Simultaneous degradation of trace antibiotics in water by adsorption and catalytic oxidation induced by N-doped reduced graphene oxide (N-rGO): synergistic mechanism

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Abstract
Aimed at current difficulties in the treatment of trace antibiotics in water, an adsorption-catalytic oxidation system was established by combining persulfate and graphene, which have the dual functions of adsorption and catalysis, for simultaneous enrichment and degradation of trace antibiotics in water. The experimental results showed that over 90% sulfamethoxazole could be degraded by the proposed system. The activation energy of the proposed system was 7.9 kJ mol⁻¹, which was significantly lower than those of typical Co catalysts and some carbon-based catalysts. Synergistic effect analysis revealed that catalytic oxidation was the key degradation kinetic of the proposed system, while adsorption showed a significant enhancement effect. Specifically, a compound with large adsorption capacity tended to be degraded preferably and rapidly. Characterization results indicated that N atoms were doped into the graphene framework, resulting in significant impacts on the activation process of potassium bisulfate by activating the sp² C system. Quenching and free radical trapping experiments revealed that degradation catalyzed by the proposed system was a non-free radical oxidation reaction dominated by singlet oxygen. In summary, the proposed design was rational, N-rGO surface provided good adsorption and catalysis sites, the synergistic effect of adsorption and catalytic oxidation led to rapid and effective enrichment and in situ degradation of trace antibiotics in water.

1. Introduction
As a typical novel pollutant, antibiotics cause potential risks to the environment and human health. Despite great attention attracted, antibiotics have not been effectively controlled. Antibiotics have been widely applied in healthcare and animal husbandry, thus making contributions to human health and socio-economic development [1–3]. Nevertheless, antibiotics are non-biodegradable compounds and prolonged exposure to antibiotics can affect endocrine, hormonal and genetic systems of the body. The key problem of the release of antibiotics into the environment is related to the development of antibiotic resistance, which has led to a reduction in its therapeutic potential against human and animal pathogens, thus the well-known antibiotic-resistant bacteria (ARBs) and antibiotic-resistant genes (ARGs) issues [4–7]. In urban water purification processes, some treatment processes (e.g., bio-active carbon and chlorine disinfection processes) and
distribution systems may enrich and promote the production of ARGs and ARBs [8, 9]. For deep, efficient treatment of antibiotics in complicated water has become a hot topic in recent years.

Currently, a key challenge in the treatment is the extremely low content of antibiotics in water, which leads to the extremely low efficiency of conventional techniques [10]. Adsorption is widely used for trace pollutant treatment, but the treatment process is long and further harmless treatment is required after adsorption [11, 12]. As one of the most powerful advanced oxidation systems used in environmental remediation, the treatment pathway of oxidation by persulfate includes free radical and non-free radical reactions. Herein, the non-free radical pathway preferentially conducts electrophilic attacks on electron-rich organic pollutants such as antibiotics, making its degradation more selective and more resistant to the adverse effects of complex components on free radical consumption in natural water environment, but its efficiency in treating trace pollutants in water is poor [13–16]. Therefore, the in situ degradation based on synergistic mechanism of adsorption and catalytic oxidation, namely adsorption–catalytic oxidation system was designed, under the synergistic mechanism of the proposed system, the trace antibiotics in water were enriched by the adsorbent, and at the same time, the adsorbent was used as the activation center to catalyze persulfate to produce a large amount of active oxygen to in situ degradation the enriched antibiotics, and then release adsorption sites and active center. Through this continuous ‘adsorption-degradation’ cycle, trace antibiotics in water were removed rapidly and efficiently. The core of this design was to find a catalyst that combines efficient adsorption and excellent catalytic performance. Ordinary adsorbent generally did not have the ability to catalyze persulfate, and the commonly used Co catalyst not only had a weak adsorption capacity, but also might cause secondary contamination by metal leaching. The emergence of graphene had brought hope to solve this problem [17–19]. Graphene, as the newest material in the carbon family, has shown many potential applications due to its unique 2D assembly and associated energy band structure. The graphene inherits the excellent adsorption performance of carbon materials, and numerous studies have confirmed the great potential of graphene in the adsorption of different antibiotics and its fast and efficient adsorption of trace antibiotics has been demonstrated [20–25]. Since the report of peroxymonosulfate (PMS) activation by rGO, graphene is expected to be a promising new catalytic material. More importantly, the number of active sites can be increased by various modification methods to enhance its catalytic performance [26–29]. Modified graphene pairs have good adsorption and catalytic performance, among which N doping has been shown to induce changes in the nature of carbon nanoparticles, creating more active sites and bringing new properties such as increased electrochemical catalytic activity, hydrophilic and highly selective oxidative dehydrogenation reactions, and oxygen reduction reactions [30–34].

