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Preparation of Cu-Ce@ γ -Al₂O₃ and Study on Catalytic Ozone Oxidation for the Treatment of RO Concentrate Water

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Abstract: In this paper, a high-efficiency and stable Cu-Ce@ γ -Al₂O₃ catalyst was prepared by taking the reverse osmosis (RO) concentrated water of a sewage treatment plant as the treatment object and activated alumina as the carrier. The preparation factors that affected the catalytic activity of Cu-Ce@ γ -Al₂O₃ were investigated. SEM, EDS, XRD, BET, XRF, and XPS techniques were applied to characterize the catalyst. Optimal working conditions, and degradation mechanism of RO concentrated water were researched. In comparison with the ozone oxidation alone, the Cu-Ce@ γ -Al₂O₃ catalytic ozonation has more reactive groups, significantly improving the treatment effect. Characterization results show that Cu and Ce are successfully supported on the surface of the activated alumina support and mainly exist in the form of oxides (e.g., CuO and CeO₂). The loading of metal led to a larger specific surface area and pore volume. The repeated use had an insignificant effect on the peaks of Cu2p and Ce3d energy spectra and caused a small loss of active components. Under these conditions, the removal rate of COD from RO concentrated water by Cu-Ce@ γ -Al₂O₃ catalyst was 85.2%. The stability and salt tolerance of Cu-Ce@ γ -Al₂O₃ catalysts were investigated by catalyst wear rate and repeated use times, respectively. The degradation of organic matter and residual tryptophan-like organic compounds were observed through UV absorption spectroscopy and 3D-EEM. Hydroxyl radicals participated in organic pollutants degradation. Finally, a multi-level-fuzzy analysis evaluation model was developed to quantitatively assess the catalytic ozone oxidation system of the Cu-Ce @ γ -Al₂O₃ catalyst for the treatment of RO concentrated water.

Keywords: ozone catalyst; catalytic oxidation; activated alumina; RO concentrated water; model evaluation



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1. Introduction

The amount of freshwater is decreasing worldwide due to population growth and accelerating industrialization. Industrial drainage policies are gradually being tightened, and the problem of water shortage is becoming increasingly serious. As more companies have begun to work on improving the reuse rate of water sources, the membrane concentration process has become more and more widely used [1]. Reverse osmosis (RO) has the advantages of simple operation, high degree of automation, and small footprint and has been widely used in seawater desalination, brackish water desalination, reclaimed water reuse, boiler make-up water preparation, and wastewater treatment [2]. The RO concentrate produced as its byproduct accounts for a third of the total water production and contains numerous pollutants, particularly toxic or bioaccumulative organic contaminants. Therefore, the treatment of RO concentrate has become an increasingly important issue [3]. The discharge of RO concentrated water has also caused a huge waste of water resources. It has brought huge challenges to wastewater treatment because it contains high concentrations of refractory dissolved organic matter (DOM), soluble minerals, and other total dissolved solids (TDS). Therefore, the development of new technology for its removal is very important [4].

In recent years, the commonly used RO concentrated water treatment methods at home and abroad have mainly included direct discharge (surface water or ocean), deep

well injection, evaporation ponds, and treatment and reuse. The direct discharge method is easy to operate and inexpensive and is currently the most common method of treatment. However, the direct or indirect discharge of RO concentrated water has far exceeded the environmental carrying capacity, and the advanced treatment and reuse of concentrated water have become a general trend. At present, commonly used advanced treatment methods include the adsorption method [5], coagulation sedimentation method [6], advanced oxidation method, and biological method [7]. Among them, advanced oxidation technology (AOPs) has unique advantages in treating refractory industrial wastewater, including fast reaction speed, complete degradation of organic matter, no secondary pollution, a wide application range of water quality, and broad application in the treatment of RO concentrated water [8].

In recent years, AOPs, such as the Fenton method, electrocatalytic oxidation method, ozone oxidation method, wet oxidation method, and supercritical water oxidation method have been used at home and abroad to treat high-concentration refractory industrial wastewater [9]. Among them, ozone oxidation technology, which can degrade most of the refractory organic substances in wastewater, and has the advantages of green and no secondary pollution, is a very effective method for treating pollutants [10]. Compared with single ozone treatment, ozone-catalyzed oxidation generates reactive groups with higher active potentials during the reaction process, which can degrade pollutants in water with higher efficiency and can oxidize almost all organic matter [11]. Compared with homogeneous ozone catalytic oxidation, heterogeneous ozone catalytic oxidation technology avoids the problem of difficult recovery, waste of resources, and secondary pollution, which limits the application of homogeneous ozone catalytic oxidation technology in practical water treatment [12]. Activated alumina has the advantages of good thermal stability, high mechanical strength, wear resistance, large specific surface area, and abundant hydroxyl groups on the surface. Alumina and metal oxides supported on alumina have been widely applied as catalysts for the treatment of industrial wastewater due to their low cost and excellent catalytic effect. Alumina catalytic ozonation exhibited significantly more effective removal of organic pollutants than ozonation treatment [13]. Li et al. found that Mg-Ce ceramic membrane increased the TOC removal rate from less than 50% by ozonation to 85.1% by catalytic ozonation [14]. Cu and Ce are considered to be loaded on the catalyst for catalytic ozonation due to their high redox potential and environmental friendliness [15,16]. In this study, activated alumina was selected as the catalyst carrier, and Cu and Ce metal active components were supported on the carrier by the impregnation-calcination method to prepare a bimetallic Cu-Ce@ γ -Al₂O₃ catalyst and used heterogeneous ozone catalysis. Oxidation technology treats RO concentrated water, which provides a theoretical basis for the actual treatment of RO concentrated water.

Catalytic ozonation is a complex process. In order to determine the optimal operation conditions, a comprehensive assessment of the influences of various factors on the environment, energy consumption, economic benefit, and other aspects is necessary and significant. The multilevel-fuzzy analysis evaluation model can be employed to evaluate the optimal operation conditions.

In this study, activated alumina was applied as the catalyst supporter, and RO concentrated water was taken as the research object. Impacts of pH, ozone dosage, catalyst dosage, and column height to diameter ratio on the treatment were investigated. Cu-Ce@ γ -Al₂O₃ catalyst improves ozone utilization rate significantly. The application of X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), scanning electron microscopy (SEM), specific surface area analysis (BET), X-ray energy spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS) are means to analyze the physicochemical properties of Cu-Ce@ γ -Al₂O₃ catalysts. The stability of the supported Cu-Ce@ γ -Al₂O₃ catalyst was explored through the repeated use and wear resistance testing of the Cu-Ce@ γ -Al₂O₃ catalyst. The mechanism of action of the Cu-Ce@ γ -Al₂O₃ catalyst was explored by radical quencher, UV absorption spectroscopy, and three-dimensional fluorescence spectroscopy. The comprehensive evaluation model of the Cu-Ce@ γ -Al₂O₃ catalyst was established by

the multilevel-fuzzy analysis method, and the optimal operation model was determined by the comprehensive evaluation of the experimental operating conditions of each group.

2. Materials and Methods

2.1. Experimental Materials

Analytically pure Copper nitrate hexahydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), and tert-butanol (TBA, $\text{C}_4\text{H}_{10}\text{O}$) were purchased from Sinopharm Group Chemical Reagent Co., Ltd (Shanghai, China). Analytical grade potassium bromate, potassium bromide, sodium thiosulfate, soluble starch, potassium iodide, potassium dichromate, silver sulfate, mercury sulfate, potassium sodium tartrate, Nessler's reagent, and hydrochloric acid were purchased from Nanjing Chemical Reagent Co., Ltd (Nanjing, China). Activated alumina is an industrial-grade product and was purchased from Henan Jiechuanghao Clean Water Treatment Materials Co., Ltd (Zhengzhou, China). The RO concentrated water was taken from a water group in Jiangsu Province. The same batch of RO concentrated water was used throughout the study. Table 1 presents water quality.

Table 1. RO concentrated water quality.

