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Efficient Degradation of Chlortetracycline by Graphene Supported Cobalt Oxide Activated Peroxydisulfate: Performances and Mechanisms

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Abstract: Cobalt oxide has good catalytic activity for peroxydisulfate (PDS) activation but poor stability and is vulnerable to inactivation because of agglomeration. In this work, the chlortetracycline (CTC) degradation by peroxydisulfate (PDS) catalysis using the reduced graphene oxide support cobalt oxide (Co₃O₄/rGO) composite catalyst was investigated. It was found that 86.3% of CTC was degraded within 120 min in the Co₃O₄/rGO-800/PDS system. The influences of catalyst dosage, PDS concentration, solution pH, and reaction temperature were systematically explored. The excellent removal performance of CTC could be attributed to the synergistic effect between adsorption and catalytic degradation. $=Co^{2+}$ and surface functional groups played as active sites to catalyze PDS, and the circulation of $=Co^{2+}/=Co^{3+}$ was achieved. Moreover, Co₃O₄/rGO-800 showed satisfactory reusability after three cycles. This research can provide useful information for the development of efficient PDS catalysts and facilitate insights into CTC degradation mechanism.

Keywords: antibiotic; advanced oxidation processes (AOPs); reduced graphene oxide; cobalt oxide; wastewater

1. Introduction

Chlortetracycline (CTC) are tetracycline antibiotics that are widely prescribed and often applied as pharmaceutical ingredients and feed additives [1]. Owing to widespread utilization, CTC were detected as common species causing water contamination world-wide [2–4]. When CTC spreads among bacteria and natural microbial populations, it may trigger the imbalance of the ecosystem and threaten human health through the food chain [5]. At the same time, changes in bacterial adaptation caused by the misuse of antibiotics were investigated and evaluated, and the environmental risks posed by the development of drug-resistant bacteria in various countries cannot be underestimated [6,7].

To ensure food safety, control water contamination and the proliferation of drug-resistant bacteria, various approaches were proposed to eliminate CTC [8,9]. Advanced oxidation processes (AOPs) use the powerful oxidative free radicals (such as •OH) to oxidize and even mineralize pollutants, it is considered as an efficient and insightful remediation technique [10]. Recently, sulfate radicals-based AOPs caused rising interests owing to the advantages of high performance and wide operation pH range [11]. Sulfate radicals (SO4•-) could be generated through activating peroxymonosulfate (PMS) and peroxydisulfate (PDS) using different activation strategies, such as UV irradiation, heat, ultrasound, alkaline, and transition metals [12]. Transition metals activation

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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/license s/by/4.0/). is widely deemed as a promising approach since it is simple, low cost, and high performance [13]. Cobalt (Co) is the most efficient PDS catalyst compared with other transition metals, and cobalt ion (Co²⁺) was frequently reported as an effective PDS activator for organic pollutants degradation [14]. However, the application of homogeneous Co²⁺ would lead to the discharge of Co²⁺. Co²⁺ is highly toxic and carcinogenic, and the remaining Co²⁺ in the aquatic solution are likely to have negative effects on human health [15].

Heterogeneous cobalt containing materials are considered promising alternative approaches. Recently, Co₃O₄ nanoparticles were widely used as PDS catalysts. For instance, Zhang et al. reported that orange G was completely degraded in the Co₃O₄/PDS system in 180 min [16]. Yang et al. investigated the effective degradation of orange G with Co₃O₄ as persulfate catalyst. They found that orange G (30 mg/L) could be almost completely removed after 10 min reaction at 0.5 g/L Co₃O₄ catalyst and 8.0 mM persulfate [17]. However, a serious agglomeration problem was observed when using Co₃O₄ nanoparticles because of the high surface energy [13]. Loading cobalt oxide onto appropriate support materials is a feasible solution to solve this problem [18]. Graphene is a two-dimensional monolayer of sp²-hybridized carbon material [19]. It is considered as a potential carrier because of large surface area and excellent electrical conductivity [20]. It was reported that the combined transition metals with graphene will undergo considerable restacking through π - π and hydrophobic–hydrophobic interactions when used directly [21].