In summary, this study established an adsorption–catalytic oxidation system using N-doped reduced graphene oxide (N-rGO) and PMS, to solve the problem of trace antibiotics treatment, exploiting the dual adsorption and catalytic effects of N-rGO. Combining adsorption with catalytic oxidation synergistic mechanism in kinetic analysis system of degradation, the effects of pH value, temperature and dosage were investigated, and the main active components in the degradation process were analyzed by free radical experiments to investigate the reaction mechanism.

2. Experimental

2.1. Preparation of N-rGO

The graphite powder (10 g) was pre-oxidized with concentrated nitric acid (20 ml), potassium persulfate (8 g) and phosphorus pentoxide (8 g) at 80 °C for 6 h. The powder was then cooled at room temperature, diluted with DI water, filtered, washed several times and dried at 60 °C for 12 h. The powder was ground and sieved through 100 mesh sieves to obtain the pre-oxidized graphite powder. 10 g of pre-oxidized graphite powder was placed into a beaker containing 180 ml of concentrated sulfuric acid and 20 ml of concentrated phosphoric acid (ice bath) and stirred for 30 min 60 g of potassium permanganate was added in small amounts. Then the beaker was transferred to a water bath and stirred at 35 °C for 1 h. Then the temperature was adjusted to 60 °C, continuously drop add 490 ml of DI water dropwise to raise the temperature to 98 °C for 30 min. The reaction was terminated by adding 25 ml of 30% hydrogen peroxide. The solution was filtered directly while it was still hot and eluted with 0.1 mol L⁻¹ hydrochloric acid. It was then subjected to ultrasonic peeling in DI water for 30 min at 100 W. After centrifugal concentration, the powder was dried at 60 °C for 12 h. After drying, the powder was ground and sieved through 100 mesh sieves to obtain graphene oxide powder. The graphene oxide was dispersed in water at a concentration of 2 mg L⁻¹ and sonicated for 1 h. 60 ml of graphene oxide was added to 2 ml of ammonia and stirred for 10 min and transferred to an autoclave for 24 h at 180 °C. The powder was collected by centrifugation and washed with DI water, dried at 60 °C for 12 h and then ground and sieved through 100 mesh to obtain N-rGO powder (N-rGO).
2.2. Adsorption-catalytic oxidation synergistic treatment

In a 120 ml brown vial, 80 ml of antibiotics solution and 10 ml of 1 mg l$^{-1}$ N$^{-1}$-rGO disperser were added, followed by 10 ml of 10 mg l$^{-1}$ PMS solution and shaken rapidly, followed by initiation of the catalytic reaction in a shaker. Meanwhile, comparative experiments were designed: one was to add potassium bisulfate when N-rGO reached adsorption equilibrium on antibiotics; the other was to use graphene oxide (GO) to catalyze degradation of antibiotics by PMS; the third was to use potassium bisulfate itself without N-rGO to degrade antibiotics. A comparative analysis of degradation kinetics was performed to identify the dominant role of antibiotics degradation process and adsorption-catalytic oxidation synergistic mechanism. The pH range of the influencing factors experiment was 3–12, the temperature range was 288.15, 298.15 and 308.15 K, and the catalyst dosage was set as 5, 10 and 20 mg 1$^{-1}$ mg. The mixed experiments were also conducted to investigate whether the capacity of the proposed system was affected by the coexistence of antibiotics and to analyze the synergistic mechanism.