Index	Unit	Content	Method
COD	mg/L	146.6	Potassium dichromate method
Ammonia nitrogen	mg/L	2.5	Nessler's reagent colorimetry
pH	/	7.49	pH meter
Turbidity	mg/L	0.25	Turbidimeter
Chroma	NTU	1.5	Colorimeter
Total nitrogen	mg/L	10.2	UV spectrophotometry
Total phosphorus	mg/L	0.95	UV spectrophotometry
Conductivity	us/cm	1695	Conductivity meter

2.2. Catalyst Preparation Process

First, pure water was used to rinse the activated alumina carrier repeatedly. When the washed solution was no longer turbid, the washed activated alumina carrier was washed into a beaker, and then 0.1 mol/L hydrochloric acid solution was added to soak for 6 h to destroy the alumina film on the surface for the next dipping. After soaking in hydrochloric acid, the washed activated alumina carrier was rinsed repeatedly with pure water until the eluted solution was no longer turbid and the eluate was neutral. The activated alumina particles were taken out and placed in an oven at 110 °C for 4 h to dry the water for later use. The catalyst was prepared by using the equal amount impregnation method. $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were weighed on an electronic balance, and a 0.8 mol/L concentration of the metal element active component precursor solution was prepared, controlling the molar ratio of Ce:Cu from 3:1 to 1:3. The pretreated activated alumina was placed in a conical flask, and the precursor solution was poured in until it was submerged in the activated alumina. The conical flask was shaken in a water bath shaker for 12 h, and the water bath temperature was set at 25 °C. The supporter was dried at 110 °C for 12 h. The catalyst was roasted in a muffle furnace at a controlled roasting temperature of 300–700 °C for 2–6 h. The Cu-Ce@ γ - Al_2O_3 catalyst was produced when the temperature cooled.

2.3. Methods for Catalyst Characterization

The surface morphology of the catalyst was characterized by SEM (ZEISS Merlin, Zeiss AG, Oberkochen, Germany). XRD (D8 Advance, Bruker, Berlin, Germany) was used to characterize the crystal morphology of transition metals in the catalyst. XRF (Axios Pw4400, PANalytical, Eindhoven, The Netherlands) was used to characterize the content of metal elements and metal oxides inside the catalyst. The pore volume, pore size, and adsorption performance of the catalysts were characterized by BET-specific surface area and pore distribution (ASAP-2020, Micromeritics, Norcross, GA, USA). Energy dispersive

X-ray spectroscopy (EDS) (Kratos AXIS Ultra DLD, Shimadzu Corporation, Kyoto, Japan) was used to characterize the content of each element in the catalyst. The element species and valence distribution of the catalysts were characterized by XPS (250xi, Perkin Elmer, Waltham, MA, USA).

2.4. Ozone Catalytic Oxidation Experiment

Figure 1 shows catalytic ozone oxidation reaction flow. First, open the oxygen cylinder and control the oxygen outlet pressure to 0.12 Mpa. Then, turn on the cooling water circulation system, then turn on the ozone generator and adjust the ozone output. Before the experiment, the ozone should be pre-blown for 10 min to discharge other impurity gases in the catalytic oxidation device. After pre-blowing, the filling rate of the reaction column catalyst is controlled to be 4%, 8%, 12%, 16%, 20%, and the amount of RO concentrated water in the column is controlled so that the ratio of the height of the water column to the inner diameter of the reaction column is 3:1, 5:1, 7:1, 9:1 and 11:1. The gas flow meter is adjusted to realize the control of the ozone dosage, and the remaining ozone is discharged to the outside through a two-stage 20% KI absorption unit. In order to investigate the adsorption of organics on activated alumina, the adsorption experiment process is performed as follows. A pretreated blank activated alumina carrier in the experimental device is added. Subsequently, a certain amount of RO-concentrated water is injected. Open the high-purity oxygen cylinder and control the oxygen discharge pressure by adjusting the pressure-reducing valve to 0.12 Mpa. A 25 mL water sample is taken every 10 min. All experiments were repeated three times.

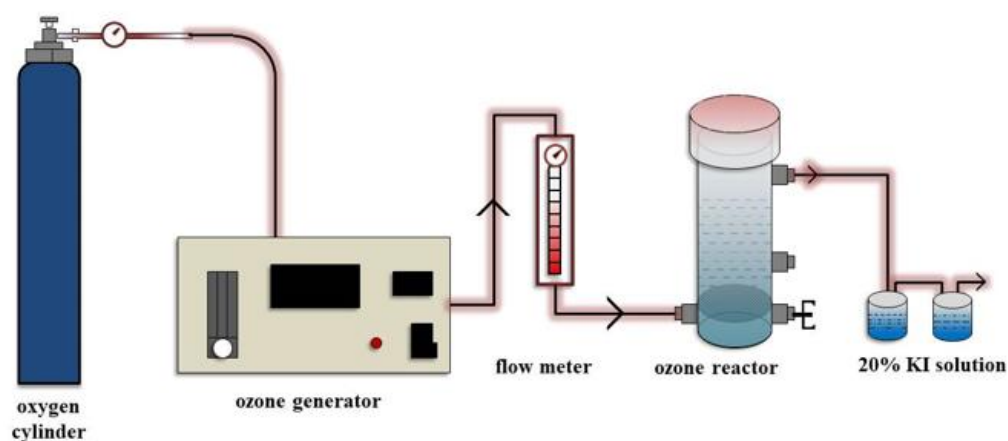


Figure 1. The schematic diagram of the catalytic ozone oxidation system.

The vibration of the water bath shaker was used to simulate the friction strength of the catalyst caused by the ozone aeration device and the combined flow friction strength of the gas and water caused by the aeration. The wear resistance of the catalyst was analyzed according to the wear rate of the Cu-Ce@ γ -Al₂O₃ catalyst, which varied with the shaking speed of the shaker. Detailed experimental procedures are shown in Text S1. The prepared Cu-Ce@ γ -Al₂O₃ catalyst was used 30 times to investigate its stability in long-term use and its degradation performance in RO concentrated water.

2.5. Water Quality Analysis Method

The iodometric method is commonly used to determine the gas-phase ozone concentration. This study uses the sodium indigo disulfonate method to measure the ozone concentration in the liquid phase. The calculation of the ozone utilization rate is shown in Text S2. The spectral analysis of the water quality conditions before and after treatment was conducted using a fluorescence spectrophotometer to investigate the consistency of the organic matter in water. The three-dimensional fluorescence spectrum testing parameters were presented as follows: the emission wavelength (EM) was 270–600 nm, the excitation wavelength (EX) was 250–450 nm, and the slit width was 5 nm. The water quality con-

ditions before and after the treatment were scanned and analyzed by a mid-ultraviolet spectrophotometer, and the detection wavelength range was 190–1100 nm.

2.6. Multilevel-Fuzzy Analysis Evaluation Model

Various complex factors and indicators in the catalytic oxidation process often have certain levels and ambiguities. For the evaluation subject of the Cu-Ce@ γ -Al₂O₃ catalyst, the evaluation indexes are selected from three aspects, namely, environmental impact, resource consumption, and energy consumption, which can reflect the environmental and economic benefits of the system. A comprehensive evaluation index system is established, that is, multilevel fuzzy analysis evaluation. The Cu-Ce@ γ -Al₂O₃ catalyzed ozone oxidation degradation of COD in RO concentrated water was evaluated by the analytic hierarchy process (AHP), and the target layer was determined as the comprehensive evaluation system for Cu-Ce@ γ -Al₂O₃ catalyzed ozone oxidation degradation of RO concentrated water called T. Environmental impact, T1, resource consumption, T2, and energy consumption, T3, which can reflect the environmental benefits and economic benefits of the system, are chosen as the criterion layer. COD removal efficiency, T11, catalyst filling rate, T21, ozone flow rate, T22, reaction pH value, T23, height-diameter ratio, T24, and reaction time, T31 are the plan layer, and the effect of individual reaction conditions on the COD removal efficiency in RO concentrated water is explored. The hierarchical structure is shown in Figure S1, and the detailed calculation is shown in Text S3.

3. Results and Discussion

3.1. Preparation and Optimization of Cu-Ce@ γ -Al₂O₃ Catalyst

As shown in Figure S2, when no ozone was introduced, the adsorption rate of the blank activated alumina catalyst was faster within 0–60 min, the adsorption saturation state was reached at 80 min, and the COD removal efficiency was 5.9%. In the catalytic ozone oxidation system, the COD removal efficiency was basically stable at 80 min, at 35.3% compared with 27.2% in the single ozone oxidation, and the presence of the blank activated alumina catalyst improved the COD removal efficiency. The blank activated alumina catalyst showed good adsorption performance for organic matter in RO concentrated water. The reason is that the particle size of the activated alumina was small, and the specific surface area and pore structure were improved after calcination and activation (as shown in Table S11). With the increase in time, the treatment effect of the three reaction systems gradually reached saturation, when the COD removal efficiency was still low. This indicates that there are many hard-to-degrade organic pollutants remaining in the RO concentrated water. Hence, it is necessary to dope an active component into the γ -Al₂O₃ to improve the catalytic activity of the catalyst. Figure S3 illustrates that the catalytic activities of the multi-component activated alumina catalysts are quite different when the ratios of Ce and Cu vary. With the increase in Cu content, catalyst degradation efficiency for RO concentrated water increases then decreases. When the doping ratio of Ce and Cu was 1:2, the catalytic activity of the catalyst reached the maximum with COD removal efficiency of 68.6% at 70 min. With the increase in Cu element content, the catalyst active components Ce and Cu are present in a relatively better morphology and dispersion [17]. However, when the doping of Cu is too high, the excess Cu blocks the pore channels inside the catalyst, which is not conducive to sufficient contact between the active components and the ozone. Figure S4 shows that the Cu-Ce@ γ -Al₂O₃ catalysts have great differences in the removal of COD by the catalytic oxidation of RO concentrated water at different calcination temperatures. When the calcination temperature was 600 °C, the catalytic degradation effect was the best, and the COD removal efficiency was 69.3% at 70 min. If the roasting temperature is too low, the high-temperature modification is not sufficient to convert Cu and Ce into the corresponding active oxides [18], and if the roasting temperature is too high, some of the crystal particles sinter and the surface activity decreases significantly. Figure S5 shows that with a calcination time of 3–5 h, the COD removal efficiency showed a significant and gradual upward trend. However, by continuing to extend the roasting time to 6.0 h, the