Recently, reduced graphene oxide (rGO) exhibited excellent persulfate activation activity for the generation of powerful reactive species [22]. It was reported that the defective structure and ketonic groups existed on rGO might play as active sites for persulfate activation [23]. For example, Olmez-Hanci et al. reported that rGO was an efficient persulfate activator for Bisphenol A degradation. They found that Bisphenol A can be completely removed by rGO/persulfate system within 10 min [23]. Cruz-Alcalde et al. developed the rGO membranes to activate persulfate for phenol and venlafaxine degradation. The results indicated that 90% and 94% of phenol and venlafaxine could be removed after treatment, respectively [24]. Therefore, the integration of rGO with Co₃O₄ nanoparticles can not only improve the dispersive forces within nanomaterial, but the catalyzing activity towards PDS could also be significantly enhanced [25]. For instance, Yan et al. developed reduced graphene oxide supported magnetite nanoparticle composite (nFe₃O₄/rGO) and used it as PDS catalyst for the degradation of trichloroethylene (TCE). The degradation rate of TCE was 98.6% within 5 min at 6.94 g/L of nFe₃O₄/rGO and 3 mM PDS [26]. Ahmad et al. developed reduced graphene oxide-iron nanocomposite (nZVI-rGO) to activate persulfate for trichloroethylene degradation. The results indicated that the nZVI-rGO/persulfate process could remove approximately 99% of trichloroethylene within 2 min [27]. However, there are no researches on the application of rGO-supported cobalt oxide composite as a PDS activator for CTC degradation.

In this work, the CTC degradation by PDS catalysis using the reduced graphene oxide support cobalt oxide (Co₃O₄/rGO) composite catalyst was studied. Co₃O₄/rGO was synthesized with a simple strategy. The crucial influencing factors, including catalyst dosage, PDS concentration, pH, and temperature on CTC degradation, were experimentally explored. CTC degradation mechanisms were investigated according to the experimental results and characterization analysis. The catalyst's reusability was examined using cyclic experiments. The main objectives of this research are to: (1) prepare and systematically characterize the Co₃O₄/rGO-800 catalyst, (2) evaluate the activity of different catalysts that are synthesized under different conditions, (3) investigate the impacts of crucial environmental factors on CTC degradation, (4) elucidate CTC degradation mechanisms in the Co₃O₄/rGO-800/PDS system. This research can provide useful information for the development of efficient PDS catalysts and facilitate insight into CTC degradation mechanism.

2. Materials and Methods

2.1. Chemicals

Urea, CoCl2•6H2O, sodium peroxydisulfate, chlortetracycline hydrochloride (CTC), and NaOH were purchased from Shanghai Macklin Biochemical Co., Ltd., Shanghai, China. Graphene oxide (GO) was obtained from JCNANO Tech Co., Ltd., Nanjing, China. Ethanol and sulfuric acid was obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Deionized (DI) water was used in the experiments.

2.2. Catalysts Synthesis

A total of 50 mg of dried GO was accurately weighed and transferred into a 100 mL beaker. An amount of 20 mL of DI water was added to the beaker, and it was sonicated and dispersed for 30 min to form a GO homogenate. Then, different amounts of CoCl2•6H2O were added to the homogenate (0.5–2 mM), and 2 g of urea was added to improve the loading success of metal atom. After stirring with an electromagnetic stirrer for 4 h, the homogenate was filtered and thoroughly washed, and dried at 60 °C. The solid was ground into powder form to obtain precursors of the material for subsequent experiments.

The above precursor materials were heated in a tube furnace under N₂ atmosphere at the heating rate of 5 °C min⁻¹. The temperature was set up to reach 700 °C, 800 °C, and 900 °C. Additionally, these temperatures were maintained for 2 h. The black powders were designated Co₃O₄/rGO-700, Co₃O₄/rGO-800, and Co₃O₄/rGO-900.

2.3. Experimental Procedures

CTC degradation was carried out in a 200 mL glass flask containing 100 mL of CTC (20 mg L⁻¹) with a constant stirring at 25 °C. Influences of crucial factors (catalyst dosage, PDS concentration, pH, temperature) were studied using single-factor experiments. A non-homogeneous system was formed by adding 50 mg of catalyst, stirring uniformly and then left to settle for 30 min under light-proof conditions. Then, solution pH was adjusted by using NaOH (1 M) and HCl (1 M). Thereafter, degradation was initiated through adding PDS to the stirred system. At the specified time interval, 1 mL of the sample solution was extracted and filtered through an aqueous microporous membrane (0.45 μ m) before the measurement of concentration. The reusability of the catalyst was examined using cycling experiments.