Excessive addition was used to investigate whether the removal effect was inhibited, with tert-butanol, methanol, P-benzoquinone, β-carotene as blockers of the active oxygen reaction. The active oxygen was captured and qualitatively analyzed by using 5,5-dimethyl-1-pyrroline-n-oxide (DMPO) as a scavenger for sulfate-free radical and hydroxyl free radicals and 2,2,6,6-tetramethylpiperidine (TEMP) as a scavenger for singlet oxygen. Electron paramagnetic resonance spectroscopy was used to capture and qualitatively analyze active oxygen.

2.3. Measurement of antibiotic concentrations

The antibiotics concentration was measured by HPLC with a C18 chromatographic column and other conditions: (1) sulfamethoxazole: The mobile phases were water, acetonitrile and triethylamine in the ratio of 799: 200: 1. The pH value was adjusted to 5.9 using sodium hydroxide or glacial acetic acid with a flow rate of 1 ml min$^{-1}$ and a wavelength of 240 nm. (2) Levofloxacin: 0.05 mol l$^{-1}$ potassium dihydrogen phosphate (pH value adjusted to 2.8 by phosphoric acid) - acetonitrile (82:18) as mobile phase at a flow rate of 1 ml min$^{-1}$ and a wavelength of 293 nm. (3) Clindamycin: The mobile phase was 0.68 g 1$^{-1}$ potassium dihydrogen phosphate (250 g l$^{-1}$ sodium hydroxide to adjust pH value to 7.5) - acetonitrile (55:45) at a flow rate of 1 ml min$^{-1}$ and a wavelength of 210 nm. (4) Tetracycline: The mobile phase was methanol – 0.02 mol l$^{-1}$ potassium dihydrogen phosphate (pH value was adjusted to 2.0 by nitric acid) at a ratio of 12:88, flow rate 1 ml min$^{-1}$, wavelength 280 nm. (5) Penicillin G, Sodium Salt: The mobile phase was 0.1 mol l$^{-1}$ potassium dihydrogen phosphate (pH was adjusted to 2.5 by phosphoric acid) - acetonitrile, 70:30 ratio, flow rate 1 ml min$^{-1}$, wavelength 225 nm. (6) Chloramphenicol: The mobile phase was methanol and water, volume ratio was 6:4, flow rate was 0.5 ml min$^{-1}$, wavelength was 272 nm.

2.4. Characterization

Surface morphology was observed on a ZEISS Gemini SEM 500 scanning electron microscope (SEM) and a Xradia 610 transition electron microscopy. Fourier transform infrared spectra (FTIR) were obtained from a Bruker instrument with ATR correction mode. X-ray photoelectron spectroscopic (XPS) analysis was conducted on a VG Multilab 2000 spectrometer (Thermo Electron Corporation) with Al Kα radiation as the exciting source (300 W). Raman spectra were obtained by using an ISA argon-laser Raman spectrometer. Electron paramagnetic resonance (EPR) from a Bruker EMS-plus was applied to probe the reactive radicals generated during activation of PMS captured by spin trapping agents 5,5-dimethylpyrroline-oxide (DMPO) and 4-Amino-2,2,6,6-tetramethylpiperidine (TEMP), operating with center field of 3515G, sweep width of 100G, microwave frequency of 9.86 GHz, power setting of 18.75 mW, and scan number of 3. The EPR spectra were analyzed by the spin-fitting package of Bruker Xeon software.

