

Hybrid Electrocatalytic Ozonation Treatment of Simulated High-Salinity Carbamazepine Wastewater with Ni_{0.2}-Ce_{0.2}/OMC Particle Electrodes

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High-salinity pharmaceutical wastewater contains refractory contaminants that can be effectively treated by hybrid electrocatalytic ozonation (3D/O₃). The salt in the wastewater provides a natural electrolyte, thus avoiding secondary pollution caused by the addition of electrolytes. In this work, we studied high-salinity pharmaceutical wastewater with carbamazepine as the main pollutant. Degradation experiments showed that the Ni_{0.2}-Ce_{0.2}/OMC/granular activated carbon (GAC) particle electrodes was effective, 3D/O₃ in combination with Ni_{0.2}-Ce_{0.2}/OMC/GAC removed carbamazepine effectively. The optimal conditions for the degradation of the simulated high-salinity wastewater containing 25 mg·L⁻¹ carbamazepine by the 3D/O₃ + Ni_{0.2}-Ce_{0.2}/OMC/GAC process were: 10 mA current, pH of 2, and a 5 g:150 mL ratio of particle electrode to solution. Under these conditions, the carbamazepine removal ratio was 99.7%, and the mineralization rate of the simulated wastewater was 75.7%. The removal of carbamazepine follows pseudo first-order reaction kinetics. The Ni_{0.2}-Ce_{0.2}/OMC/GAC particle electrodes exhibit good stability, and the main active species in the 3D/O₃ + Ni_{0.2}-Ce_{0.2}/OMC/GAC process is ·OH.

Keywords: Ni_{0.2}-Ce_{0.2}/OMC/GAC; hybrid electrocatalytic ozonation treatment; high-salinity pharmaceutical wastewater; carbamazepine; conditions optimization

1. INTRODUCTION

The widespread use of drugs results in water pollution. Drugs that persist in the environment cause endocrine disorders in humans and a wide range of environmental problems [1]. High-salinity pharmaceutical wastewater is usually the concentrated effluent from membrane separations. Common types include antibiotic wastewater and pharmaceutical fermentation wastewater. One of the drugs most commonly found in high-salinity pharmaceutical wastewater is carbamazepine, a neuroregulatory drug

that is widely used to treat epilepsy [2, 3]. Carbamazepine has a complex molecular structure (Figure 1) [4]. However, the high salinity of pharmaceutical wastewater makes biological treatment [5], adsorption [6, 7], and other traditional processes ineffective in removing the main pollutants [8]. It is therefore important to develop efficient and environmentally friendly methods to remove carbamazepine from high-salinity pharmaceutical wastewater.

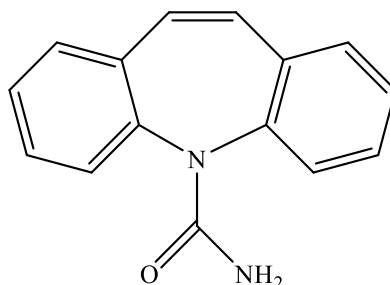


Figure 1. Molecular structure of carbamazepine.

In recent years, advanced oxidation methods have become attractive methods for treating high-concentration refractory organic pollutant wastewater. Ozone process could increase the biodegradability of carbamazepine wastewater, but do not achieve efficient degradation [9]; Electric-Fenton could effectively remove carbamazepine but has a low degree of mineralization [10]. Hybrid electrocatalytic ozonation treatment (3D/O₃) is considered to be an ideal process for toxic and refractory organic pollutants due to its advantages such as no secondary pollution, environmental friendliness, and complete degradation [11]. However, the removal ratio of pollutants by activated carbon as particle electrodes was low [11]. Therefore, the development of suitable particle electrodes with electrocatalysis and ozonation for the complete degradation of carbamazepine has great significance.

Nickel-based catalysts are widely used in electrochemical processes to promote redox reactions [12]. The conversion of Ce⁴⁺ to Ce³⁺ also increases the reaction rate of ozone catalysis. Ordered mesoporous carbon (OMC) modified with Ni-Ce disperses metal oxides well and creates oxygen vacancies that improve redox reaction rates and effectively promote electron transfer [12, 13]. In the 3D/O₃ process, an electric field is used to polarize the particle electrodes into many bipolar microelectrodes, which increases the reaction rate of the process. The high specific surface area of the particle electrodes increases their capacity to adsorb and degrade pollutants [14, 15]. At the surface of the particle electrode, O₂ is reduced to H₂O₂ (Eq. (1)), which subsequently decomposes to ·OH [16, 17]. At the same time, O₃ in the reactor oxidizes organic matter, which has active double bonds. More importantly, 3D/O₃ may synergistically produce ·OH, thus enhancing the oxidation performance of the oxidation system. The particle electrode reduces O₃ to O₃⁻ (Eq. (2)) [18] and further converts it to ·OH (Eq. (3)), increasing the reaction rate of the system [19, 20].