COD removal efficiency decreased. When the roasting time was 5.0 h, the COD removal efficiency reached the highest of 80.6% at 70 min. The complete conversion of the active components to metal oxides requires a long roasting time. However, when the roasting time is too long, the Cu and Ce oxides tend to sinter, forming large areas of coverage and causing a certain degree of reduction in the specific surface area of the catalyst [19]. When Ce:Cu = 1:2, the roasting temperature is 600 °C, and the roasting time is 5 h, the elements Cu and Ce can be converted to the corresponding metal oxides better, and the catalytic activity of the catalyst is higher.

3.2. Characterization and Analysis of Cu-Ce@ γ -Al₂O₃ Catalysts

Figure 2 shows the SEM of the catalysts. When the calcining temperature is lower than 600 °C, a great quantity of obvious crystal particles is not observed compared with the blank sample, indicating less generated active components. When the calcination temperature reached 600 °C, generous crystal particles were formed on the surface of Cu-Ce@ γ -Al₂O₃, and the crystal particles were relatively dispersed. A lower calcination temperature is not conducive to the formation of crystal particles. The rise of calcining temperature properly increases the surface roughness and enhances the catalytic activity [20]. However, the crystal particles generated on the surface of the catalyst increase significantly at a calcination temperature of 700 °C, thereby causing certain crowding of the voids inside the catalyst and affecting the catalytic performance [21]. After 30 repetitions, the pore structure of the Cu-Ce@ γ -Al₂O₃ catalyst was blocked by substances in the RO concentrated water, reducing the catalytic oxidation effect.

Figure 3a suggests that the catalyst has the typical diffraction peaks of Al₂O₃ at $2\theta = 33.16^\circ, 33.16^\circ, 37.68^\circ, 47.06^\circ, 56.19^\circ$, and 66.52° and show the same strength. At $2\theta = 29.15^\circ, 28.75^\circ, 33.22^\circ, 48.35^\circ$, and 57.21° , obvious fluctuations are observed compared with the blank carrier, which are typical CeO₂ and Ce₂O₃ diffraction peaks. Furthermore, at $2\theta = 36.15^\circ, 39.15^\circ$ is the diffraction peak of CuO. When roasting temperature rises, the diffraction peak intensities of CeO₂ at $2\theta = 29.15^\circ, 28.75^\circ, 33.22^\circ, 48.35^\circ, 57.21^\circ$, and CuO at $2\theta = 36.15^\circ, 39.15^\circ$ showed a trend of increasing gradually. The intensity of the corresponding diffraction peaks is highest when the roasting temperature reaches 600 °C. When the roasting temperature reaches 700 °C, the intensity of the diffraction peaks decreases to some extent. The reason is that the ratio of Ce³⁺/Ce⁴⁺ generated in Cu-Ce@ γ -Al₂O₃ is the highest at 600 °C, the amount of Cu²⁺ is also the largest, and the electron transfer rate in the catalytic oxidation process is also the highest [22]. However, excessively high roasting temperatures can cause damage to the structure of Cu-Ce@ γ -Al₂O₃, and the crystal forms of the generated Ce⁴⁺ and Cu²⁺ metal oxides will gradually disappear. Furthermore, repeated use will reduce the CuO and CeO₂ crystal forms [23]. This phenomenon may be due to the loss of metal components caused by repeated use, which in turn affects the size of the diffraction peaks of CuO and CeO₂.

Figure 3b depicts that the electronic binding energy of O1s is 531.1 eV, C1s is 284.8 eV, Al2p is 74.26 eV, Cu2p is 933.4 eV, and Ce3d is 883.8 eV. According to Figure S6, the electronic binding energies corresponding to the peaks of Cu2p_{3/2} and Cu2p_{1/2} are 933.68 eV and 953.5 eV. Meanwhile, the binding energies corresponding to the peaks of Ce3d_{5/2} and Ce3d_{3/2} are 882.85 eV and 905.10 eV. The valence state of Cu supported in the Cu-Ce@ γ -Al₂O₃ catalyst is +2, and the valence of Ce is +4. In addition, compared with the full XPS spectrum of Cu-Ce@ γ -Al₂O₃ catalyst after repeated use 30 times, there seems to be no significant decrease in the characteristic peaks of Cu and Ce. The loss of loading metal due to 30 repetitions did not have a significant effect on the magnitude of the peaks in the Cu2p and Ce3d energy spectra, indicating that the Cu-Ce@ γ -Al₂O₃ catalysts still had high catalytic activity after repeated use.

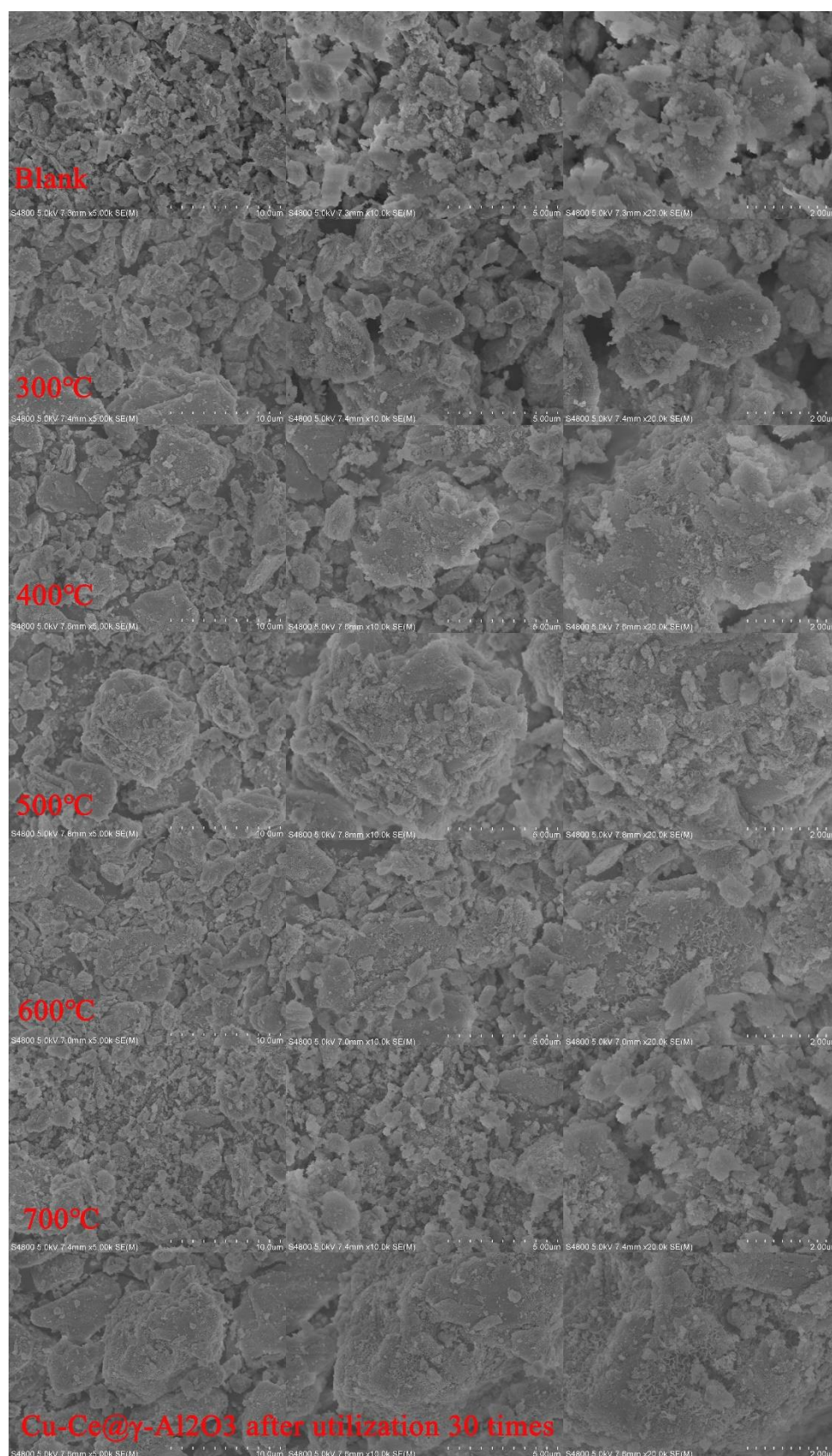


Figure 2. SEM characterization of catalysts ($\times 5000$, $\times 10,000$, $\times 20,000$ from left to right).