3. Result and Discussion

3.1. Characterization

Scanning electron microscope (SEM) coupling energy dispersive spectrometer (EDS) (ZEISS Sigma 300) was applied for the analysis of surface morphology of catalyst. According to the SEM images (Figure 1a–d), the Co₃O₄/rGO-800 presented an irregular and curled flake structure, which was consistent with the results in other researches [28,29], indicating the reduction in GO was successful. Additionally, the rough and wrinkled surface of graphene flakes increased the effective contact area of the material and exposed more surface active sites, which was significant for the adsorption properties of the Co₃O₄/rGO-800 [23]. In addition, the loading of cobalt was also observed on the surface of the material, and the more uniform spherical or ellipsoidal particles were distributed on the surface of the graphene sheets. According to EDS images (Figure 1e–h), C, N, O, and Co elements were uniformly distributed on the catalyst surface, indicating that reduced graphene oxide-supported cobalt was successfully prepared, which was consistent with the SEM results.



Figure 1. (a–d) SEM images of Co₃O₄/rGO-800; (e–h) the corresponding EDS mapping of Co₃O₄/rGO-800).

X-ray diffraction (XRD, Panalytical Empyrean) was used to determine the composition of the catalyst. One sharp peak at $2\theta = 10.4^{\circ}$ attributed to the (001) crystal plane was observed at the XRD pattern of GO (Figure 2) [30]. For Co₃O₄/rGO-800, the peak at $2\theta = 10.4^{\circ}$ disappeared, and there were three peaks at $2\theta = 25.1^{\circ}$, 39.5° , and 49.8° , corresponding to the (002) facet of stacked graphene sheets [28], the (222) and (331) crystal faces of the cobalt oxide (Co₃O₄) nanoparticles, respectively (JCPS No. 76-1802) [31]. These results were in accordance with the SEM results and elemental mapping results. In conclusion, the characterization analysis results demonstrated that cobalt oxide was successfully loaded onto rGO.



Figure 2. XRD patterns of GO and Co₃O₄/rGO-800.

3.2. Evaluation of Catalytic Performance

The catalytic activity of Co₃O₄/rGO-800 was evaluated (Figure 3). Clearly, CTC could not be efficiently removed with PDS alone and Co₃O₄/rGO-800 alone. Without Co₃O₄/rGO-800, only 6.8% of CTC was removed after 120 min, suggesting that CTC could not be efficiently degraded with unactivated PDS, and a catalyst was needed to catalytic reaction [28]. Additionally, the addition of Co₃O₄/rGO-800 only removed 23.6% CTC within 120 min. This demonstrated that adsorption was involved in CTC removal process but it was not the predominant mechanism [32]. Meanwhile, CTC degradation efficiency reached 86.3% within 120 min in the Co₃O₄/rGO-800/PDS system. These results clearly demonstrated that CTC removal was mainly driven by the catalytic degradation, and Co₃O₄/rGO-800 was a promising PDS catalyst. The enhanced CTC degradation in the Co₃O₄/rGO-800/PDS system might be attributed to the improved physiochemical characteristics after Co loading [33]. In addition, Co species could also play as active sites for PDS activation to generate powerful reactive oxygen species (ROS) [34].

The experimental result obtained in this research is in accordance with the previous reports. For example, Liu et al. developed carbon-coated Mn₃O₄ nanocube (Mn₃O₄/C) as a persulfate activator for the degradation of 2,4-dichlorophenol (2,4-D). They found that the adsorption removal of 2,4-D by Mn₃O₄/C was about 37%, the direct degradation of 2,4-D by persulfate alone was approximately 26%, and the degradation rate of 2,4-D by Mn₃O₄/C/PS system was 95% [35]. Ren et al. synthesized fishbone-derived biochar (FBBC) as an efficient persulfate catalyst for phenol degradation. They reported that 10.7% of phenol was removed by FBBC adsorption, persulfate could hardly degrade phenol, and the combination of FBBC and persulfate significantly improved phenol removal performances, phenol was completely removed within 60 min in the FBBC/persulfate system [36].

