Study on the synthesis and characterization of CoTiO\textsubscript{3} catalysts and their catalytic properties in Oxone activation for the degradation of tetracycline antibiotic in water

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Abstract

The chemical degradation of sulfate by activated Oxone has the advantages of high degradation capacity, wide pH range and convenient transportation and storage, making it one of the most attractive advanced oxidation processes (AOPs). Besides, Co is the metal most capable of activating Oxone to produce sulfate. Therefore, it is critical to develop Co-based catalyst, an effective and recyclable heterogeneous catalyst, for activating Oxone to degrade tetracycline. In this study, CoTiO\textsubscript{3} was extensively investigated for the activation of Oxone to generate sulfate radicals and degrade tetracycline antibiotics. The results showed that more than 95% of tetracyclines could be degraded at the amount of CoTiO\textsubscript{3} catalyst of 0.02 g, the Oxone reagent concentration of 0.4 mmol l\textsuperscript{−1}, and the pH value of 7. The removal rate of tetracyclines could still reach more than 85% after the CoTiO\textsubscript{3} composite was repeatedly used for four consecutive cycles. These results indicate that CoTiO\textsubscript{3}/Oxone can be explored as an effective system for degrading long-lived organic pollutants.

1. Introduction

Over the last decades, antibiotics have been widely used in human healthcare as well as livestock and poultry breeding industries. They were released to the environment, causing widespread contamination to aquatic systems and threatening human health [1]. According to statistics, the global annual per capita consumption of antibiotics was 15 g and even reached 50–150 g in some countries. After being ingested by humans or animals, a small part of antibiotics were metabolized, and most of them were excreted into the external environment in the form of original drugs through urine or feces [2]. Tetracycline (TC) has become a widely used antibiotic due to its stability and persistence [3, 4]. In recent years, residual tetracycline antibiotics have been frequently detected in the water environment. This is mainly related to the landfills and wastewater from pharmacy, aquaculture, and livestock and poultry breeding. The existing conventional sewage treatment processes cannot effectively degrade and remove the micro-polluted tetracycline from water. Without in-depth treatment, these long-lasting organic pollutants can easily induce the emergence of antibiotic-resistant bacteria and antibiotic-resistant genes in the environment, which will in turn threaten the balance of the ecosystem and the health of human beings [5, 6].

At present, the methods for deep removal of micro-polluted antibiotics from water mainly include coagulation [7], biological treatment [8, 9], photoelectric catalysis [10], ozone oxidation [11], Fenton oxidation [12], photocatalytic oxidation [13], Oxone oxidation and constructed wetland treatment [14, 15]. Coagulation treatment is most likely to generate solid waste and cause secondary pollution among these methods. Biological treatment is specific, and constructed wetland treatment occupies a large area. Compared with the above methods, advanced oxidation processes can produce many active free radicals to mineralize and degrade the persistent organic pollutants. This has stimulated enormous enthusiasm and interest in recent years. Amongst
various advanced oxidation processes, advanced persulfate oxidation technology (SR-AOPs) is particularly attractive because sulfate radicals (SO$_4^{2-}$) possess several significant advantages, such as higher oxidative potential and longer half-life period (2.5 ~ 3.1 V and 30 ~ 40 μs) compared to hydroxyl radicals (1.8 ~ 2.8 V and 20 ns), and broader pH applicability (pH = 2 ~ 9) [16–18]. Generally, the Oxone reagent as a commercially available reagent can be used to generate SO$_4^{2-}$. Nonetheless, the generation of SO$_4^{2-}$ from Oxone is relatively slow and thus various activation methods, such as heat [19], ultra-sound [20], UV irradiation [21], transition metals [22], etc, have been proposed to quickly generate SO$_4^{2-}$. Transition metals have the advantages of high activation efficiency and low energy requirement. Therefore, the activation of Oxone by transition metal has become a research hotspot [20, 23, 24].