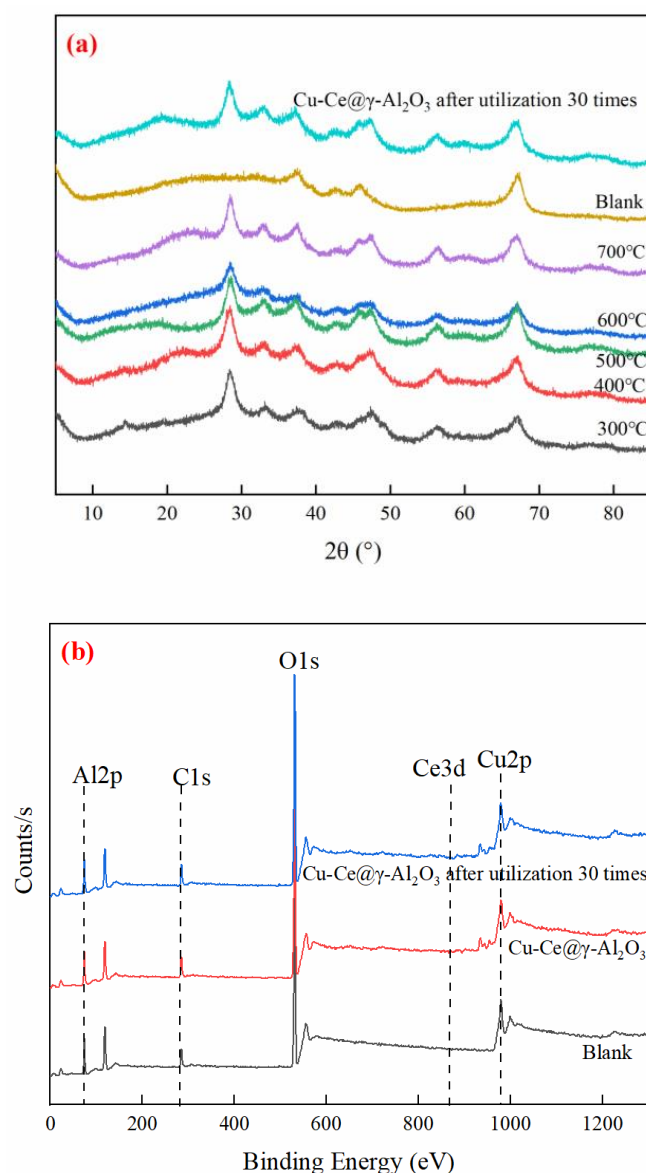


Figure 3. Characterization of the catalyst in different states: (a) XRD, (b) XPS.

Figure 4 shows that the three adsorption and desorption isotherms are all typical type IV isotherms compared with the adsorption-desorption isotherm of N₂. When the relative pressure P/P_0 was around 0.8, the three adsorption and desorption isotherm curves all showed obvious inflection points. According to Table S11, the specific surface area of Cu-Ce@γ-Al₂O₃ is 181.93 m²/g, the average pore volume is 0.44, and the average pore diameter is 9.73 nm. Compared to the blank carrier, the Cu-Ce@γ-Al₂O₃ has a larger surface area and average pore volume, with a small reduction in the average pore size. However, after repeated use for 30 times, Cu-Ce@γ-Al₂O₃ showed a slight decrease in various indexes. This result indicates that Cu and Ce form corresponding metal oxides through calcination activation, which are successfully loaded on the surface and inside of activated alumina. However, in the process of catalytic oxidation treatment of RO concentrated water, with the flow of liquid in the system, a small number of metal oxides of Cu and Ce will penetrate into the pores of the carrier, which will block the pores of the carrier and reduce the specific surface area, thereby affecting the catalytic performance of Cu-Ce@γ-Al₂O₃.

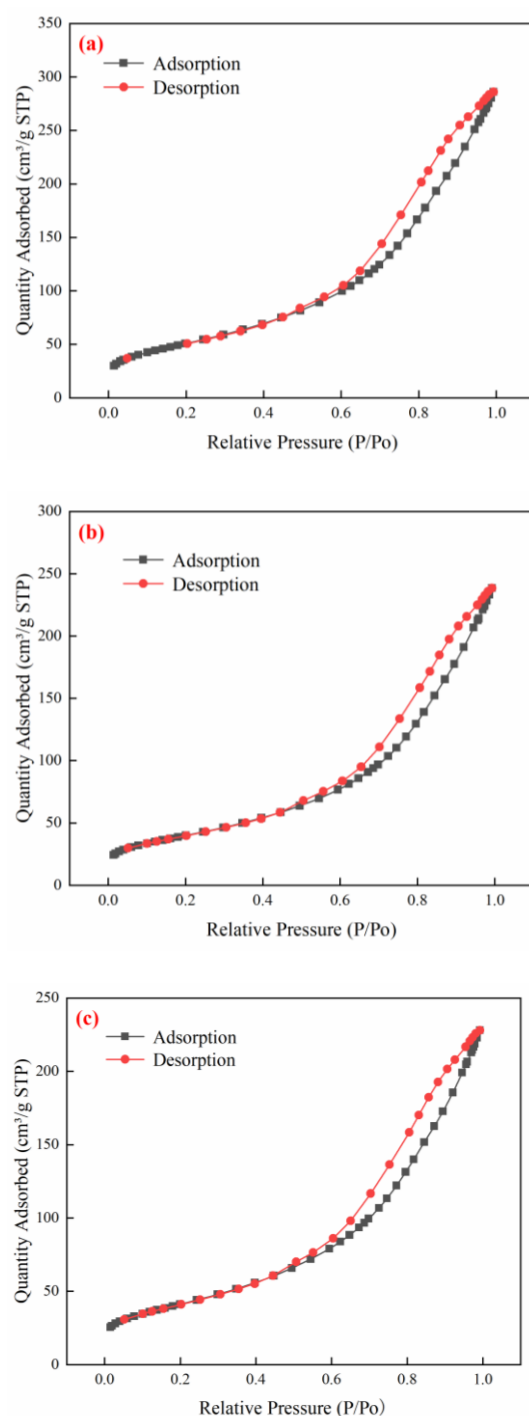


Figure 4. Adsorption and desorption isotherms of Cu-Ce@ $\gamma\text{-Al}_2\text{O}_3$ catalyst: (a) $\gamma\text{-Al}_2\text{O}_3$, (b) Cu-Ce@ $\gamma\text{-Al}_2\text{O}_3$, (c) Cu-Ce@ $\gamma\text{-Al}_2\text{O}_3$ after utilization 30 times.

Table 2 presents that the weight percentages of active metal elements Cu and Ce supported in Cu-Ce@ $\gamma\text{-Al}_2\text{O}_3$ are 3.42% and 3.92%, respectively, and their atomic percentages are 1.16% and 0.60%, respectively. Compared to the blank carrier, the metal active fraction content on the catalyst surface is substantially higher, indicating that two metal active fractions, Cu and Ce, have been successfully loaded onto the active alumina supporter. After repeated use of Cu-Ce@ $\gamma\text{-Al}_2\text{O}_3$ for 30 times, the weight percentages of Cu and Ce are 3.23% and 3.59%, and their atomic percentages are 1.04% and 0.54%, respectively. Compared with Cu-Ce@ $\gamma\text{-Al}_2\text{O}_3$, the weight percentages decreased by 0.19% and 0.33%, indicating that the Cu-Ce@ $\gamma\text{-Al}_2\text{O}_3$ catalyst will lose a small number of active components

Cu and Ce in the process of treating RO concentrated water, and it also has good stability, which can be applied to the actual high-salt wastewater treatment [24].

Table 2. EDS characterization of Cu-Ce@ γ -Al₂O₃ catalyst.