In the paper, simulated high-salinity pharmaceutical wastewater containing carbamazepine as the main pollutant was selected to evaluate the catalytic performance of Ni-Ce co-modified OMC ($\text{Ni}_{0.2}\text{-Ce}_{0.2}/\text{OMC}$) particle electrodes. The effects of pH, initial carbamazepine concentration, particle electrode and solution ratio, and current on the reaction were studied, and the optimal reaction conditions were determined. The effects of using $\text{Ni}_{0.2}\text{-Ce}_{0.2}/\text{OMC}/\text{GAC}$, $\text{Ni}_{0.2}/\text{OMC}/\text{GAC}$, and $\text{Ce}_{0.2}/\text{OMC}/\text{GAC}$ particle electrodes on the removal of pollutants were compared. A reaction mechanism is proposed based on the determination of the active species.

2. MATERIALS AND METHODS

2.1 Materials

Carbamazepine (>98%, Macklin Biochemical Co., Ltd) and other chemicals (Na_2SO_4 , CaCl_2 , NaOH , and KCl) were obtained from Sinopharm and were used without further purification. The acetonitrile solvent used in these experiments was of HPLC grade from Sinopharm.

2.2 Hybrid electrocatalytic ozonation degradation experiment

SBA-15 was synthesized using an optimized version of a previously reported procedure [21]. The $\text{Ni}_{0.2}\text{-Ce}_{0.2}/\text{OMC}/\text{GAC}$, $\text{Ni}_{0.2}/\text{OMC}/\text{GAC}$, and $\text{Ce}_{0.2}/\text{OMC}/\text{GAC}$ catalysts were synthesized using a one-step method. Analysis of the morphology, structure, and performance of the catalysts revealed that a bimetallic catalyst with 0.2% metal oxide content and a Ni to Ce ratio of 1:1 was the best of the catalysts tested. All experiments were carried out until adsorption on the particle electrodes reached saturation. In the degradation experiments, the removal of carbamazepine was mainly caused by catalytic degradation rather than adsorption onto the catalyst.

The experimental apparatus was a plexiglass container ($10\text{ cm} \times 5\text{ cm} \times 7.5\text{ cm}$) with a volume of about 150 mL (schematic diagram Figure 2). The anode and cathode consisted of a $\text{RuO}_2/\text{IrO}_2/\text{Ti}$ plate and a Ti plate, respectively. The inter-electrode gap was 2.5cm. The $\text{Ni}_{0.2}\text{-Ce}_{0.2}/\text{OMC}/\text{GAC}$ particle electrode was loaded into the apparatus and all experiments were performed at a constant current from a digital DC power supply (DH1718E-4, Dahua, China). In the $3\text{D}/\text{O}_3$ treatment, the O_3 was generated by using an ozone generator purchased from Xuzhou Jinyuan Ozone Equipment Company (JY-SY20). The O_3 flowed continuously into the bottom of the reactor at a flow rate of $0.1\text{ L}\cdot\text{min}^{-1}$. The water quality characteristics of the simulated high-salinity pharmaceutical wastewater containing carbamazepine are shown in Table 1. The high salinity of the wastewater provided a natural electrolyte for degradation, and no additional electrolyte was required. The treatment was performed for 60 min and the catalyst stability was evaluated by cyclic degradation experiments.

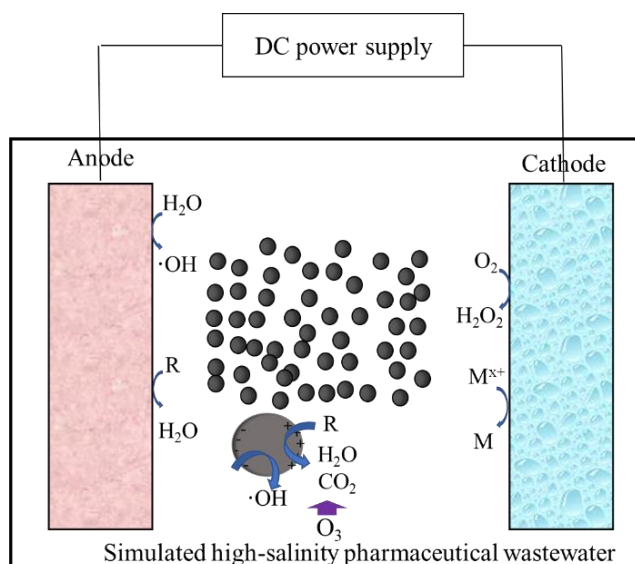


Figure 2. Schematic of hybrid electrocatalytic ozonation treatment reaction device.

Table 1. The parameters of simulated high-salinity pharmaceutical wastewater with carbamazepine as the main pollutant.

Indicator	pH	carbamazepine ($\text{mg}\cdot\text{L}^{-1}$)	Cl^{-} ($\text{mg}\cdot\text{L}^{-1}$)	CON ($\text{mS}\cdot\text{cm}^{-1}$)
Values	12.8	25	1490	38

2.3 Measurements

High-performance liquid chromatography (HPLC, LC 2030, Shimadzu) was used to determine the concentration of carbamazepine. An ODS-SPC18 column (250 mm \times 4.6 mm, 5 μm) was used at a column temperature of 30 $^{\circ}\text{C}$. The mobile phase containing carbamazepine was acetonitrile and water in a ratio of 60:40 (1 mL $\cdot\text{min}^{-1}$). The detection wavelengths were set at 286 nm and 280 nm and the sampling volume was 20 μL . A total organic carbon analyzer (TOC4000, Shimadzu, Japan) was used to determine the total organic carbon (TOC) content. Ion chromatography (IC-3000, USA) with a separation column (AS11-HC), was used to test the chlorine ion concentration. The mobile phase for ion chromatography was 250 mmol $\cdot\text{L}^{-1}$ aqueous NaOH solution (1.2 mL $\cdot\text{min}^{-1}$).