3. Results and analysis

3.1. Characterization results

Both GO and N-rGO showed transparent lamellar structures, and the folds were distributed in large numbers on the basal plane, forming more gully areas, and these folds and planar structures could provide more adsorption sites. N doping did not change the intrinsic structure of graphene, but the transparency of the lamellae increased and the porous structure became more prominent, which might represent an increase in intra- and interlayer repulsion and a decrease in stacking, which was consistent with the apparent difference between the two in transmission electron microscopy (figure 1). The elemental composition in table 1 showed that N-rGO had been successfully doped with nitrogen, and the oxygen content had decreased due to the reduction of ammonia, and some of the oxygen-containing functional groups had been reduced during the doping process.
N doping changed the IR spectrum, both GO and N-rGO had a very distinct absorption peak at 3390 cm\(^{-1}\), which was attributed to the stretching vibration of OH, COOH. The IR spectra of N-rGO showed three new absorption peaks at 1627 cm\(^{-1}\), 1397 cm\(^{-1}\), 1032 cm\(^{-1}\), among which the absorption peaks at 1627 cm\(^{-1}\), 1397 cm\(^{-1}\) might be caused by C=O, C=C, indicating that N doping might not only cause the reduction of oxygen-containing functional groups in graphene oxide, but also might cause the transfer of oxygen-containing functional groups (figure 2). The absorption peak at 1032 cm\(^{-1}\) might be caused by -OH or C-N BONDS, both C-N BONDS and -OH infrared absorption peaks were between 1014 and 1165 cm\(^{-1}\). Infrared spectroscopy did not effectively distinguish between these two absorption peaks, and further investigation was needed\[35\].

Figure 3(a) shows XPS full spectrum scans of as-prepared N-rGO. As observed, both GO and N-rGO showed C1s and O1s peaks at 298 and 533 eV, and the O1s peak of N-rGO was significantly weaker than that of GO, indicating the decrease of oxygen-containing functional groups during N doping, forming a more reducing graphene surface, which was consistent with the decrease of oxygen content after N doping in the elemental analysis. Meanwhile, the N1s peak at 400 eV appears in the full spectrum of N-rGO, demonstrating the successful integration of the nitrogen atom into the graphene framework. Further scanning of the N spectrum at 400 eV revealed that the nitrogen atoms were connected to the carbon atoms in graphene by three carbon-nitrogen structures (pyridinic N, pyrrolic N and graphitic N, as shown in figure 3(b)), which was consistent with previous studies\[36, 37\].

As shown in figure 4, two characteristic peaks appeared at 1307 cm\(^{-1}\), 1598 cm\(^{-1}\), which corresponded to the D-band and G-band, respectively, and this was a sign of successful graphene preparation. The intensity ratio of D band to G band (\(I_D/I_G\)) clearly indicated the degree of defects in the carbon materials. In most cases, the introduction of dopant atoms into the graphene network resulted in more defects, which in turn increased the \(I_D/I_G\). The structural defects of N-doped graphene became larger, which changed the spin structure and charge distribution of graphene, thus breaking the chemical inertia of graphene and improving its chemical catalytic performance. This increase in defect structure might be due to the disruption of the carbon lattice, the removal of oxygen and the release of edge sites, which facilitated the activation of PMS\[38, 39\].

3.2. Kinetic analysis

Figure 5 shows features of the adsorption-catalytic oxidation system under different degradation modes. As observed, the processing rates and effects of the adsorption-catalytic oxidation system under different degradation modes showed great differences. Apparently, the removal rate of N-rGO/PMS adsorption-catalytic oxidation system was high (>91%), and the reaction was extremely rapid (in 16 min). The removal rate of sulfamethoxazole by adding PMS after adsorption equilibrium was basically the same as that of the N-rGO/PMS adsorption-catalytic oxidation system, but the overall reaction rate was significantly slower, indicating that PMS was catalyzed by N-rGO, and the resulting active oxygen could degrade the remaining antibiotics after adsorption. However, the degradation rate of this method of adding oxidant after adsorption was overly dependent on the previous adsorption process, resulting in low efficiency. In contrast, neither PMS nor GO/PMS systems were effective in treating antibiotics, in which the removal rate was still less than 10% when PMS was not activated for more than 60 min, and the amount of active oxygen produced was very small. The removal rate of antibiotics by GO/PMS system was close to 70%, but the reaction rate was low and it took a long time to
reach equilibrium, although GO itself had certain adsorption and catalytic ability, it was weaker than N-rGO. This could be seen from the small difference in removal rate between different degradation modes triggered by GO. In summary, the proposed adsorption–catalytic oxidation system had an efficient processing capacity for simultaneous adsorption and oxidation.