Sample	γ -Al ₂ O ₃		Cu-Ce@ γ -Al ₂ O ₃		Cu-Ce@ γ -Al ₂ O ₃ after Utilization 30 Times	
Element	Weight percent (%)	Atomic percent (%)	Weight percent (%)	Atomic percent (%)	Weight percent (%)	Atomic percent (%)
OK	44.48	59.82	42.58	56.83	45.21	60.73
AlK	44.18	38.42	40.32	35.19	38.08	33.75
CK	10.13	1.85	9.24	3.81	8.39	3.62
CuK	/	/	3.42	1.16	3.23	1.04
CeK	/	/	3.92	0.60	3.59	0.54

Table 3 presents the main elements contained in the blank sample are Na, Al, and Ca, mainly in the form of Na₂O, Al₂O₃, and CaO, and also contain trace elements, such as Si, Fe, S, and other elements, with the form of SiO₂, Fe₂O₃, and SO₃. Compared with the blank, the content of oxides contained in the Cu-Ce@ γ -Al₂O₃ catalyst changed significantly, and the supported CuO and CeO₂ contents were 6.25% and 6.44%, respectively. Thus, Cu and Ce in the immersion solution have been successfully loaded on the surface and inside of the activated alumina supporter and successfully converted into the active components of CuO and CeO₂ after calcination. During the preparation process, the impregnation ratio of Cu and Ce was 1:2, whereas the content ratio of CuO and CeO₂ was approximately 1:1, and the ratio of the generated metal oxides was basically the same as the actual feeding ratio. This finding indicates that the Cu and Ce metal oxides can stably exist in the interior and surface of Cu-Ce@ γ -Al₂O₃, but a small amount of loss will occur during the preparation process. After repeated use for 30 times, the contents of CuO and CeO₂ decreased by 6.41% and 1.24%, respectively, indicating that the surface and internal active components of the catalyst would be lost irreversibly. However, the loss of active metal components is small, and the loss of the Ce element is very small. The results show that the Cu-Ce@ γ -Al₂O₃ catalyst has good stability and can meet the requirements of practical engineering wastewater treatment.

Table 3. XRF characterization of Cu-Ce@ γ -Al₂O₃ catalyst (wt.%).

Sample	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃	SO ₃	CuO	CeO ₂
γ -Al ₂ O ₃ (%)	0.33	98.93	0.07	0.12	0.03	0.07	/	/
Cu-Ce@ γ -Al ₂ O ₃ (%)	0.11	87.29	0.06	0.07	0.02	0.08	6.25	6.44
Cu-Ce@ γ -Al ₂ O ₃ after utilization 30 times (%)	0.29	85.53	0.21	0.29	0.02	0.50	5.85	6.36

3.3. Optimization of Ozone Catalytic Oxidation Conditions

Figure 5a suggests that with prolonged catalytic reaction time, the content of COD in the RO concentrated water gradually decreased. When the reaction time was 10–50 min, the COD removal efficiency increased and reached the value of 80.9%. The COD removal efficiency increased slowly with reaction time proceeding and increased by 2.7% at 100 min. This result is due to the high concentration of organic matter in the RO concentrated water of the system in the first 60 min of the reaction. At this time, the Cu-Ce@ γ -Al₂O₃ catalyst is in rapid and substantial effective contact with the organic pollutants in the system, degrading them at a fast reaction rate. After 60 min, with the prolongation of reaction time, the concentration of organic pollutants in the system gradually decreased, the effective contact efficiency between Cu-Ce@ γ -Al₂O₃ and pollutants also decreased, and the removal efficiency of COD in wastewater increased gently. Figure 5b suggests that the COD removal efficiency has a positive correlation with pH. The COD removal efficiency reaches the highest value of 80.3% at pH 11. However, when pH = 9–11, the

Cu-Ce@ γ -Al₂O₃ catalyst only increased the COD removal efficiency of RO concentrated water by 0.5%. Under alkaline conditions, the COD removal efficiency of RO concentrated water was higher than that under acidic conditions. This phenomenon is due to the fact that many OH[−] exist in alkaline conditions, which can combine with ozone to generate more •OH, thereby improving the degradation effect [25]. Furthermore, the alkaline conditions can possibly destroy the structure of the organic matter in the wastewater, thereby causing it to be dissociated and oxidized faster. Figure 5c shows that when the ozone ventilation rate increases from 0.1 to 0.5 L/min, the COD removal efficiency in the RO concentrated water shows a trend of rapid increase first and then slow. When the ozone flow rate was 0.5 L/min, the highest removal efficiency was 86.3% at 70 min. The reason is that with the increase in ozone flow rate, the gas–liquid–solid three-phase contact is sufficient, thereby increasing the volume mass transfer coefficient, accelerating the generation of •OH in the system, and improving the COD removal efficiency [26]. Figure 5d shows that with the increase in the Cu-Ce@ γ -Al₂O₃ catalyst filling rate, the COD removal efficiency also increased. When the catalyst filling rate was 4–12%, the COD removal efficiency of Cu-Ce@ γ -Al₂O₃ catalyst to RO concentrated water was faster. The COD removal efficiency reached 82.2% at 70 min when the Cu-Ce@ γ -Al₂O₃ catalyst filling rate was 12%. When the catalyst filling rate continued to increase to 20%, the COD removal efficiency only increased by 2.5% compared with the catalyst filling rate of 12%. The reason for this may be that an increase in catalyst fill rate provides more active sites and increases the effective contact area with ozone, enabling the reaction system to generate more •OH per unit of time, increasing the efficiency of catalytic degradation [27]. However, when the active sites provided by the Cu-Ce@ γ -Al₂O₃ catalyst almost meet the demand of ozone, increasing the catalyst fill rate will not significantly improve the catalytic effect. Figure 5e depicts that with the increase in the height-diameter ratio of the reaction column, the COD removal efficiency showed a trend of first increasing and then decreasing. When the height-diameter ratio of the reaction column was 5:1, the removal efficiency of COD was the highest, which was 85.1%. The retention time of ozone in the reactor is shorter with the smaller height-diameter ratio of the reactor. Meanwhile, the ozone utilization rate is also low due to the limit of mass transfer of ozone and the content of •OH produced by catalysis. However, when the H/D of the reactor is too large, the catalyst cannot react with the water sample uniformly to a certain extent due to the constant aeration, which reduces the degradation efficiency.

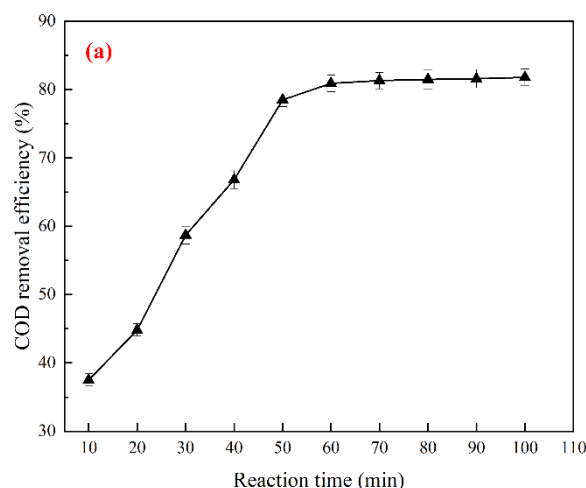


Figure 5. Cont.

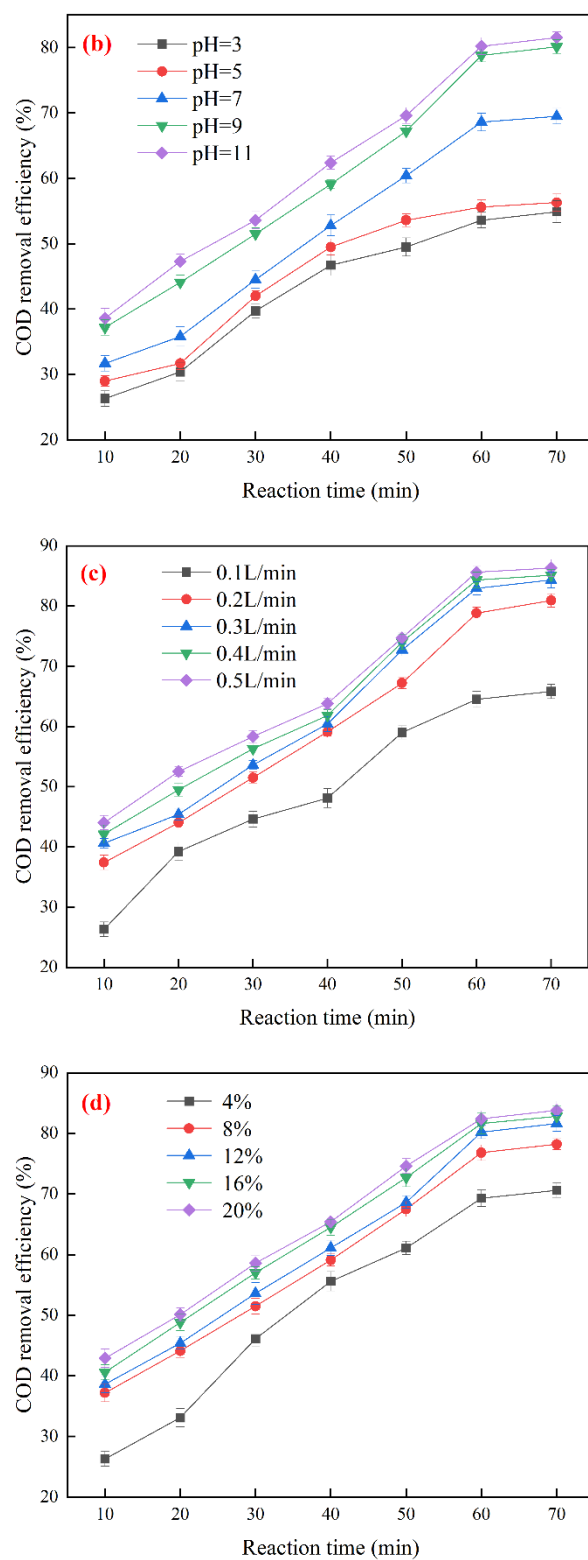


Figure 5. Cont.

