**Original Research** 

# Study on Treatment of Organic Wastewater from Cutting Fluid by Electro-Flocculation-Multiphase Fenton/Ultrasonic System

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#### Abstract

The composition of cutting fluid wastewater is complex, containing oil and various additives. Due to different production processes, various metal particles will be mixed, which has caused great difficulties in wastewater treatment. In this study, electro-flocculation-multiphase Fenton/ultrasound system was used to treat cutting fluid organic wastewater. Firstly, the demulsification pretreatment was carried out by electroflocculation method, which achieved 97.4% COD<sub>er</sub> removal efficiency. Afterwards, a multiphase Fenton/ultrasonic system was used for advanced treatment. By comparing the SEM results, BET results, XRD results and COD<sub>er</sub> removal efficiency of the catalysts prepared by different supports and methods, CuO/CeO, catalyst prepared by the deposition precipitation method was used in this experiment. The dissolution rate of copper in the catalyst CuO/CeO, was only 1.29% after 4 hours of reaction. After 5 times of recovery, the recovery rate of the catalyst was still 95%, and the removal efficiency of COD<sub>er</sub> was 29.8%. It proved that the catalyst CuO/CeO, had good stability. Compared with a separate multiphase Fenton or ultrasound system, the multiphase Fenton/ultrasonic system had a better processing effect. Under the conditions of an ultrasonic frequency of 800 KHz, a reaction time of 180 min, a catalyst dosage of 1.6 g/L, a hydrogen peroxide dosage of 0.5 mol/L, and an initial pH of 8, the multiphase Fenton/ultrasonic system could achieve 65% COD<sub>er</sub> removal efficiency. This study found that electro-flocculation-multiphase Fenton/ultrasonic system could finally achieve 99.09% COD<sub>er</sub> removal efficiency.

**Keywords**: high concentration cutting fluid wastewater, electro-flocculation, catalyst CuO/CeO<sub>2</sub>, multiphase Fenton/ultrasonic system

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#### Introduction

In the process of cutting, grinding and grinding of metals and alloys, cutting fluid is often used to lubricate and cool metal objects and tools [1]. In the production process, the cutting fluid needs to be replaced regularly to remove various impurities mixed in, and the cutting fluid residue on the surface needs to be cleaned after the metal workpiece is processed, which lead to the generation of a large amount of cutting fluid wastewater. The composition of the cutting fluid wastewater is complex, containing oil and various additives. Due to the difference in the production process, various metal particles may be mixed in, which causes great difficulties in the treatment of the wastewater.

The emulsification state of cutting fluid wastewater is very stable, so pretreatment experiments are usually carried out first. By reducing the interfacial tension, neutralizing the surface charge of the interfacial film, and breaking the interfacial film, the water-in-oil (W/O) or oil-in-water (O/W) state could be removed to achieve oil-water separation and demulsification effect [2]. Common demulsification methods include salting out method [3], acid precipitation method [4], coagulation method [5], membrane filtration method [6] and electric demulsification method [7]. Electric flocculation technology has a long history of development in water treatment, and it has been widely used in the treatment of emulsified wastewater [8], printing and dyeing wastewater [9], heavy metal wastewater [10] and other wastewater [11, 12]. In the electro-flocculation method, the compound produced by cationic hydrolysis has a strong flocculation effect. It can combine with suspended solids, oily substances, colloids and other pollutants in the raw water to form larger floccules, and then remove various pollutants in the wastewater through air flotation and precipitation. Its working principle is similar to that of chemical flocculants, including processes such as electric neutralization, compression of double electric layers, net compensation and aggregation, and adsorption bridging. In this experiment, electro-flocculation was used to demulsify. The flocculant was produced at the expense of the electrode plate during the electro-flocculation process to achieve demulsification.