The adsorption of organic pollutants by carbon-based catalyst in persulfate catalyze degradation are very common [37]. The synergistic effect between adsorption and catalyze degradation in sulfate radicals-based AOPs were widely reported previously [38]. In most cases, the adsorption of organic contaminants onto a catalyst's surface is a pre-

requisite for persulfate catalysis degradation. In brief, the organic contaminants existing in the reaction matrixes are enriched onto the surface of catalyst. Subsequently, the active sites on the catalyst can catalyze persulfate to generate surface-bound reactive oxygen species (\bullet OH and SO₄ \bullet ⁻). Then, the adsorbed organic pollutants are rapidly degraded by the attached reactive oxygen species [39]. Therefore, there is no doubt that both adsorption and catalyzed degradation contributed to CTC removal, and this conclusion was not only supported by the experimental results, but it could also be justified by the related scientific references.



Figure 3. Different reaction systems on the degradation of CTC. (Reaction condition: CTC = 20 mg/L, PDS = 1 g/L, catalyst = 0.5 g/L, T = 25 °C and pH = 5.0).

The effect of calcination temperatures on the activation activity of Co₃O₄/rGO catalyst was investigated (Figure 4a). When pyrolysis temperature increased from 700 °C to 800 °C, CTC degradation efficiency increased from 76.03% to 86.3%. This might be attributed to the formation of higher sp² carbon contents under high pyrolysis temperature [40]. However, as the calcination temperature further increased from 800 °C to 900 °C, CTC degradation rate declined from 86.3% to 78.97%. The collapse of carbon structure could be caused at excessively high pyrolysis temperature, and then, limit the catalytic activity [41]. Additionally, PDS activation and CTC degradation reactions occurred at the surface of catalyst, the adsorption of PDS and CTC onto the surface of catalyst is the prerequisite for CTC degradation [32]. The collapse of carbon skeleton would decrease the pore sizes and surface areas of catalysts, and the adsorption performances would be negatively affected [41]. Based on this, a catalyst calcined at 800 °C was selected for the subsequent experiments.

The effect of Co on the catalytic performance was systematically explored with catalyst synthesized using different amounts of Co for CTC degradation (Figure 4b). It could be found that CTC degradation efficiency enhanced with Co content increasing, and the degradation rate enhanced from 67.91% to 87.2% when the amount of Co increased from 0.5 mmol to 2 mmol. This suggested that the catalytic ability of Co₃O₄/rGO could be improved through the addition of an appropriate amount of Co; therefore, the CTC degradation efficiency was enhanced [42]. In addition, CTC degradation performance increased slightly from 86.3% to 87.2% when the Co content increased from 1 mmol to 2



mmol. This might be because of the aggregation of nanomaterial [43]. Thus, 1 mmol was adopted for the subsequent experiments.

Figure 4. Influences of (**a**) calcination temperature, (**b**) Co loading amounts, (**c**) dosage of Co₃O₄/rGO-800, (**d**) concentration of PDS, (**e**) initial pH, (**f**) reaction temperature on the degradation of CTC. (Reaction condition: CTC = 20 mg/L, PDS = 0.5–2.0 g/L, catalyst = 0.2–0.5 g/L, T = 15–35 °C, and pH = 3–9).

3.3. Influence of Reaction Parameters

3.3.1. Dosage of Catalyst

Figure 4c illustrated the influence of catalyst dosage on CTC degradation. Clearly, CTC degradation improved with the increase in catalyst dosage. When the Co₃O₄/rGO-800 dosage was 0.2 g/L, CTC degradation ratio was 57.9% within 120 min. As the dosage increased from 0.2 g/L to 0.5 g/L, CTC degradation significantly enhanced

from 57.9% to 86.3%. This implied that the increase in catalyst dosage resulted in more active sites to catalyze PDS for CTC degradation [43]. However, it was reported that the degradation rate would not enhance significantly when the catalyst dosage further increased to a certain amount, which might be explained by the fact that the active sites were enough for PDS catalysis [44]. Consequently, the optimal dosage for Co_3O_4/rGO -800 was 0.5 g/L.