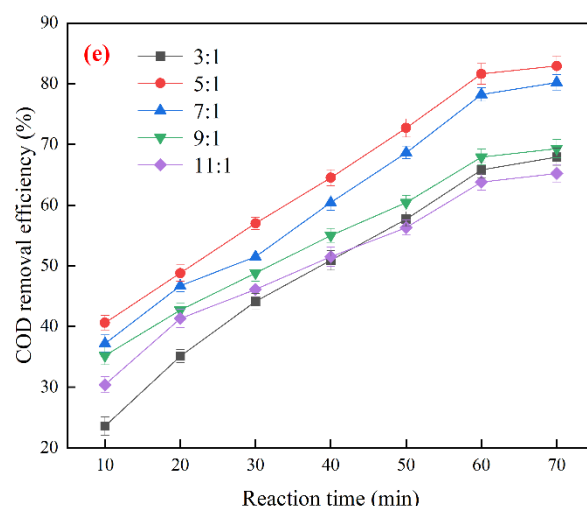


Figure 5. Effects of different conditions on COD removal efficiency: (a) reaction time, (b) pH, (c) ozone aeration, (d) catalyst filling rate, (e) reaction column height-diameter ratio.

In Figure 6, before the reaction time reaches 60 min, the ozone concentration in the exhaust gas keeps rising because in the initial stage, ozone will cooperate with the $\text{Cu-Ce@}\gamma\text{-Al}_2\text{O}_3$ catalyst, or ozone itself will decompose to generate a large number of $\bullet\text{OH}$ to react with pollutants [28]. After the reaction time reached 60 min, the concentration of pollutants in the RO concentrated water continued to decrease due to the oxidation reaction. At this time, the ozone could not be used again. Therefore, the exhaust ozone concentration was high and did not fluctuate much. When the reaction reached the stable stage of 60 min, the ozone utilization rate of the single ozone catalytic oxidation system was 18.5%, and the ozone utilization rate of the $\text{Cu-Ce@}\gamma\text{-Al}_2\text{O}_3$ ozone catalytic oxidation system was 47.6%, which increased by 29.1% compared with the ozone system.

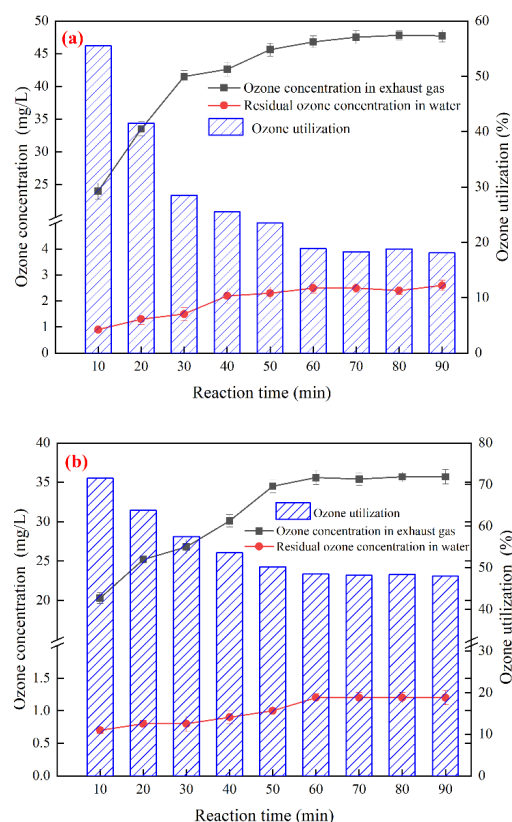


Figure 6. Ozone utilization rate: (a) ozone system, (b) catalytic ozone oxidation system.

3.4. Effects of Free Radical Quenchers on Ozone Catalytic Oxidation

Figure 7 shows that when the concentration of TBA is 0 mg/L, the COD removal efficiencies in the ozonation system and the catalytic ozonation system are 18.2% and 80.7%, respectively. The COD removal efficiency in both systems decreased significantly with increasing TBA concentration, but the rate of decrease gradually became gentle. At a TBA concentration of 120 mg/L, the COD removal efficiencies for the two systems were 10.4% and 34.3%, respectively, which were 7.8% and 46.4% lower compared to the TBA concentration of 0 mg/L. The reason is that TBA, as an inhibitor of $\bullet\text{OH}$, can shield the effect of free radicals in water on the degradation of COD. The COD removal efficiency of the ozone catalytic oxidation system is more affected by TBA, which indicates that $\bullet\text{OH}$ dominates in the Cu-Ce@ $\gamma\text{-Al}_2\text{O}_3$ ozone-catalyzed oxidation reaction system to a certain extent. Therefore, the catalytic oxidation of ozone follows the action mechanism of $\bullet\text{OH}$; that is, ozone is chemically adsorbed on the active site of the catalyst surface to generate $\bullet\text{OH}$, thereby degrading organic pollutants in water.

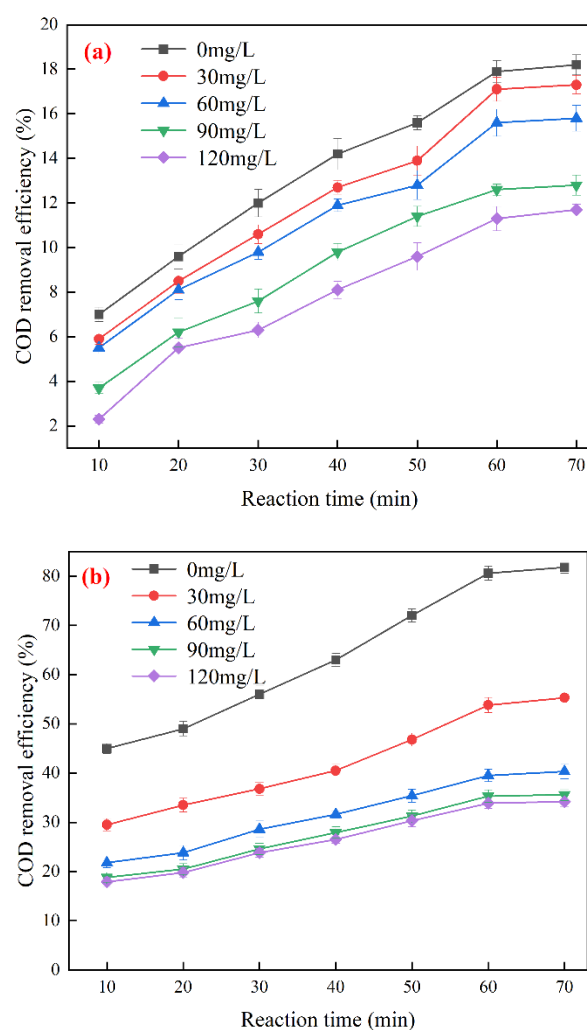


Figure 7. Effect of TBA dosage on COD removal efficiency: (a) ozonation system, (b) ozone catalytic oxidation system.

3.5. UV Absorption Peak of Tail Water

Figure 8 demonstrates that the UV absorption peak of the effluent sample treated with RO concentrated water has a significant decrease in the range of $\lambda = 190\text{--}220\text{ nm}$, indicating that the conjugated structure and unsaturated organic matter in the RO concentrated water are effectively degraded. In addition, after 60 min of reaction, the decrease in UV absorbance is small, indicating that most organic compounds have been degraded, the reaction rate of

catalytic ozone oxidation has gradually become flat, and the number and peak of absorption peaks have also gradually stabilized. The reaction time was prolonged continuously, and the degradation effect was not large, which is consistent with the changing trend of COD removal efficiency. Therefore, UV absorbance can measure the catalytic performance of the Cu-Ce@ γ -Al₂O₃ catalyst for the degradation of RO concentrated treated water.