The $\cdot\text{OH}$ concentration was measured using an EMXplus electronic paramagnetic resonance (ESR) spectrometer (Bruker, Germany). The test conditions were as follows: selected x-band, experimental temperature 20 $^{\circ}\text{C}$, central magnetic field 3522 G, modulation amplitude 0.5 G, reception gain 20 dB, sweep duration 80 s, and sweep width 100 G. For each sample, the signal attenuation was 10 dB and the energy was 20 MW. The samples were loaded into 1 mm quartz capillary tubes for testing. The concentration of capture agent DMPO (Sigma, USA, stored at -20 $^{\circ}\text{C}$) was 0.08 mol $\cdot\text{L}^{-1}$.

3. RESULTS AND DISCUSSION

3.1 Optimization of carbamazepine degradation in 3D/O₃ with Ni_{0.2}-Ce_{0.2}/OMC/GAC particle electrode

3.1.1 Effect of particle electrodes

To evaluate the effects of bimetal modified catalysts on the carbamazepine degradation, GAC, Ni_{0.2}/OMC/GAC, Ce_{0.2}/OMC/GAC, and Ni_{0.2}-Ce_{0.2}/OMC/GAC particle electrodes were compared (Figure 3).

After 60 min of reaction, the final removal ratio of carbamazepine by the GAC particle electrode was 69.5%. For the Ni_{0.2}-Ce_{0.2}/OMC/GAC particle electrode, the removal ratio of carbamazepine was 99.7%, which was higher than those of the Ni_{0.2}/OMC/GAC and Ce_{0.2}/OMC/GAC particle electrodes. This indicates that the Ni_{0.2}-Ce_{0.2}/OMC/GAC particle electrode has higher electrocatalytic and ozonation performance in high-salt environments. The introduction of Ni and Ce bimetallic oxides improves the dispersion of metal oxides and the exposure of active sites, which enhance catalytic performance [22]. The Ni_{0.2}-Ce_{0.2}/OMC/GAC particle electrode containing Ni²⁺ species produced more H₂O₂ in the course of the degradation process than the other particle electrodes. In addition, the oxidation of Ce³⁺ to Ce⁴⁺ in the Ni_{0.2}-Ce_{0.2}/OMC catalyst continuously produces oxygen vacancies, which react with O₃ and increase ·OH formation in the system. As shown in Figure 3 (inset), the effect of different particle electrodes on carbamazepine degradation followed first-order reaction kinetics. The Ni_{0.2}-Ce_{0.2}/OMC/GAC particle electrode had the highest degradation rate constant and was consequently chosen as the best particle electrode.

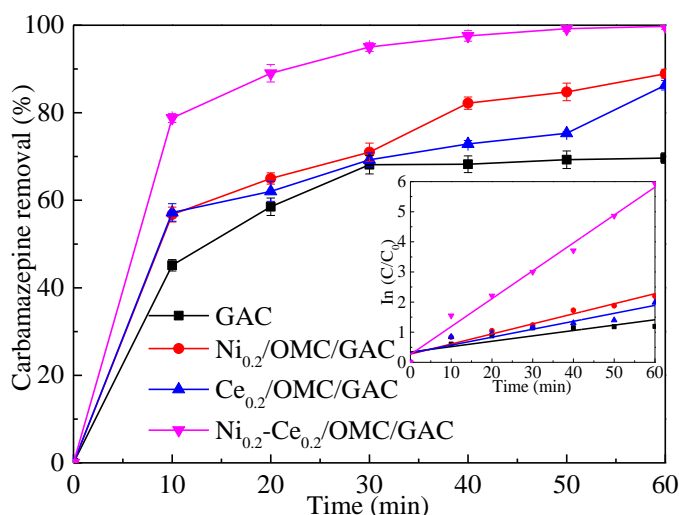


Figure 3. Effects of different particle electrodes on carbamazepine degradation. The inset was the kinetic analysis of carbamazepine removal.