To further investigate the features of the proposed adsorption–catalytic oxidation system, a lateral comparison of different degradation modes was performed using reaction rate constant. In common kinetic equation, first-order kinetic equation was often used for kinetic fitting of persulfate catalytic oxidation, and the fitting was good, so in this paper, first-order kinetic equation was also used to fit the above experimental process [40]:

\[
\ln \frac{C}{C_0} = -k_1 t
\]

where \(C\) and \(C_0\) refer to antibiotic concentrations at Moment t and the initial moment, respectively (mg l\(^{-1}\)); \(k_1\) is the first-order kinetic rate constant (min\(^{-1}\)).

Figure 6 and table 2 illustrated fitting results and kinetic parameters, respectively. As observed, the reaction rate constant of the N-rGO/PMS adsorption–catalytic oxidation system was significantly higher than other reaction types, with a reaction rate constant of 0.1686, while the reaction rate constant for adsorption followed by adding PMS was about 0.0533, suggesting that by simultaneous adsorption, the catalytic oxidation reaction rate was increased by more than 3 times compared to the activation method after adsorption. This was probably due to the fact that the N-rGO surface after adsorption saturation was covered by antibiotics, which affected the active sites of the catalyst, resulting in the decrease of catalytic efficiency. The reaction rate constant of N–rGO during adsorption was 0.0309, while the reaction rate constant of GO/PMS system was 0.0181, and it could be found that the adsorption rate by N-rGO was faster than the reaction rate of GO/PMS system, and this rapid adsorption was one of the reasons for the higher reaction rate of simultaneous adsorption and catalytic oxidation. The rapid and effective enrichment ability of N-rGO solved the problem that the concentration of trace antibiotics in water to degradation was too small, which was not conducive to the reaction and the reaction condition of high pollutant concentration in local areas was formed near the catalyst, which was beneficial to improve the effect of pollutant oxidation by active oxygen produced by catalytic PMS. At the same time, during the degradation process of pollutant, this timely oxidative degradation could not only remove antibiotics quickly, but also avoided the problem of catalyst surface absorbing too much pollutant, which led to the decrease of active sites and thus the decrease of catalytic efficiency, and the purpose of simultaneous adsorption, catalytic oxidation degradation was achieved.

Figure 2. FT-IR spectra of GO and N-rGO.

Table 1. Physical and chemical properties of GO and N-rGO.

|       | C, at% | O, at% | N, at% | SSA, m\(^2\) g\(^{-1}\) |
|-------|--------|--------|--------|--------------------------|
| GO    | 62.74  | 0      | 37.83  | 197                      |
| N-rGO | 61.85  | 34.75  | 2.99   | 232                      |
Figure 3. (a) XPS surveys of GO and N-rGO, (b) N1s high resolution spectra of N-rGO.

