration efficiency was that cavitation promoted the occurrence of R1–3. Besides, NO_x might react with •OH, as shown in R5-R8. And then ClO₂ would oxidize NO₂⁻ to NO₃⁻.

Fig. 10b showed the NO₂ concentration with time. NO₂ concentration first increased and then stabilized. The highest concentration of NO₂ was only 34 ppm. One of the reasons might be R8. HC enhancing ClO₂ non-circulation denitration solved the residual NO₂ concentration being too high. This research has important guiding significance for the practical application of the one-step HC enhancing ClO₂ denitration method.

3.8.2. Analysis of anions on denitration

We took samples at an interval of 40 s, and Fig. 11 showed the analysis results of anion products containing nitrogen atoms in the samples. It could be found from Fig. 11 that the anion product containing nitrogen atoms was only NO₃⁻ after 280 s non-circulation denitration, which meant that most of the absorbed NO_x were converted to NO₃⁻. The NO₃⁻ was the natural composition of seawater and was non-polluting to the ocean. We did not detect NO₂⁻, which was very toxic [59]. It was also observed that the trend of the measured values and the theoretical ones was the same.

4. Conclusions

We carried out a detailed study to check the effects of various parameters on denitration using HC enhancing ClO₂. Results showed that the HC reactor mainly enhanced the mass transfer process to enhance the removal of NO_x by ClO₂. In a wide pH range of 3–11, the η_{NO_x} was more than 90% during the HC enhancing ClO₂ circulation denitration experiments. The duration for η_{NO_x} over 90% initially increased to a maximum value and then decreased with the rise of operating conditions like solution temperature and ΔP. The duration for η_{NO_x} over 90% decreased with increasing NO initial concentration and gas flow rate and increased with increasing initial ClO₂ concentration. Considering the application to the practical engineering, based on the results of HC enhancing ClO₂ circulation denitration, the HC enhancing ClO₂ non-circulation denitration experiment was carried out under conditions of gas flow rate 1.0 L/min, NO initial concentration 1000 ppm, ΔP 270 kPa, solution temperature 25 °C, and 11.12 mmol/L ClO₂ feeding at a rate of 4 ml/min. The results showed that η_{NO} and η_{NO_x} reached 93% and 90%, respectively. The NO₃⁻ was the only final product of denitration and was non-polluting to the ocean. The research findings showed that the HC enhancing ClO₂ denitration method had huge potential for industrial application in flue gas cleaning.

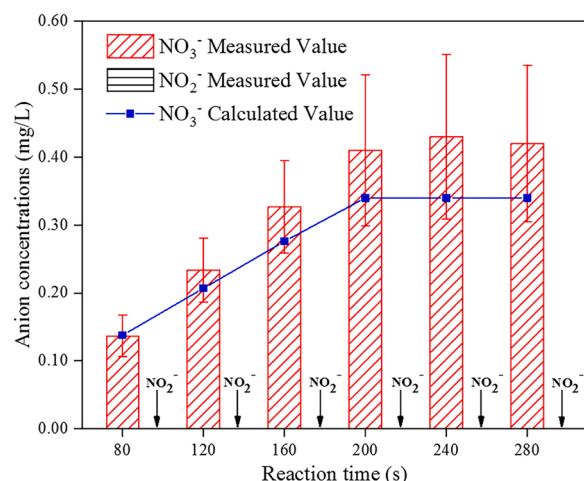


Fig. 11. Analysis of anion products containing nitrogen atoms in the samples. (Conditions: gas flow rate 1.0 L/min, NO initial concentration 1000 ppm, 11.12 mmol/L ClO₂ feeding at a rate of 4 ml/min, solution temperature 25.0 °C, ΔP 270 kPa.).

Credit author statement

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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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