3.3.2. PDS Concentration

In Fenton-like reaction systems, apart from the amount of catalyst, the amount of oxidant was equally important. The influence of PDS concentration on CTC degradation was explored. As seen in Figure 4d, as the concentration of PDS gradually increased from 0.5 g/L to 2 g/L, the degradation rate markedly improved from 59.1% to 88.0%. It can be seen that the greater the dosage of PDS in a certain range, the more obvious the effect. At the same time, it can also be observed that there was no significant difference in the degradation ratio when PDS concentration increased from 1 g/L to 2 g/L, which might be explained that the excessive PDS would result in the self-quenching effect (Equations (1) and (2)) [45]. In addition, the excessive PDS would compete with CTC for the adsorption active sites on the surface of $Co_3O_4/rGO-800$ catalyst [32]. So, 1.0 g/L PDS was selected as the optimal concentration.

$$SO_4^{\bullet-} + SO_4^{\bullet-} \to S_2O_{8^{2^-}} \tag{1}$$

$$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{2-}$$
 (2)

3.3.3. Solution pH

Solution pH could significantly affect the surface charge of catalyst [46,47], leach of metal ions [32], ionization of CTC [48], and PDS activation [12]; thus, the impact of solution pH on CTC degradation was explored. As depicted in Figure 4e, CTC degradation rate reached the highest at pH 3 (90.2%), and it gradually declined to 71.2% when pH increased from 3 to 9. The results were in line with the previous reports [45,49]. The ineffective consumption of SO4.- and •OH under high pH conditions might be a major reason responsible for the decreased CTC degradation efficiency (Equations (3)–(6)) [49]. In addition, CTC is an amphiphilic molecule, the pKa values for CTC were pKa1 = 3.3, pKa2 = 7.44, pK_{a3} = 9.5. CTC was negatively charged (CTC⁻ and CTC²⁻) at high pH conditions, and positively charged (CTC⁺) under acidic condition [50]. The surface of Co₃O₄/rGO-800 was positively charged at acidic condition like other carbon materials [51,52]; therefore, it was expected that the strong electrostatic repulsion could occur between CTC and Co₃O₄/rGO-800. The excellent CTC degradation performances might because the leached Co²⁺ promoted PDS activation through homogenous catalysis [32]. However, 71.2% of CTC was degraded at pH 9 in the Co₃O₄/rGO-800/PDS system, demonstrating that the Co₃O₄/rGO-800/PDS system could remain high stability at a wide range of pH.

$$SO_4^{\bullet-} + H_2O \rightarrow HSO_4^- + \bullet OH$$
 (3)

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + \bullet OH$$
 (4)

$$\bullet OH + \bullet OH \to H_2O_2 \tag{5}$$

$$S_2O_{8^{2-}} + H_2O_2 \rightarrow 2 SO_{4^{2-}} + O_2$$
 (6)

3.3.4. Reaction Temperature

Temperature was also considered as an important factor. The effect of solution temperature (T = 15 °C, 25 °C and 35 °C) on CTC degradation was studied. As revealed in

Figure 4f, the optimal degradation effect was achieved when the solution temperature was 35 °C, reaching 89.2% in 120 min. With the solution temperature gradually decreased from 35 °C to 15 °C, the degradation rate also decreased from 89.2% to 73.5%, which demonstrated that the system had a good degradation effect on CTC under a wide range of temperatures. The temperature accelerated the movement of molecules and the contact between the catalyst and PDS was more frequent, which promoted the faster generation of free radicals and the corresponding increase in the degradation rate of CTC [53].

3.4. Reusability of Catalyst

The durability and reusability of the Co₃O₄/rGO-800 catalyst were significant indicators to be considered in practical applications. Recyclable materials will considerably reduce disposal costs and lower costs [54]. As displayed in Figure 5, the degradation rates of CTC reached 86.3%, 71.1%, and 63.7% in the first, second, and third cycle tests, respectively. The decrease in degradation rate in the second and third cycles was presumed because the active sites of the material were worn out or consumed during the previous experiments and part of the structure was destroyed, which led to the decrease in catalytic effect [32]. However, the removal rate in the third cycle was still higher than the related previous paper. For example, Su et al. developed graphene oxide-carbon nanotubes anchored α -FeOOH hybrid catalyst (α -FeOOH@GCA) as a persulfate activator for the degradation of Orange II. The degradation rate obtained in the first run in the α -FeOOH@GCA/persulfate system was 99.1%, and the rate then decreased to 38.4% in the third cycle [55]. Pedrosa et al. prepared metal-free graphene-based catalytic membrane for persulfate activation to degrade phenol, they found that the degradation rate decreased from 94% to 27% after three cyclic experiments [30]. Olmez-Hanci et al. reported the degradation of Bisphenol A by reduced graphene oxide (rGO)/persulfate system. In the first run, Bisphenol A can be completely removed within 10 min. Additionally, the degradation rate gradually decreased to 68%, 33%, and 35% in the second, third, and fourth cycles after 30 min reaction, respectively [23]. Jiang et al. developed graphene-like carbon sheet supported nanoscale zero-valent iron (nZVI@CS) as a persulfate catalyst for the degradation of atrazine. The removal ratio of atrazine in the nZVI@CS/persulfate system was 84.27% in the first run, and then, it decreased to 82.0%, 63.1%, and 14.2% in the second, third, and fourth cycles, respectively [38]. Therefore, the as-synthesized Co3O4/rGO-800 catalyst was superior or comparable to the previous related papers. Additionally, it exhibited good stability and reusability in cyclic experiments. In fact, the decline in the catalyze reactivity of the carbon-based catalyst in sulfate radicals-based AOPs is very common, and it was extensively reported. Leaching of metal species, consumption of active sites, and the destruction of structure might all contribute to the decreased catalytic reactivity [56]. To further increase the stability of the catalyst, great efforts should be dedicated in future research.