3.1.2 Effect of degradation processes

Different degradation processes can have different effects on the degradation of carbamazepine. With the other parameters held at their optimal values, the effects of O₃, 3D, 3D/O₃, O₃ + Ni_{0.2}-

$Ce_{0.2}/OMC/GAC$, $3D + Ni_{0.2}-Ce_{0.2}/OMC/GAC$, and $3D/O_3 + Ni_{0.2}-Ce_{0.2}/OMC/GAC$ on the degradation process of carbamazepine were studied (Figure 4). Compared with O_3 and $3D$ electrolysis, the $3D/O_3$ process had a better removal rate of carbamazepine. The removal rate of carbamazepine in the $3D/O_3 + Ni_{0.2}-Ce_{0.2}/OMC/GAC$ system was higher than in the other two systems. The removal rate of carbamazepine by O_3 alone after 60 min was only 21.5%. Ozone is a selective oxidant that rapidly oxidizes active double-bonded organic compounds such as alkenes, amines, and reduced sulfides [12, 23]. However, ozone oxidation degradation of polycyclic refractory substances in high-salinity pharmaceutical wastewater is less efficient [24]. The main products of the reaction with O_3 are 1-(2-benzaldehyde)-4-hydro-(1H,3H)-quinazoline-2-one and 1-(2-benzaldehyde)-(1H,3H)-quinazoline-2,4-dione [25]. Although $Ni_{0.2}-Ce_{0.2}/OMC/GAC$ can react with ozone to produce $\cdot OH$, the required removal efficiency cannot be achieved at a high enough removal rate. The removal rate of carbamazepine is higher in the combined $3D/O_3 + Ni_{0.2}-Ce_{0.2}/OMC/GAC$ process, with the salinity of the wastewater providing a natural electrolyte. This enhancement is due to the $\cdot OH$ generated by the $3D/O_3$ process. The $\cdot OH$ attacks carbamazepine from multiple positions and may generate some intermediate products such as 5H-dibenzo[b,f]azepine, 5H-dibenzo[b,f]azepin-5-ol, 5-carbamoyl-10,11-dihydro-5H-dibenzo[b,f]azepin-10-ylum-11-olate, and others [26, 27].

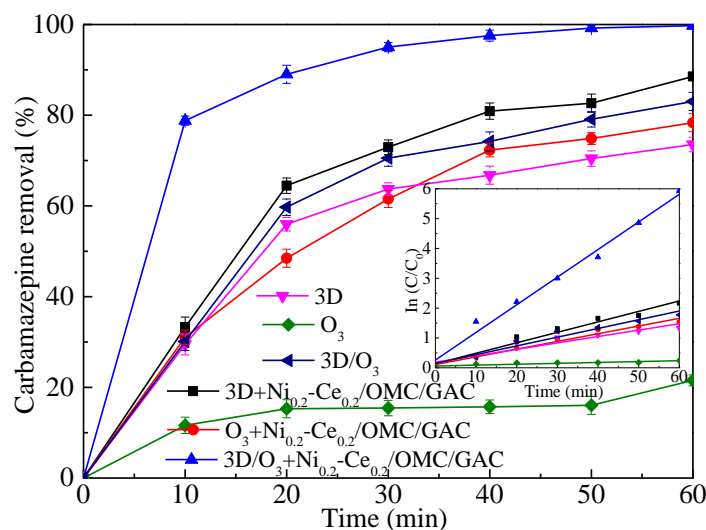


Figure 4. Effects of different degradation processes on carbamazepine degradation. The inset shows the kinetic analysis of carbamazepine removal.

Because the ozone generator can only convert part of the O_2 gas input into O_3 , it discharges a mixture of O_2 and O_3 [28]. In the $3D/O_3$ process, O_2 is reduced to H_2O_2 (Eq. (1)) on a particle electrode [18, 29], O_3 is reduced to O_3^- (Eq. (2)), and then react to produce $\cdot OH$ (Eq. (3)) [19, 20]. The same reaction occurs on the particle electrode, where oxygen vacancies and O_3 react to produce $\cdot OH$, further improving the degradation efficiency of the $3D/O_3$ process. In this process, carbamazepine may be further degraded to acridine, hydroxycarbamazepine, quinazoline-2,4-(1H, 3H)-dione, 2,4,10-trihydroxy-10,11-dihydro-5H-dibenzo[b,f]azepine-5-carboxamide, and 2,20-(carbamoylazanediyl)dibenzoic acid, after which it undergoes ring-opening to form small molecular

acids [26, 30]. The Ni_{0.2}-Ce_{0.2}/OMC/GAC particle electrode has a high surface area and good Ni-Ce distribution on the surface. The exposed active sites on the particle electrode increase the electron transfer capacity and thus increase the removal rate of carbamazepine. The kinetic analysis (Figure 4 (inset)) shows that the 3D/O₃ process had the highest reaction rate and was therefore the best degradation process.

3.1.3 Effect of particle electrode and solution ratios

The effects of the ratio of particle electrode mass to solution volume on the degradation of carbamazepine was investigated. Different masses of Ni_{0.2}-Ce_{0.2}/OMC/GAC particle electrode (1 g, 2 g, 3 g, 4 g, 5 g, 8 g, and 10 g) were used to remove carbamazepine from 150 mL of simulated wastewater solution (Figure 5). The carbamazepine removal ratio increases with the mass of particle electrode in the solution volume, which increases the mass transfer rate and improves the carbamazepine removal rate by promoting the decomposition of O₃, increasing the oxygen vacancy content in the system, and producing more ·OH. Figure 5 shows that when the ratio of particle electrode and solution volume was greater than 5 g:150 mL, the removal ratio of carbamazepine was close to 100% after 10 min of treatment. The dynamic analysis (Figure 5 (inset)) shows that when the ratio of particle electrode to solution volume was lower than 5 g:150 mL, the reaction kinetics were first order. The maximum reaction rate was obtained when 5 g of particle electrode were used per 150 mL of solution.