Up to date, Co$^{2+}$ has been considered the most effective activator of Oxone among these transition metals, which include Cu, Co, Mn, Ni, Fe, Ru and so forth [25]. However, the direct use of homogeneous Co ions to activate Oxone can lead to serious problems, such as difficult recovery and strong toxicity [22]. Thus, it is necessary to develop more practical heterogeneous-phase Co catalysts for activating Oxone. Different materials have been explored as supports for cobalt ions and cobalt oxides. Several studies have investigated heterogeneous cobalt oxide catalysts as Oxone activators [24, 26, 27]. In addition, Co$^{3+}$ can be immobilized on a variety of solid materials as supported heterogeneous Co catalysts, which improves catalytic activity, enhance stability, increase reusability and prevent the release of Co$^{2+}$ into the environment [28, 29]. Very recently, several scholars have been devoted to coupling the cobalt ions with the specific inert transition metals M (such as Ni, Zn, Al and Ti) to construct the novel Co–O–M-based heterogeneous catalyst for Oxone activation, which consequently exhibits a significantly lower-level cobalt leaching under the premise of catalytic activity [30–33]. For example, Tian et al reported that NiCo$_2$O$_4$ microspheres were used to activate PMS to degrade humic acid, thus achieving better degradation effect than Co$_2$O$_4$ as a catalyst under the same conditions (degradation rate of 90% versus 50%) [30]. Hu et al found that ZnCo$_2$O$_4$/PMS system could degrade more than 99% of bisphenol A within 5 min [31]. Zhu et al reported that CoAl$_2$O$_4$/PMS system showed excellent effect of degrading metronidazole [32]. Due to the abundant reserves, perovskite cobalt titanate (CoTiO$_3$) has been widely applied in gas sensing, pigment preparation, semiconductor devices, catalysts and other fields [34, 35]. However, only a small part of studies on activation of Oxone by CoTiO$_3$ were found through literature investigation. Lin and co-worker synthesized CoTiO$_3$ via a co-precipitation method and employed it as a heterogeneous catalyst for activating Oxone to degrade acid azo dyes, achieving an excellent degradation effect [18]. In addition, Wei and co-workers reported that over 85% of nimesulide could be removed after 5 consecutive cycles through Fe–doped CoTiO$_3$/SiO$_2$ catalysts in the presence of PMS, and the cobalt leaching rate of catalyst is low (<0.054 mg l$^{-1}$) because of the intrinsic stable crystalline between Co and Ti in the Co–O–Ti unit of catalyst [33], as verified by recent works [36, 37]. Therefore, CoTiO$_3$ seems to be a promising catalyst for the activation of Oxone to degrade tetracycline. However, to the best of our knowledge, the study of Oxone activation by CoTiO$_3$ for the application of tetracycline degradation in water treatment is very limited. This deserves further investigation. Herein, CoTiO$_3$ was selected and prepared to activate Oxone to degrade tetracycline.

In this paper, CoTiO$_3$ catalysts were synthesized through hydrothermal method, and the structures and chemical properties of CoTiO$_3$ catalysts were characterized and further discussed. Tetracycline was then chosen as a model antibiotic contaminant to evaluate the catalytic performance of the CoTiO$_3$ catalyst in the presence of Oxone. The tetracycline degradation efficiency in the CoTiO$_3$/Oxone process was systematically investigated at various conditions, including catalyst dosage, Oxone dosage, solution pH and reaction temperature. Furthermore, the dominating reactive species were explored, and the potential catalytic oxidation mechanism was also proposed. Finally, the reusability of CoTiO$_3$ catalysts was tested.

2. Materials and methods

2.1. Materials

Cobalt nitrate hexahydra, tetrabutyltitanate, isopropyl alcohol (IPA) and tert-butyl alcohol (TBA) were all purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All other reagents, including sodium hydroxide, hydrochloric acid, Oxone (2KHSO$_5$, KH$_2$SO$_4$, K$_2$SO$_4$), citric acid and anhydrous ethanol were of analytical grade and purchased from Tianjin Kemiu Chemical Reagent Co. Ltd (China). Tetracycline (96% purity) was purchased from Aladdin.

2.2. Synthesis of CoTiO$_3$ catalysts

CoTiO$_3$ catalysts were obtained using traditional hydrothermal methods. In brief, 4 ml tetrabutyltitanate was slowly added to 50 ml anhydrous ethanol and stirred at room temperature for 10 min. Then, 3.41 g Co(NO$_3$)$_3$·6H$_2$O and 6.75 g citric acid were added to this solution, stirred continuously for 1 h, and transferred...
The CoTiO3 catalysts were synthesized by the simple hydrothermal method and then calcined at 600 °C to obtain powdered CoTiO3.