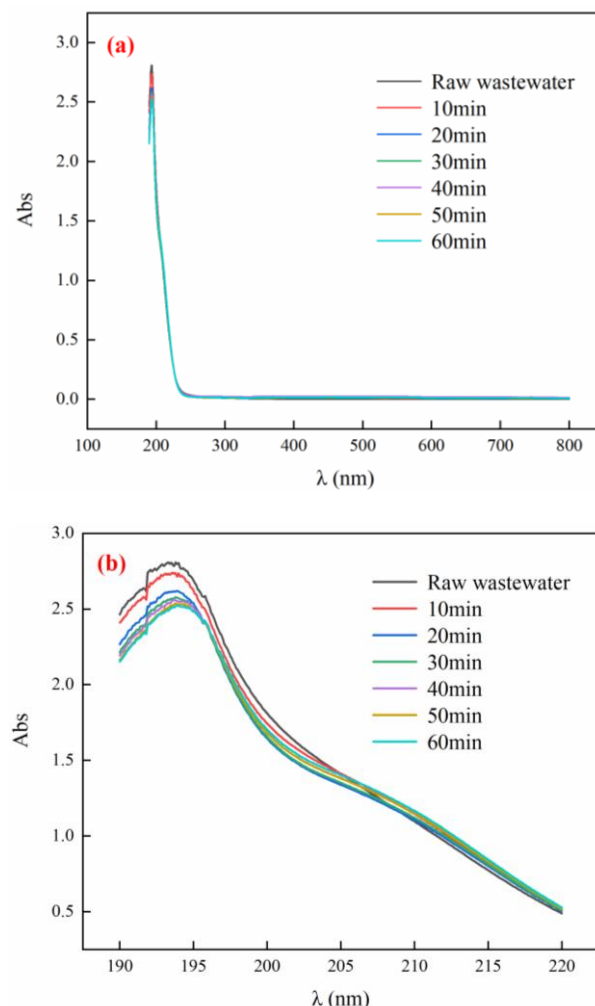


Figure 8. UV-Vis analysis results: (a) 190~1100 nm, (b) 190~220 nm.

3.6. 3D-EEM Spectrum Analysis of Tail Water

Figure 9 shows that the pollutants in RO concentrated water are mainly tryptophan-like organics and fulvic acid-like and humic-like acids, and the fluorescence intensity of tryptophan-like organics can reach up to 9850. After Cu-Ce @ γ -Al₂O₃ ozone catalytic oxidation treatment of RO concentration for 60 min, fulvic acid-like and humic-like acids were effectively removed, and only tryptophan-like organic compounds remained. The maximum fluorescence intensity value is 3050. It shows that ozone catalytic oxidation has a good removal effect on these three types of substances. The unsaturated bonds of the three species are broken, resulting in a reduction of the fluorescent light peak. The comparison of 3D-EEM of the raw water and the treated water suggests that after the Cu-Ce@ γ -Al₂O₃ ozone catalytic oxidation treatment, in addition to removing most of the pollutants, some weak fluorescence peaks still exist in the spectrum. This is due to the fact that some difficult intermediates are produced during the degradation of the large organic compounds in the RO concentrated water. However, such substances remain in the wastewater because of the limited reaction time [29].

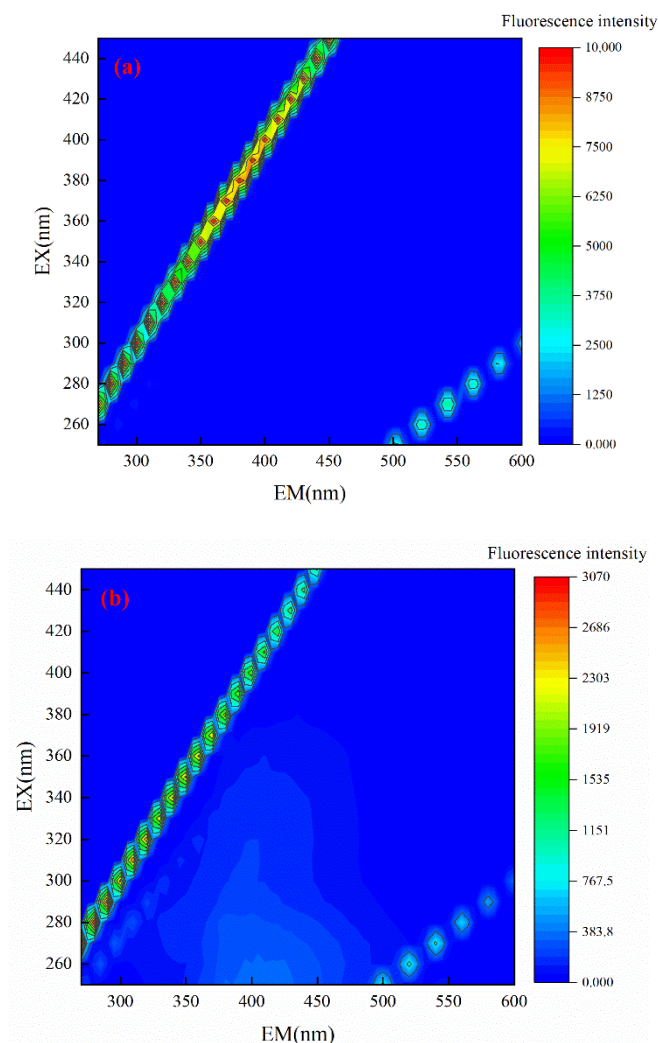


Figure 9. 3D-EEM: (a) RO concentrated water, (b) effluent after 60 min degradation of RO concentrated water.

3.7. Cu-Ce@ γ -Al₂O₃ Catalyst Stability

Figure 10a displays that when the dosage of the Cu-Ce@ γ -Al₂O₃ catalyst is constant, the wear rate increases with the shaking speed of the shaker. The experimental results show that when the shaking speed is in the range of 20–150 rpm, the wear rate of the Cu-Ce@ γ -Al₂O₃ catalyst increases slowly with the shaking speed of the shaking table. When the shaking speed was 20 rpm, the wear rate of the Cu-Ce@ γ -Al₂O₃ catalyst was 0.45%, and when the oscillation speed was 150 rpm, the wear rate was 2.5%. When the oscillation speed was in the range of 150–210 rpm, the wear rate of the Cu-Ce@ γ -Al₂O₃ catalyst increased rapidly. When the vibration speed was 180 rpm, the wear rate was 5.3%, and when the vibration speed was 210 rpm, the wear rate was 7.6%. At this time, the loss of Cu-Ce@ γ -Al₂O₃ catalyst was serious, and more damaged catalysts appeared in the conical flask. In the practical application of Cu-Ce@ γ -Al₂O₃ catalyst for the treatment of RO concentrated water, the friction strength of the catalyst caused by the ozone aeration device is weaker than that caused by the shaking speed of the water bath shaking table, and it is far smaller than the friction strength when the shaking speed of the water bath shaker is 150 rpm. Therefore, the loss of Cu-Ce@ γ -Al₂O₃ catalyst in the practical application of RO concentrated water treatment is relatively small, meeting the wear and tear requirements of its practical application. Figure 10b shows that the performance of the Cu-Ce@ γ -Al₂O₃ decreases slightly with the increase of reused times. The first-used Cu-Ce@ γ -Al₂O₃ catalyst has a COD removal efficiency of 85.1% when treating RO concentrated water. After repeated

use of Cu-Ce@ γ -Al₂O₃ catalyst for 5 times, the COD removal efficiency of RO concentrated water became 82.5%, and the COD removal efficiency only decreased by 2.6%. After repeated use of Cu-Ce@ γ -Al₂O₃ 30 times, the COD removal efficiency of RO concentrated water is 68.9%, which still has a high removal efficiency. This is due to the reduction and separation of the active components on the surface of the Cu-Ce@ γ -Al₂O₃ catalyst due to friction between the particles over a long period of time, and the loss of active components leads to a reduction in the performance of the Cu-Ce@ γ -Al₂O₃ catalyst. However, the catalytic performance of the Cu-Ce@ γ -Al₂O₃ catalyst did not decrease significantly after repeated use for 30 times. Therefore, its mechanical strength and catalytic activity are relatively stable, which has certain practical application significance.