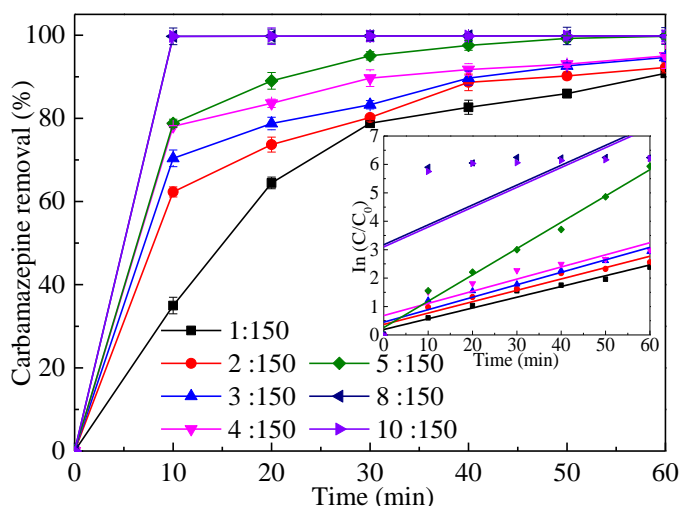


Figure 5. Effects of different ratios of particle electrode mass to solution volume on carbamazepine degradation. The inset shows the kinetic analysis of carbamazepine removal.

3.1.4 Effect of currents

In the 3D/O₃ + Ni_{0.2}-Ce_{0.2}/OMC/GAC process, the current played an important role in enhancing the strong oxidation species. An appropriate current polarizes the particle electrode to form bipolar microelectrodes, which directly affects the removal rate of pollutants. In the 3D/O₃ system, catalysis at

the particle electrodes, and ozone oxidation combine with the effects of Ce^{3+} conversion to Ce^{4+} in the particle electrode, which produces oxygen vacancies that react with ozone reaction to generate $\cdot OH$, to increase the pollutant degradation efficiency of the system [31]. The effects of currents of 5, 10, 15, 20, 50, and 100 mA on the degradation of carbamazepine were studied while other experimental conditions were held at their optimal values (Figure 6).

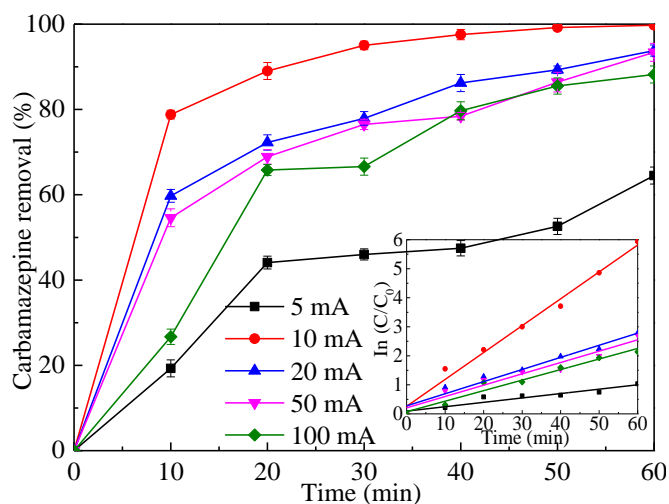


Figure 6. Effects of different levels of current on carbamazepine degradation. The inset shows the kinetic analysis of carbamazepine removal.

Figure 6 shows that when the current was increased from 5 mA to 10 mA, the carbamazepine removal ratio increased to 99.7%, which was consistent with previous results [32]. A high current increases the electron transfer efficiency of the system, increases the mass transfer capacity of the system through the polarization of the particle electrode, and produces more $\cdot OH$ through the redox and catalytic action of the particle electrode. However, with further increases in the current, the removal rate of carbamazepine decreased. Although high current density tends to produce more active species, a large number of these active species do not participate in the oxidative degradation of organic compounds other than in some side reactions such as hydrogen evolution or oxygen evolution. Moreover, high current increases the temperature of the system and reduces the current efficiency. The fitted removal rate curves of carbamazepine are shown in Figure 6 (inset). The fitted carbamazepine rate constant k first increased and then decreased with increasing current [32]. When the current was 10 mA, the maximum rate constant was 0.0983 min^{-1} , with fast carbamazepine degradation.

3.1.5 Effect of pH

In the 3D/O₃ system, the pH of the solution has great influence on the performance of the particle electrodes and ozone reactions [33]. The effects of varying initial pH between 2.0 and 13.0 on carbamazepine degradation is shown in Figure 7. Figure 7(a) shows the removal rate sequence of carbamazepine at different pH values. Both acid and alkaline conditions were good for the

carbamazepine degradation. Alkaline conditions are conducive to the decomposition of O_3 , and OMC can initiate or promote an O_3 decomposition chain reaction that generates more $\cdot OH$. The Ce^{4+} in the particle electrode has a high oxidation capacity, which increases the pollution degradation in the system [34]. The degradation effect of carbamazepine was better when the pH value was 13. Under acidic conditions, the rapid transformation of Ce^{3+} to Ce^{4+} in the particle electrode increases the generation of oxygen vacancies and accelerates the reaction with O_3 [35, 36]. The removal rate of carbamazepine reached 99.7%, indicating that the $Ni_{0.2}-Ce_{0.2}/OMC/GAC$ particle electrode had excellent degradation performance under acidic conditions.