2.3. Characterization of the prepared CoTiO3
FEI Quanta 250FEG field emission scanning electron microscope (SEM) was applied to analyse the micromorphology of the prepared sample CoTiO3. The crystal structure was analysed by X-ray diffraction (XRD) patterns (Bruker D8 Advanced diffractometer) with Cu Kα radiation between 20° and 70°. The chemical composition of CoTiO3 samples and the changes in chemical valence and content of surface elements were analysed by high-resolution X-ray photoelectron spectrometry (XPS; AXIS Ultra DLD, UK). The energy standard of C 1s = 284.80 eV was used for charge correction. The relative contents of different valence states of the same elements were obtained by peak fitting from the spectra of related elements. Raman spectra of CoTiO3 were collected by a Raman spectroscopy (HORIBA, French). Chemical structures were determined using Fourier transform infrared (FT-IR) spectroscopy (ISS) in the 4000 and 400 cm⁻¹ regions. The specific surface area, pore size distribution and specific pore volume of CoTiO3 were analysed using Micromeritics ASAP2020 HD88 surface area analyser. The samples were pretreated at 80 °C before testing.

2.4. Reaction procedures
250 ml tetracycline wastewater with an initial concentration of 20 mg l⁻¹ was placed in a 500 ml conical flask. And then a certain amount of CoTiO3 and Oxone reagents were added. The reaction temperature was set. The pH value of the solution was adjusted. And samples were taken every 10 min. Liquid chromatography was used to analyse the change in concentration of tetracycline and calculate the rate of removal from the wastewater. All data were the average of three replicate experiments. Ct was used to assess the change in concentration of tetracycline, where C₀ (mg/l) was the initial concentration of tetracycline, and Ct (mg/l) was the concentration of tetracycline at that time. In addition, isopropyl alcohol and tert-butanol as the free radical scavengers were added to the aqueous solution containing tetracycline at the very beginning to reveal the contributions of different active radicals to degradation of tetracycline. The reusability of the CoTiO3 catalyst was tested by degrading tetracycline in multiple cycles.

3. Results and discussion
3.1. Characterization of the prepared CoTiO3
The CoTiO3 catalysts were synthesized by the simple hydrothermal method and then calcined at 600 °C. The morphology and size distribution of the CoTiO3 catalysts were observed via SEM images (figure 1(a)). It could be seen that CoTiO3 particles were uniform with small size, and the agglomeration phenomenon was not obvious. The results of elemental analysis clearly confirmed the uniform distribution of Co, Ti and O elements in CoTiO3 nanoparticles (figure 1(b)). To further verify the phase and detailed structure, the as-prepared CoTiO3 materials were characterized by XRD. Figure 1(c) shows that the diffraction angles 2θ are 23.9°, 32.8°, 35.4°, 40.5°, 49.0°, 53.5°, 57.0°, 61.9°, 63.9°, and 68.8°, which are corresponded to the characteristic peaks of CoTiO3 (012), (104), (110), (113), (024), (116), (212), (124), (300) and (208) crystal planes, and matches well with the standard pattern of CoTiO3 (JCPDS no. 77-1373). Besides, the characteristic peak of the prepared CoTiO3 material is sharp and the peak intensity is high, which implies that the crystallinity of the material is high. The detailed elemental composition and surface chemical state of CoTiO3 catalyst characterized by XPS are exhibited in figure 2. As shown in figure 2(a), the peaks of Co, Ti and O can be observed in the XPS full spectrum of CoTiO3 samples. Differential-mode analysis of the XPS peaks show the XPS photoelectron peaks of Co 2p, Ti
2p and O 1s (figures 2(b)–(d)). Figure 2(b) displays Co 2p core-level spectrum, which can be deconvoluted into two main peaks at binding energy of 779.7 eV and 794 eV, signifying the Co 2p$\frac{3}{2}$ and Co 2p$\frac{1}{2}$ states of Co$^{2+}$ respectively in this product [38, 39]. Figure 2(c) shows the Ti 2p core levels can be deconvoluted to the typical peaks located at 455.6 eV (Ti 2p$\frac{3}{2}$) and 461.3 eV (Ti 2p$\frac{1}{2}$), which indicates the presence of normal states of Ti (IV) [35, 40]. The O 1s core-level spectrum is also measured and shown in figure 2(d), which is deconvoluted to exhibit two peaks. The O 1s peaks at 527.3 eV and 529.4 eV are ascribed to the lattice oxygen of Co-O and Ti-O of the CoTiO$_3$, respectively [41].