Figure 4. Raman spectra of GO and N-rGO.
3.3. Influencing factors

3.3.1. pH value
At pH $= 4 \sim 12$, the N-rGO/PMS adsorption-catalytic oxidation system showed a good treatment effect on antibiotics and demonstrated strong adaptability to pH value changes. Compared with N-rGO adsorption, the removal rate was significantly increased in the full pH value range, especially in the case of pH deviation from neutral. The reason for the decreased treatment effect of N-rGO/PMS at lower pH values was the presence of a large number of hydrogen ions in the system, which would compete with the sulfamethoxazole that presented in the ionic form in water for active oxygen, resulting in the poor degradation effect. At high pH values, the effect of alkali activation on the persulfate system gradually manifested itself, filling the gap in the treatment demand caused by insufficient graphene adsorption capacity under alkaline conditions [41, 42]. The pKa of SMZ is 2.28 and 7.42, respectively. When pH $< 2.28$, the substance exists as a positive charge, and when pH $> 7.48$, it exists in the form of negatively charged substance, and there is coexistence between the two. When the pH increases from 2 to 7, the electrostatic attraction of the surface hydroxyl-protonated N-rGO to SMZ is enhanced, resulting in an increase in the adsorption capacity. As the pH value gradually approaches 7, the protonated SMZ is more stable than the deprotonated SMZ. SMZ is more hydrophobic, and at the same time, the number of $\pi$ electrons attracted by neutral SMZ increases, which leads to the enhanced $\pi-\pi$ EDA interaction between $\pi$ electrons and deionized groups in the graphitic carbon structure, and the adsorption capacity reaches the maximum. If pH $> 7$, with pH value increases, the electrostatic interaction changes from attraction to repulsion, making the adsorption of SMZ less favorable, and the adsorption process is suppressed [43, 44].

3.3.2. Temperature
As shown in figure 7(b), increasing the temperature was beneficial for adsorption-catalytic oxidation to degrade sulfamethoxazole. Thermal activation was one of the methods of PMS activation, but the free radical chain reaction was usually triggered at temperatures above 323.15 K. Therefore, in practice, the activation of PMS by pure thermal activation was rarely used, but only as a supplementary activation method, or by using the heat of the wastewater for activation. The activation energy was one of the indicators of catalyst performance. The activation energy of N-rGO calculated by the Arrhenius equation was $7.9 \text{kJ mol}^{-1}$, which was significantly smaller than that of typical Co catalyst ($59.7 \sim 69.7 \text{kJ mol}^{-1}$), and exhibited great advantages over carbon-based catalysts, including CNT ($33.3 \text{kJ mol}^{-1}$), $\text{N}^{-1}$-CNT ($39.2 \text{kJ mol}^{-1}$), $\text{N}^{-1}$G$^{-1}$50 ($19.7 \text{kJ mol}^{-1}$), and NG-700 ($18.6 \text{kJ mol}^{-1}$), demonstrating that N atoms could significantly activate the $sp^2$ carbon system and reduce the activation energy of electron transfer from graphene surface to PMS, which had a significant effect on the activation process of PMS [45, 46].

3.3.3. N-rGO dosage
When the catalyst dosage was increased from 0.05 mg l$^{-1}$ to 0.1 mg l$^{-1}$, the processing rate and effect of the system on sulfamethoxazole were improved. Increasing the catalyst content provided more active sites and enhanced the pollutant adsorption effect, and also enhanced the PMS active effect. The simultaneous effects on the adsorption-catalytic oxidation system were all positive, which could greatly improve the degradation ability.
of the system to pollutant. When the catalyst dosage was increased from 0.1 mg l$^{-1}$ to 0.2 mg l$^{-1}$, the changes in removal rate and reaction equilibrium time were not significant for two reasons. First, from the perspective of adsorption, too many adsorbents might generate cause overlap/stacking, which reduced the effective surface area and active adsorption sites that could be utilized, and the adsorption effect would not be enhanced. Second, from the catalytic point of view, although the number of active sites for PMS catalysis increased, the quantity of PMS and pollutant in the system was certain, the increase of active sites was single, the PMS and pollutant concentration did not match it, so the increase of activation rate was not obvious. Therefore, the experimental selection of a reasonable catalyst dosage could improve the reaction process quickly and avoid unnecessary waste.