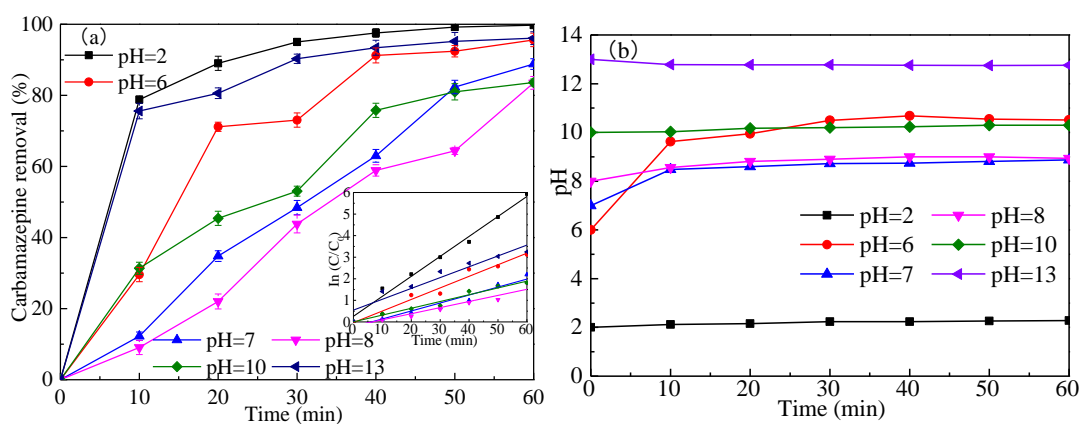


Figure 7. Effects of different pH (a) on carbamazepine degradation (inset is the kinetic analysis of carbamazepine removal); and (b) changes in pH during the degradation.

When $7 < \text{pH} < 10$, the ozone has a long half-life of 15–25 min, and the decomposition rate of O_3 was low in this pH range [37]. The direct oxidation of O_3 and electrocatalysis at the particle electrodes play a major role in this range, and the removal rate was lower than that under strongly basic or strongly acidic conditions. The kinetic analysis (Figure 7(a) (inset)) shows that the reaction rate was highest at a pH value of 2.0.

Figure 7(b) shows that the pH increased with time and then reached a stable state from an initial pH of 6. This is because the oxidation of O_3 under weakly acidic conditions accelerates the generation of OH^- , while the reaction of O_3 decreases with increasing pH and tends to be stable [37].

3.1.6 Effect of carbamazepine concentrations

The initial concentration of carbamazepine was also a major factor affecting the degradation process. The effects of initial concentrations of 5, 10, 15, 20, 25, and $50 \text{ mg}\cdot\text{L}^{-1}$ on the degradation of carbamazepine were studied under optimal reaction conditions, as shown in Figure 8.

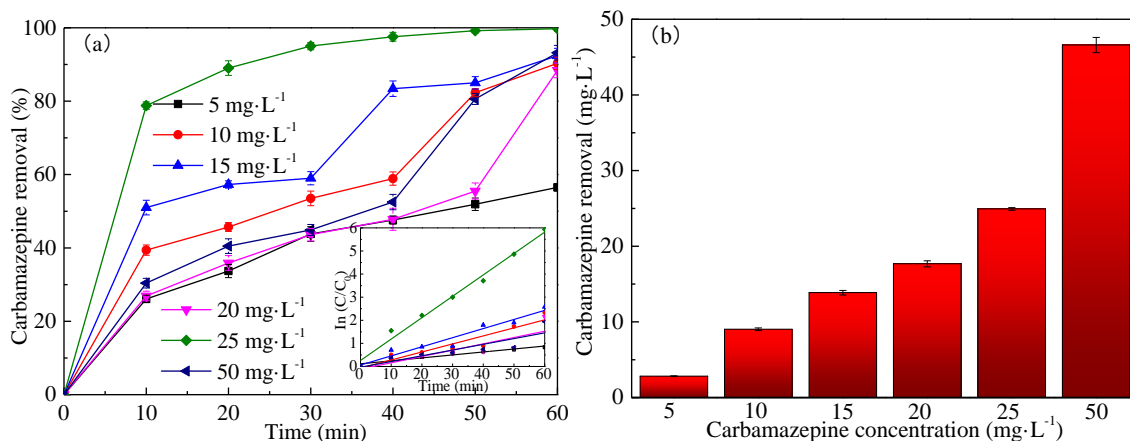


Figure 8. Effects of carbamazepine concentration on carbamazepine removal rate (a) (the inset was the kinetic analysis of carbamazepine removal); and on absolute removal after 60 min (b).