In addition, Raman spectra have been also measured to further investigate the microstructure of CoTiO$_3$ materials as displayed in figure 3(a). All the Raman peaks of the sample are consistent with the characteristic peaks of CoTiO$_3$. The most typical characteristic peak (around 700 cm$^{-1}$) of CoTiO$_3$ can be observed, which comes from the highest frequency vibration mode of CoO$_6$ octahedron, namely the symmetric stretching mode [42]. Phonon modes below 300 cm$^{-1}$ belong to lattice vibration [43]. This further illuminates the formation of the CoTiO$_3$ sample. Fourier transform infrared spectrum (FT-IR) was conducted to obtain further information on the surface structure and functional group information of CoTiO$_3$ materials. As shown in figure 3(b), the absorption peak at 3441 cm$^{-1}$ was caused by the tensile vibration of the O-H group within the water molecules absorbed on the sample surface. And the absorption peak at 1627 cm$^{-1}$ was the H-O-H bending vibration [44, 45]. The absorption peaks at 564 cm$^{-1}$ and 533 cm$^{-1}$ represent Ti-O stretching vibrations, corresponding to TiO$_6$ groups [46, 47]. The absorption peak at 445 cm$^{-1}$ was caused by Co-O stretching vibration [47]. In addition, the N$_2$ adsorption–desorption isotherm curve was also measured in figure 3(c). As can be seen, the
CoTiO₃ catalyst exhibits a type III adsorption–desorption isotherm with an elongated H1 type hysteresis loop, indicating the presence of uniform cylindrical mesopore and low porosity in the sample. Therefore, the specific surface area of the as-prepared CoTiO₃ catalyst is relatively small at 10.57 m² g⁻¹. At a higher relative pressure (above 0.95), the cumulative adsorption capacity of nitrogen suddenly increases, indicating the existence of a certain number of large pores in the sample. Pore distribution of CoTiO₃ was estimated by the Barrett–Joyner–Halenda (BJH) method. As shown in figure 3(d), the size distribution of most of the pores is in the range of 0–40 nm, which indicates the mesoporous nature of the catalyst.

3.2. Tetracycline degradation performance

3.2.1. Effect of different catalytic processes

The initial concentration of tetracycline wastewater was set as 20 mg l⁻¹. The pH value was 7. The reaction temperature was 25 °C. The concentration of Oxone reagent was 0.4 mmol l⁻¹. And the dosage of CoTiO₃ was 0.02 g. Before evaluating the catalytic activity of the CoTiO₃ catalyst to activate Oxone oxidation, it is critical to determine whether tetracycline can be removed from water by the CoTiO₃ catalyst. As seen in figure 4, tetracycline was not eliminated when the CoTiO₃ catalyst alone was present, indicating that the degradation of the CoTiO₃ catalyst has almost no influence on tetracycline. In addition, Oxone oxidation alone only removed a part of the tetracycline, which was also evaluated in terms of the degradation of tetracycline. This indicated that the inactivated Oxone oxidation was ineffective in the degradation of tetracycline. However, when CoTiO₃ was applied in combination with Oxone oxidation, tetracycline was rapidly degraded. And the degradation and removal rate could reach more than 95% after 80 min of reaction. The CoTiO₃ catalysts and Oxone alone did not eliminate tetracycline. Therefore, it can be concluded that the CoTiO₃ catalyst can successfully activate Oxone to generate free radicals for the degradation of tetracycline. Therefore, in this study, CoTiO₃/Oxone oxidation system was successfully used to remove tetracycline from aqueous solution. And the relevant influencing factors were also investigated.

3.2.2. Effect of the dosage of CoTiO₃

Degradation was carried out upon tetracycline at the tetracycline concentration of 20 mg l⁻¹, the pH value of 7, the reaction temperature of 25 °C and the Oxone reagent dosage of 0.4 mmol l⁻¹ using different levels of CoTiO₃. As shown in figure 5, the removal rate of tetracycline gradually increases with the increase of the amount of CoTiO₃ because increasing the amount of catalysts could help to provide more active sites for the activation of Oxone reagent and increase the formation of the active radicals like SO₄·⁻. However, when the dosage of CoTiO₃ was increased to 0.02 g, the removal effect of tetracycline was not significantly improved. Therefore, 0.02 g CoTiO₃ catalyst was adopted for the further investigation on the degradation of tetracycline.