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Figure 5. Cyclic degradation of CTC by the recycled $Co_3O_4/rGO-800$ (reaction condition: CTC = 20 mg/L, PDS = 1 g/L, catalyst = 0.5 g/L, T = 25 °C, and pH = 5.0). 3.5. Proposed degradation mechanisms.

According to the aforementioned results, CTC degradation mechanisms in the Co₃O₄/rGO-800/PDS system were concluded (Figure 6). Generally, CTC removal in the Co₃O₄/rGO-800/PDS system could be attributed the synergistic effect between adsorption and catalyze oxidation. The predominant mechanism that was responsible for CTC removal was the catalyzed oxidation. Firstly, PDS and CTC were adsorbed onto the surface of Co₃O₄/rGO-800 catalyst. Thereafter, PDS was activated by the active sites existing on Co₃O₄/rGO-800 material to generate powerful radicals including •OH and SO₄•-. \equiv Co²⁺ and surface functional groups played as active sites for PDS catalysis (Equations (7) and (8)) [11,57]. Meanwhile, \equiv Co²⁺ could be regenerated during the reaction, and the circulation of \equiv Co²⁺/ \equiv Co³⁺ was achieved (Equations (9) and (10)) [58]. CTC was finally decomposed by powerful oxidative radicals to form small molecule compounds with less toxic.

$$\equiv Co^{2+} + S_2O_8^{2-} \rightarrow \equiv Co^{3+} + SO_4^{\bullet-} + SO_4^{2-}$$
(7)

$$SO_4^{\bullet-} + H_2O \rightarrow H^+ + \bullet OH + SO_4^{2-}$$
 (8)

$$SO_4^{\bullet-} + \bullet OH \to HSO_5^-$$
 (9)

$$\equiv \operatorname{Co}^{3+} + \operatorname{HSO}_{5^{-}} \to \equiv \operatorname{Co}^{2+} + \operatorname{SO}_{5^{\bullet-}} + \operatorname{H}^{+} \tag{10}$$



Figure 6. Proposed mechanism for CTC degradation in the Co/rGO/PS system.

4. Conclusions

In the present research, reduced graphene supported cobalt oxide (Co₃O₄/rGO) catalyst was successfully synthesized using a simple strategy to catalyze persulfate (PDS) for the degradation of chlortetracycline (CTC). The Co₃O₄/rGO-800 presented an irregular and curled flake structure, large surface area, and abundant functional groups, which provided an excellent degradation performance for CTC (86.3% in 120 min). The excellent catalyze ability of Co/rGO material could be attributed to the synergistic effect between graphene and cobalt oxide. The study showed that both adsorption and catalyzed oxidation were involved in the removal process, and catalyze oxidation was the predominant mechanism. PDS was activated by the active sites (cobalt oxide and oxygen-containing functional groups) on the surface of Co₃O₄/rGO-800 catalyst, and the generated powerful radicals (SO4.- and •OH) could attack CTC into byproducts with less toxic. Co₃O₄/rGO-800 showed good stability in the cyclic experiments (63.7% removal of CTC after 3 cycles of reuse). This research demonstrated the practical application potential of Co₃O₄/rGO as a PDS catalyst material with the advantages of simple production process and high catalytic performance. This work could provide a scientific basis for the future development and research of environmentally functional materials applied in wastewater treatment.

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