### 3.3.4. Presence of multiple antibiotics

In practical cases, water usually contains multiple antibiotics. In order to investigate the effect of the system on the treatment of antibiotics in the coexistence of multiple antibiotics and to examine whether there was a sequence of degradation, a mixture of sulfamethoxazole, levofloxacin, clindamycin, tetracycline, penicillin and chloramphenicol was treated. The results demonstrated that the proposed system was effective in treating multiple antibiotics. However, the degradation process had a certain sequence, in the initial stage of the reaction, the removal rate of antibiotics was ranked from high to low as tetracycline, levofloxacin, sulfamethoxazole, clindamycin, penicillin, chloramphenicol. The heterogeneous catalytic process included at least diffusion, adsorption, reaction, desorption and re-diffusion. Each step controlled the overall catalytic reaction, especially in the adsorption-catalytic oxidation system, adsorption was an important control process. A discussion of the effects of this part would be presented in the next section.

### 3.4. Synergistic effect

In the adsorption-catalytic oxidation system, N-rGO embodies the dual efficacy of adsorption and catalysis, firstly, it enriches trace antibiotics in water by its powerful adsorption ability, and then it is degraded *in situ* by the large amount of active oxygen produced by PMS catalyzed by N-rGO in this core region, and at the same time, it releases the pre-occupied active sites until all antibiotics are degraded. The experimental results have confirmed

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**Table 2. First order kinetic model parameters of different degradation modes.**

|                      | $k_1$ (min$^{-1}$) | $R^2$   |
|----------------------|--------------------|---------|
| N-rGO adsorption     | 0.0309             | 0.9326  |
| Degradation (N-rGO)  | 0.0533             | 0.9546  |
| N-rGO + PMS          | 0.1686             | 0.9842  |
| GO adsorption        | 0.0171             | 0.9982  |
| Degradation (GO)     | 0.0063             | 0.9560  |
| GO + PMS             | 0.0181             | 0.9614  |
| PMS                  | 0.0009             | 0.8722  |
the effectiveness of this system, but the dominant role needs to be further verified. As shown in figures S1(a) (available online at stacks.iop.org/MRX/9/065601/mmedia) and (b), the differences in the removal rate of sulfamethoxazole between adsorption adding PMS and adsorption followed by catalytic oxidation were not significant, but the reaction rate constant was much different. The reaction rate constant when both act at the same time was much higher than that of adsorption followed by catalytic oxidation, suggesting that catalytic oxidation was the key role in the degradation process. The large difference in the reaction rate constant might be due to the addition of PMS after adsorption saturation, although the antibiotics did not completely shield the active sites, there was a certain shielding effect, resulting in a less rapid catalytic reaction. In the process of simultaneous degradation of adsorption and catalytic oxidation, the antibiotics adsorbed to the surface by N-rGO could be degraded rapidly by the active oxygen generated by the simultaneous catalysis, and no barrier was formed on the catalyst surface, so the degradation rate was accelerated.

The previous analysis illustrated the important role of catalytic oxidation in the system by comparing two degradation modes, and the role of adsorption in the proposed system was analyzed below. The results of kinetic analysis were used to correlate the removal effect, first-order kinetic reaction constant and adsorption capacity, and to find the contribution of adsorption in the system through this correlation analysis and to investigate the reaction mechanism more deeply. The removal rate and reaction rate constant of antibiotics degraded in the system alone in figures S1(c) and (d) showed that the removal rate and reaction rate constant of antibiotics being degraded alone in the system. It can be seen that, except for clindamycin, the changes of these two parameters were positively correlated with the changes in adsorption capacity. Both parameters increased with the increase of N-rGO adsorption capacity of antibiotics, indicating that the adsorption effect on the system was enhanced. There were π-π interactions and charge transfer between the antibiotics and the catalyst, and the charge transfer effect might increase the degradation rate of the antibiotics on the catalyst surface under the same catalytic capacity of N-rGO. The magnitude of this charge transfer was directly related to the adsorption capacity, so it showed that the removal rate and reaction rate constant increased when the adsorption capacity was large.