After 60 min of reaction, the removal rates of carbamazepine from low to high initial concentrations were 56.5%, 90.3%, 92.4%, 88.4%, 99.7%, and 93.2%, respectively. At initial carbamazepine concentrations between 5 mg·L⁻¹ and 25 mg·L⁻¹, the carbamazepine removal rate increased gradually. However, when the initial carbamazepine concentration was 50 mg·L⁻¹, the carbamazepine removal rate decreased. It is possible that as the concentration of carbamazepine increases, more pollutant molecules are degraded at the electrode and particle electrode until all reaction sites are saturated [38]. However, the particle electrode still had a good removal rate (93.2%) for carbamazepine at high concentration, and may be capable of a higher removal rate with longer reaction time.

Although the carbamazepine removal rate decreased at an initial carbamazepine concentration of 50 mg·L⁻¹, the absolute amount of carbamazepine removed increased from 24.9 to 46.6 mg·L⁻¹ when the initial pollutant concentration was increased from 25 to 50 mg·L⁻¹ (Figure 8(b)). Analysis of the reaction kinetics curve (Figure 8(a) (inset)) revealed that the rate constant was largest when the initial carbamazepine concentration was 25 mg·L⁻¹. This concentration was consequently chosen for the other experiments.

3.2 Mineralization efficiency and the Cl⁻ concentration of simulate high-salinity pharmaceutical wastewater

Under optimal degradation conditions, the TOC removal rate and the change in Cl⁻ concentration of simulated high-salinity pharmaceutical wastewater are shown as functions of time in Figure 9. Figure 9(a) shows that the Ni_{0.2}-Ce_{0.2}/OMC/GAC particle electrode combined with 3D/O₃ technology strongly decreased the level of TOC in the simulated wastewater. The mineralization rate increased with reaction time. After 60 min, the TOC removal rate was 75.5% with a high mineralization rate. This suggests that carbamazepine was degraded into small-molecules acid (such as oxalic acid, mesaconic acid, acrylic acid, formic acid and others) and further mineralized into water and carbon dioxide [26]. The changes in Cl⁻ concentration during degradation were measured under optimal degradation conditions (Figure

9(b)). The Cl^- concentration does not decrease with reaction time, showing that it is not involved in the degradation reaction, and possibly that no halogenated organic intermediates are produced by the degradation process.

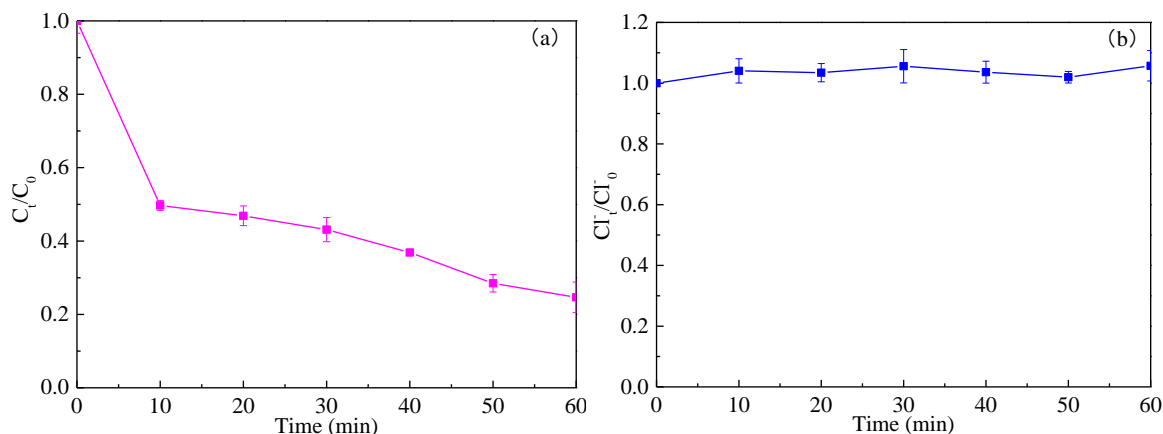


Figure 9. TOC removed rate (a) and the changes in Cl^- concentration (b) of simulation high-salinity pharmaceutical wastewater with $\text{Ni}_{0.2}\text{-Ce}_{0.2}/\text{OMC}/\text{GAC}$ particle electrode.

3.3 Stability of $\text{Ni}_{0.2}\text{-Ce}_{0.2}/\text{OMC}/\text{GAC}$ particle electrode

The stability of particle electrodes affects the applicability of the $3\text{D}/\text{O}_3$ process. Under optimal conditions, the stability of the $\text{Ni}_{0.2}\text{-Ce}_{0.2}/\text{OMC}/\text{GAC}$ particle electrode was investigated through recycling experiments. Figure 10 shows the changes over seven consecutive trials of the removal rate of carbamazepine by a $\text{Ni}_{0.2}\text{-Ce}_{0.2}/\text{OMC}/\text{GAC}$ particle electrode. The carbamazepine removal rate was still about 97% after seven repeated degradation experiments (Figure 10), indicating that the prepared $\text{Ni}_{0.2}\text{-Ce}_{0.2}/\text{OMC}/\text{GAC}$ particle electrode has good stability.