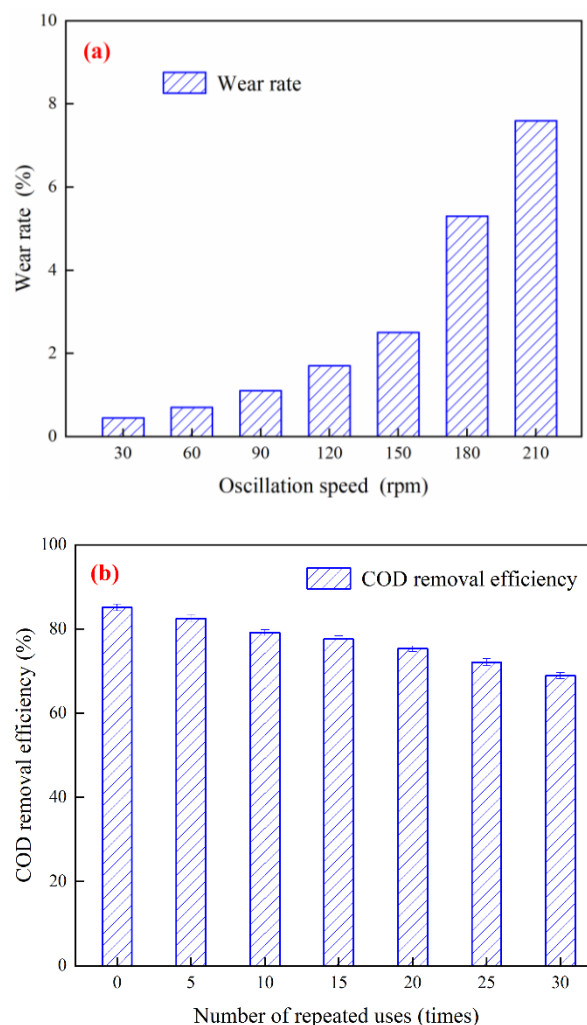


Figure 10. Catalyst stability (a) wear resistance analysis of Cu-Ce@ γ -Al₂O₃ catalyst, (b) effect of repeated use on COD removal efficiency.

3.8. Multilevel-Fuzzy Analysis Evaluation Model

The six indexes are classified according to quantitative and qualitative indexes. The quantitative indexes include the COD removal efficiency, catalyst dosage, ozone flow rate, height-diameter ratio, and reaction time, and the qualitative indexes include the reaction pH. The calculation of qualitative and quantitative indexes is shown in Text S3, and the summary of the experimental results of the Cu-Ce@ γ -Al₂O₃ catalyst for oxidative degradation of RO concentrated water is presented in Table S10. The scores and ranking of each experimental order in the multilevel-fuzzy comprehensive evaluation can be seen in Table 4. Table 4 shows that the highest score in this evaluation is the 19th group (the experimental conditions are: the catalyst filling rate is 12%, the ozone flow rate is 0.2 L/min,

the reaction pH is 9, and the H/D is 5, the reaction time is 60 min, the COD removal efficiency is 85.2%), ranking first. Under this working condition, resource consumption can be low, and the energy consumption and environmental impact are the lowest. Therefore, in the system of Cu-Ce@ γ -Al₂O₃ catalyst for catalytic oxidation and degradation of RO concentrated water, the optimal operation conditions are as follows: the catalyst filling rate is 12%, the ozone flow rate is 0.2 L/min, the reaction pH is 9, the H/D is 5, and the reaction time is 60 min.

Table 4. Comprehensive evaluation score and ranking of each experiment order.

Serial Number	Environmental Impact T1	Resource Consumption T2	Energy Consumption T3	Overall Score	Scoring Order
1	0.0661	0.1626	0.1634	0.3921	17
2	0.2007	0.1626	0.0812	0.4444	14
3	0.3726	0.1626	0.0403	0.5755	10
4	0.3846	0.1626	0.0200	0.5672	11
5	0.0908	0.1495	0.0403	0.2805	22
6	0.1025	0.1535	0.0403	0.2963	21
7	0.2196	0.1603	0.0403	0.4202	16
8	0.4055	0.1718	0.0403	0.6176	8
9	0.4164	0.1912	0.0403	0.6179	3
10	0.1834	0.2055	0.0403	0.4292	15
11	0.4437	0.1519	0.0403	0.6359	6
12	0.4604	0.1401	0.0403	0.6408	4
13	0.4880	0.1331	0.0403	0.6615	2
14	0.1873	0.2284	0.0403	0.4561	13
15	0.4604	0.1383	0.0403	0.6390	5
16	0.4653	0.1185	0.0403	0.6241	7
17	0.4703	0.1068	0.0403	0.6173	9
18	0.1685	0.1537	0.0403	0.3626	18
19	0.5396	0.1422	0.0403	0.7221	1
20	0.3553	0.1353	0.0403	0.5309	12
21	0.1694	0.1313	0.0403	0.3410	19
22	0.1516	0.1289	0.0403	0.3208	20

In comparison, the performance and degradation of other wastewater by catalytic oxidation processes were evaluated in this study (Table 5). In view of the results and AHP model analysis, it can be seen that the Cu-Ce@ γ -Al₂O₃ catalyst exhibited higher catalytic ozonation capacity, suggesting that the Cu-Ce@ γ -Al₂O₃ catalyst is a promising catalyst for the treatment of RO concentrate.

Table 5. Treatment of wastewater with different catalytic oxidation processes.

Wastewater Type	Index	Method	Initial Concentration (mg/L)	Removal Efficiency	Reference
RO concentrate	COD	Catalytic ozonation by Cu-Ce@ γ -Al ₂ O ₃ catalyst	146.6	85.2%	This study
RO concentrate	TOC	Catalytic ozonation coupling with activated carbon adsorption	66	58%	[30]
RO concentrate	COD	Catalytic ozonation with core/shell Fe ₃ O ₄ @SiO ₂ @Yb ₂ O ₃ catalyst	100 (thymol)	57%	[31]
RO concentrate	COD	A hybrid process of Fe-based catalytic ozonation and biodegradation	108	63%	[32]
RO concentrate	DOC	Catalytic ozonation by Fe-oxide@Al ₂ O ₃ catalyst	30	47%	[33]
RO concentrate	Rh B	Photocatalytic by Fe-TiO ₂ mixed-phase nanocomposite thin films	4.1	69%	[34]
Coal chemical biochemical tail water	TOC	Catalytic ozonation by Fe-Mn@Bt	210	53.5%	[35]

4. Conclusions

The Cu-Ce@ γ -Al₂O₃ catalyst was prepared using activated alumina as a carrier, and the RO concentrated water was treated by heterogeneous ozone catalytic oxidation technology. The optimal working conditions and the degradation mechanism of the Cu-Ce@ γ -Al₂O₃ catalyst catalytic oxidation system were systematically explored to treat RO concentrated water. The optimal preparation conditions of the Cu-Ce@ γ -Al₂O₃ catalyst are presented as follows: the active metal loading ratio is Cu:Ce = 2:1, the calcining temperature is 600 °C, and the roasting time is 5.0 h. Through characterization, activated alumina supported with Cu and Ce in the form of CuO and CeO₂ was observed. The optimal working conditions for Cu-Ce@ γ -Al₂O₃ ozone catalytic oxidation treatment of RO concentrated water system was optimized and screened. The decline of COD removal caused by TBA indicated that the degradation process follows the reaction mechanism of •OH. UV spectroscopic analysis and 3D-EEM analysis showed that most organic substances were almost degraded after catalytic ozonation treatment. However, a few organic substances were residual as protein-like fluorophores and fluorophores and tryptophan-like and other new substances. The Cu-Ce@ γ -Al₂O₃ exhibited excellent stability. The mechanical strength and catalytic activity of the Cu-Ce@ γ -Al₂O₃ catalyst are relatively stable. The results of the multilevel-fuzzy analysis evaluation model show that the optimal working conditions of the Cu-Ce@ γ -Al₂O₃ for catalytic oxidation and degradation of RO concentrated water is as follows: the catalyst filling rate is 12%, the ozone flow rate is 0.2 L/min, the reaction pH is 9, the H/D is 5, and the reaction time is 60 min. The Cu-Ce@ γ -Al₂O₃-catalyzed ozone oxidative degradation in the RO concentrated water treatment reaction system has a good treatment effect and stability. It provides theoretical support for the practical treatment of saline wastewater.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w14182881/s1>, Figure S1: Comprehensive evaluation index system of Cu-Ce@ γ -Al₂O₃ catalysts for catalytic oxidative degradation of RO concentrated water; Figure S2: Effect of different reaction systems on COD removal efficiency; Figure S3: Effect of active component proportion on COD removal efficiency; Figure S4: Effect of calcination temperature on COD removal efficiency; Figure S5: Effect of calcination time on COD removal efficiency; Figure S6: XPS characterization: (a) Cu2p spectrum, (b) Ce2d spectrum, (c) Cu2p spectrum after repeated use 30 times, (d) Ce2d spectrum after repeated use 30 times; Table S1: 1–9 scaling method; Table S2: The judgment matrix of criterion layer to target layer; Table S3: Judgment matrix for environmental impact at the scheme layer; Table S4: Judgment matrix for resource consumption at the scheme layer; Table S5: Judgment matrix for energy consumption at the scheme layer; Table S6: The value standard of RI; Table S7: Consistency test; Table S8: The total ranking weight of each index layer; Table S9: Qualitative index evaluation standard; Table S10: Summary of experimental data; Table S11: BET characterization of Cu-Ce@ γ -Al₂O₃ catalyst; Text S1: Catalyst wear rate; Text S2: Ozone utilization; Text S3: The calculation of index weight and consistency check, the calculation of index membership, and the structure of factor evaluation set R.

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