Figure S1(e) shows that the reaction rate constant of each antibiotic in the mixed antibiotics solution exhibits a positive correlation with the adsorption capacity, and the greater the adsorption capacity, the more rapidly and preferentially it can be degraded. Meanwhile, as shown in Figure S1(f), compared with the case of single antibiotic being degraded, the reaction rate constant decreased when mixed, and the reaction process was inhibited, but relatively speaking, the larger the adsorption capacity was, the less it was inhibited, indicating that in the coexistence of multiple antibiotics, the preferentially adsorbed ones would be preferentially degraded, indicating that adsorption played an enhanced role in the adsorption-catalytic oxidation process. The above differences might reflect a synergistic effect between adsorption and catalytic degradation: the easier the degradation, the more antibiotics will be adsorbed in solution, which in turn kept the corresponding pollutant in the solution of the easier (faster) degradation mixture.
3.5. Catalytic mechanism
Active oxygen inhibition revealed that the adsorption-catalytic oxidation system was a non-free radical dominated persulfate system. As shown in figure 8(a), Tert-butanol, methanol, P benzoquinone had almost no effect on the reaction process, and the removal rate was only slightly reduced, indicating that ·SO₄⁻, ·OH, and superoxide free radicals were not present in large quantities. β-carotene was used for singlet oxygen inhibition because its reaction rate with ¹O₂ is an order of magnitude higher than that of NaN₃ and was less susceptible to oxidation by PMS [47]. The degradation capacity after the addition of β-carotene was drastically reduced, suggesting that ¹O₂ was a main active oxygen form in the proposed adsorption-catalytic oxidation system. Meanwhile, degradation rate in presence of β-carotene was higher than that with adsorption only, although its trend was similar with the adsorption curve. In this case, ¹O₂ was completely inhibited and ·SO₄⁻, ·OH, ·O₂⁻ etc. were almost ineffective in the system, indicating that there might also be electron transfer between pollutant and oxidant in the catalyst carrier, which was also one of the non-free oxidation pathways. This speculation was confirmed by the EPR spectra of the reaction system, which showed a triple peak in place of ¹O₂ in the TEMP system, and the presence of the signal was very obvious, which was consistent with the characteristic peak formed by TEMP with ¹O₂ in figure 8(b) and the literature [48]. The characteristic peaks representing ·SO₄⁻ and ·OH were very weak, suggesting that no significant amount of ·SO₄⁻ and ·OH was produced.

4. Conclusions
The experimental results showed that over 90% sulfamethoxazole could be degraded by the proposed system within 16 min, the degradation process followed the first-order kinetic equation. The antibiotics were brought
close to the core of the catalytic reaction by adsorption with the catalyst, where they were rapidly degraded by the large amount of active oxygen produced by the catalyst and PMS. It was possible to produce charge transfer between antibiotics and catalyst, which increased the degradation rate of antibiotics on the catalyst surface. Additionally, it exhibited excellent degradation performance on sulfamethoxazole, levofloxacin, clindamycin, tetracycline, penicillin and chloramphenicol, and the sequence and extent of degradation were related to adsorption capacity of N-doped reduced graphene oxide (N-rGO). Synergistic effect analysis revealed that catalytic oxidation was the key degradation kinetic of the proposed system, while adsorption showed a significant enhancement effect. Specifically, a compound with large adsorption capacity tended to be degraded preferably and rapidly. Characterization results indicated that N atoms were doped into the graphene framework, resulting in significant impacts on the activation process of potassium bisulfate by activating the sp² C system. Quenching and free radical trapping experiments revealed that degradation catalyzed by the proposed system was a non-free radical oxidation reaction dominated by singlet oxygen. The above results demonstrate the correctness of the design, synergistic effect of adsorption and catalytic oxidation provides a new strategy for removal of trace pollutant in water.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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