3.2.3. Effect of the dosage of Oxone

When the concentration of tetracycline in water was 20 mg l⁻¹, the pH value was set as 8.0, the reaction temperature was 25 °C, and the amount of CoTiO₃ was 0.02 g, the effect of the amount of Oxone reagents on the degradation and removal of tetracycline was investigated. It can be seen from figure 6 that the degradation rate of tetracycline increases significantly when the concentration of Oxone reagent is increased from 0 mmol l⁻¹ to
The reason may be that when the amount of Oxone reagents is smaller, the concentration formed in the liquid phase is lower. With the increase of Oxone reagent, bigger and bigger amounts were generated from the solution, and its concentration became higher. This in turn triggered the chain reaction of tetracycline decomposition. As a result, the removal rate of tetracycline continued to increase. However, when the Oxone reagent was increased from 0.4 mmol l\(^{-1}\) to 0.8 mmol l\(^{-1}\), the tetracycline removal rate did not change significantly. Oxone acted as a bursting agent for SO\(_4\)\(^{-}\) (redox potential 2.5–3.1 V). The bursting effect of the generated excess Oxone could produce less reactive radicals (SO\(_5\)\(^{-}\)) (redox potential 1.1 V) (equation (1)), thus reducing the concentration of free radicals in the reaction system [48, 49]. Therefore, an Oxone concentration of 0.4 mmol l\(^{-1}\) was applied to achieve the best catalytic performance in the following tests.

\[
{\text{HSO}_5}^- + {\text{SO}_4}^2^- \rightarrow {\text{SO}_5}^- + {\text{SO}_4}^2^- + {\text{H}}^+ \quad (1)
\]

3.2.4. Effect of pH value
It was shown that the pH value of the solution plays a key role in the catalytic decomposition reaction of aqueous pollutants and the non-homogeneous activation of Oxone. In this study, the concentration of tetracycline was 20 mg l\(^{-1}\), the reaction temperature was 25 °C, CoTiO\(_3\) was 0.02 g and the amount of Oxone reagents was 0.4 mmol l\(^{-1}\). It can be seen from figure 7 that the pH value of the solution has a certain influence on the removal of tetracycline. Under acidic conditions, the degradation and removal rate of tetracycline increased significantly with the increase of the pH value of the solution. When the pH value increased to 7, the degradation rate was more than 95%. However, when pH increased to 8, tetracycline’s degradation and removal rate reduced. The
reason may be that with the mediation of $\text{OH}^-$, the sulfate produced during Oxone activation can be partially converted to hydroxyl radicals ($\cdot\text{OH}$) (equation (2)), reducing the concentration of free radicals [50].

$$\text{SO}_4^{2-} + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \cdot\text{OH} \quad (2)$$

3.2.5. Effect of temperature
For catalytic reactions, reaction temperature is a key operating parameter. Thus, the effect of temperature on the degradation and removal of tetracycline was then investigated within the range of 15 °C–35 °C at the tetracycline concentration of 20 mg l$^{-1}$, the CoTiO$_3$ dosage of 0.02 g, the Oxone reagent dosage of 0.4 mmol l$^{-1}$, and the pH value of 7. It can be seen from figure 8 that the temperature has a certain influence on the degradation of tetracycline. The removal rate of tetracycline was also increased with the increase in temperature. The reason may be that the higher the temperature is, the more the energy will be absorbed by the Oxone reagent, and the easier the O-O bond is to be broken to generate free radicals, which promotes the degradation of tetracycline. Figure 8 also shows that at the temperatures of 15 °C, 25 °C, and 35 °C, the removal rate of tetracycline reaches above 90% after 80 min reaction. Considering the actual temperature of the waste water, the economic cost and the practical application, 25 °C is appropriate.

3.2.6. Identification of radicals and catalytic mechanism
$\cdot\text{OH}$ and $\text{SO}_4^{2-}$ are possible active radicals during the activation of Oxone by CoTiO$_3$. The radicals can be used as the main oxidants for degradation of tetracycline during CoTiO$_3$/Oxone activation, which was determined by...
played a critical role in decomposing O-O bond in Oxone. Specifically, a new component especially for the quench test. And the results are shown in figure 9(a). Two quenchers, Tert-butanol (TBA) and isopropyl alcohol (IPA) were used as active radical scavengers of -OH, -OH and SO4−, respectively. IPA was an effective scavenger for SO4− and -OH (the bimolecular rate constants (k) for the reaction of IPA with -OH and SO4− are 1.9 × 109 M−1 s−1 [51] and 8.5 × 107 M−1 s−1 [52], respectively). TBA quenched -OH significantly faster (the k values for the reaction of TBA with -OH and SO4− are 6.0 × 108 M−1 s−1 [51] and 4.0 × 108 M−1 s−1 [52], respectively) than SO4−. After 80 mm TBA was introduced into CoTiO3/Oxone system, the removal rate of tetracycline was slightly reduced by 3.3%, indicating that -OH had little influence on the oxidation process. In the presence of 80 mm IPA, the removal rate of tetracycline decreased by 29.6%, indicating that SO4− is more important for degradation of tetracycline. Therefore, for the degradation of tetracycline in CoTiO3/Oxone system, SO4− dominates the reaction, and -OH has a small contribution.