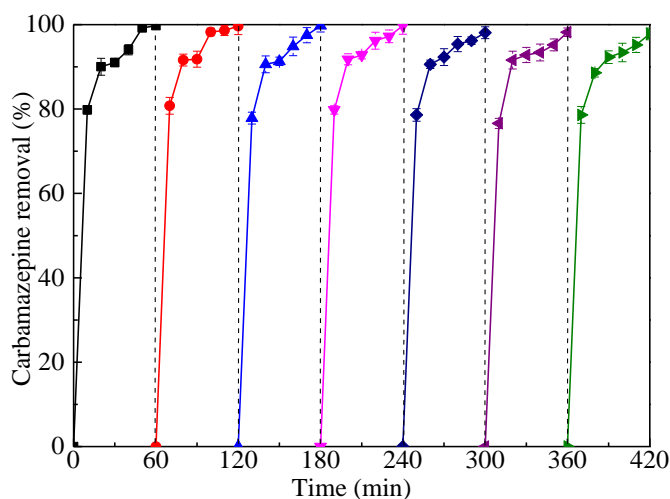


Figure 10. Removal rate of carbamazepine at a particle electrode for 7 cycles.

3.4 Analyses of active species

The existence of $\cdot\text{OH}$ radical was confirmed and the generation of $\cdot\text{OH}$ in $3\text{D}/\text{O}_3$ by the particle electrode technology was studied in order to prove that the active species in the degradation process was $\cdot\text{OH}$. In the hybrid electrocatalytic ozonation treatment process, the degradation of organic pollutants is mainly achieved through indirect electrocatalytic oxidation, especially by generated oxidant $\cdot\text{OH}$ [32]. In the $3\text{D}/\text{O}_3 + \text{Ni}_{0.2}\text{-Ce}_{0.2}/\text{OMC}/\text{GAC}$ system, the generation of $\cdot\text{OH}$ is mainly derived from the reaction of O_3 at the particle electrode, and oxygen reduction causes the decomposition of H_2O_2 [11]. The generation of $\cdot\text{OH}$ in the $3\text{D}/\text{O}_3$ device was measured by ESR (Figure 11). The ESR spectra of $\cdot\text{OH}$ -DMPO were measured under the $\text{Ni}_{0.2}\text{-Ce}_{0.2}/\text{OMC}/\text{GAC}$ particle electrode catalysis system after the reaction for 10 min without adding pollutants. The additive $\cdot\text{OH}$ -DMPO has four peaks in a ratio of 1:2:2:1, indicating that $\cdot\text{OH}$ was produced in the system [39]. The $\cdot\text{OH}$ radicals were detected within 10 minutes of the reaction, indicating that the particle electrode can catalyze the rapid formation of $\cdot\text{OH}$.

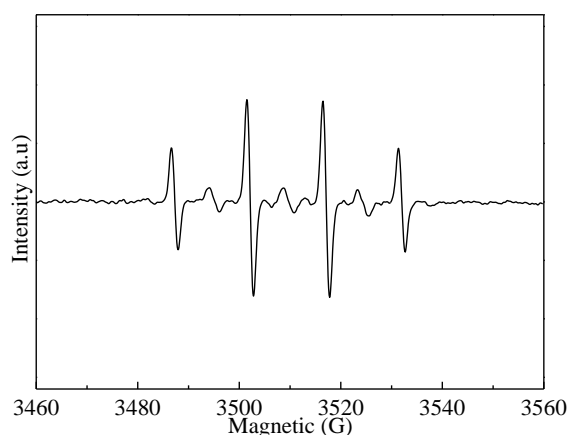


Figure 11. ESR spectrum of $\cdot\text{OH}$ -DMPO additive measured in 0.08 mol L^{-1} DMPO solution in $3\text{D}/\text{O}_3 + \text{Ni}_{0.2}\text{-Ce}_{0.2}/\text{OMC}/\text{GAC}$.

4. CONCLUSIONS

The effects of different degradation conditions on the degradation process of simulated high-salinity pharmaceutical wastewater containing carbamazepine by $\text{Ni}_{0.2}\text{-Ce}_{0.2}/\text{OMC}/\text{GAC}$ combined with $3\text{D}/\text{O}_3$ technology were analyzed. The process used electrolytes that occur naturally in wastewater. The highest carbamazepine removal efficiency and the fastest reaction rate occurred when the degradation current was 10 mA, the pH of the solution was 2, the initial concentration of carbamazepine was $25 \text{ mg}\cdot\text{L}^{-1}$, and the ratio of particle electrode mass to solution volume was 5 g:150 mL. The degradation rates of carbamazepine by $3\text{D}/\text{O}_3 + \text{Ni}_{0.2}\text{-Ce}_{0.2}/\text{OMC}/\text{GAC}$ show that the process has first-order reaction kinetics. The system had the highest carbamazepine conversion rate and TOC removal ratio. The stability of $\text{Ni}_{0.2}\text{-Ce}_{0.2}/\text{OMC}/\text{GAC}$ particle electrode was tested by repeated cycling. The particle electrode still had a high carbamazepine removal ratio after multiple cycles, proving its stability for practical application.

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