For the CoTiO3/Oxone system, as demonstrated by the above radical quenching experiments (figure 9(a)), the active radical species dominated the degradation process. In the radical mechanism, the surface active Co2+ played a critical role in decomposing O-O bond in Oxone. Specifically, the active Co2+ species reacted with HSO3− directly to generate SO4− (equation (3)). Simultaneously, the Co2+ was transferred into Co3+. This deduction could be well demonstrated by the XPS Co2p spectra as given in figure 9(b). Comparing the XPS Co2p spectra of CoTiO3 before and after reaction, almost no change was observed from the positions of peaks. Nevertheless, a new component (780.8 eV) occurred after the oxidation reaction, which signified the exclusive presence of Co3+ in octahedral sites [38]. This solidly demonstrated that Co2+ species in CoTiO3 participated in Oxone activation for the generation of SO4−, and were transformed to Co3+. Due to the reducing nature of Oxone, the regeneration of Co2+ could be promoted accompanied by the formation of SO4− as given in equation (4). The generated SO4− could interact with H2O to release -OH (equation (3)). Therefore, tetracycline pollutants were degraded into intermediate products by reactive oxygen species such as SO4− and -OH. In summary, the activation pathway of the CoTiO3-Oxone process for degradation of tetracycline can now be represented by the following reaction mechanism diagram (figure 9(c)).

Co2+ + HSO3− → Co3+ + SO4− + OH−  
(3)

Co3+ + HSO3− → Co2+ + SO4− + H+  
(4)

SO4− + H2O → SO42− + -OH + H+  
(5)

3.2.7. Reusability of CoTiO3 materials

The reusability of the catalyst is an important indicator for its application. In view of this, four-consecutive-cycle experiments for degradation of tetracycline were conducted using CoTiO3/Oxone activation system under the optimized conditions. As shown in figure 10, the removal efficiencies of tetracycline in four cycles were 95.3%, 88.0%, 87.3%, and 86.2%, respectively. It was clear that there was a 7.3% decrease after the second run compared to the first run. And the efficiency of removal of tetracycline by CoTiO3/Oxone activation system remains more than 85% after four cycles. This indicates that the CoTiO3 catalyst has good stability. It can be further used as a reusable catalyst for degradation of tetracycline. However, the deactivation of the CoTiO3

Figure 9. (a) Effect of radical scavengers on propanil degradation in the pyrite/Oxone process; (b) High-resolution XPS Co 2p spectra of CoTiO3 before and after oxidation reaction; (c) Reaction mechanistic scheme of CoTiO3-activated Oxone for degradation of tetracycline.
catalyst might attribute to two reasons. On one hand, the possible loss of active components of the catalyst might lead to reduction in efficiency of degradation of tetracycline during washing and drying after each run [53, 54]. On the other hand, the possible absorbed intermediate products may be attached to the surface of the CoTiO3 catalyst, thus affecting the further catalytic reaction [54, 55].

4. Conclusion

The CoTiO3 prepared by the hydrothermal synthesis method had uniform particles, small particle size, sharp XRD characteristic peaks, high peak intensity, and high crystallinity after being calcined at 600 °C. The effect of removal of tetracycline from water by catalytic oxidation using CoTiO3 activating Oxone reagent was better than that by CoTiO3 adsorption and Oxone oxidation alone. Besides, it was found that the degradation rate was dependent on the dosage of CoTiO3 and Oxone, the pH value, and the temperature of tetracycline in water. Under the condition of the initial concentration of tetracycline of 20 mg l−1, the amount of CoTiO3 was 0.02 g, the concentration of Oxone reagent of 0.4 mmol l−1, the pH value of 7, and the temperature of 25 °C, the degradation rate of tetracycline in water by CoTiO3-activating Oxone oxidation could reach more than 95%. Moreover, the quenching studies confirmed that SO4− was the dominating active species generated in the CoTiO3/Oxone process and ·OH had a small contribution. The degradation rate could still reach more than 85% when CoTiO3 was reused for the fourth time. Therefore, based on its high degradation efficiency, reusability and cost-effectiveness, CoTiO3/Oxone system has great promising applications in the degradation of long-lasting organic pollutants in aqueous solution.

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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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