After pretreatment, the cutting fluid still fails to meet the emission standards, so further advanced treatment is required. Advanced treatment is mainly to remove oily substances and soluble substances in water. Common advanced treatment methods include adsorption [13], air flotation [14], biological treatment [15], advanced oxidation [16], etc. Fenton oxidation technology is currently a hot topic in domestic and foreign research and is widely used [17-19]. The principle is that the hydroxyl radicals (•OH) produced in the reaction process could be used to oxidize the organic pollutants in the wastewater non-selectively, and then oxidatively decompose the refractory organic matter in the wastewater into CO<sub>2</sub>, H<sub>2</sub>O and other inorganic salts [20]. In recent years, researchers have become more mature in the research of heterogeneous Fenton technology. It not only retains the traditional homogeneous Fenton technology's features of simple operation, high oxidation, large processing capacity and non-selectivity, but also solves the problems of secondary pollution and demanding pH value. Ultrasound technology is a multi-disciplinary emerging science and technology, and it is the focus of the field of sonochemical research. It is generally believed that when a solution is irradiated by ultrasonic with a frequency of 16 KHz~1 MHz, many chemical changes would occur and the chemical reaction would be accelerated. It is considered as ultrasonic cavitation, which is an extremely complex physical and chemical change in the liquid. In recent years, ultrasonic technology has been widely used in water treatment. It is often used to treat difficult-to-degrade organic wastewater and has achieved good application results [21-24]. However, due to the complex composition of some industrial wastewater and a large amount of refractory organic matter, it is difficult to achieve the desired effect if only a single ultrasound technology is used. Therefore, researchers use ultrasound combined with other technologies to jointly treat refractory wastewater [25-27]. Fenton/ultrasonic technology, as an efficient advanced oxidation technology, combines the cavitation effect of ultrasound and Fenton's free radical oxidation mechanism, which greatly improves the degradation effect of organic pollutants. Fenton/ultrasonic technology is easy to operate, easy to implement, and has a wide range of applications. It has a good application prospect in the field of water treatment [28].

At present, the research on catalysts at home and abroad has made rapid progress in transition metals and their oxides, which are divided into catalysts containing precious metals and catalysts containing non-precious metals. Compared with other metal catalysts, noble metal catalysts have many advantages, but they also have problems such as poor stability, higher price, and easy sintering and agglomeration at high temperatures. Therefore, the application of noble metal catalysts is limited. However, the cost of supporting transition metals (copper, zinc, iron, nickel, etc.) and their oxides on the catalyst carrier would be much lower. They are easier to obtain and have better catalytic performance, which have been extensively researched in the field of heterogeneous Fenton catalysts. Therefore, in this experiment, transition metal oxide CuO was selected as the active component of the heterogeneous Fenton catalyst, and a supported oxide catalyst with better performance was screened out based on the performance of COD<sub>a</sub> degradation and characterization methods such as BET, SEM and XRD.

This article focused on the treatment of cutting fluid wastewater produced in the actual production process of a precision instrument and machinery processing plant in Shenzhen. The electro-flocculation process was used for pretreatment. The self-made CuO/CeO<sub>2</sub>

catalyst was used as a solid phase catalyst, combined with  $H_2O_2$  to form a heterogeneous Fenton system, and combined with ultrasound to increase the degradation rate of organics. A multi-phase Fenton/ultrasonic system was constructed to provide theoretical basis and technical support for the development and application of new electro-flocculation/multi-phase Fenton/ultrasonic processes.

#### **Material and Methods**

The wastewater used in this experiment was cutting fluid wastewater generated during the actual production process of a precision instrument and machinery processing plant in Shenzhen. The wastewater was collected three days before the experiment to ensure that the wastewater did not undergo secondary deterioration and the experimental results had certain reliability. The water used in the experiment was all ultra-pure water with a resistivity of 18 M $\Omega$ ·cm. In this experiment, the inoLab pH 730 desktop precision pH meter produced by WTW in Germany was used to determine the pH value of the water sample. The instrument needed to be calibrated before use. Using the Micromeritics TriStar II3020 specific surface area analyzer produced by the Americould Mike Company, under low temperature (using liquid nitrogen cooling) conditions, the specific surface area and pore volume of the catalyst were measured, and the relationship between them and the degradation effect was studied. The specific surface area was measured by the Brunauer-Emmer-Teller (BET) method. The specific surface area was measured by isothermal adsorption under low temperature conditions in a liquid nitrogen structure. SEM was used to analyze the particle shape and surface characteristics of the catalyst, and the detection was performed on the SEM of JSM-6460LV of Japan JEOL Company. Detection conditions: acceleration voltage was 20 KV; working distance was 10 mm; and magnification was 5000 times. The phase structure and type of the catalyst were precisely measured by XRD method. The detection was carried out on the X'pert Pro X-ray diffractometer produced by PANalytical Corporation in the Netherlands. Detection parameters: X-ray was Cu Ka; the target voltage was 40 kV; the target current was 40 mA; the diffraction angle was scanned between 2 Theta 10° and 80°.

The electroflocculation experiment steps were as follows. First of all, took 3 L of cutting fluid wastewater in the reaction tank to determine the initial  $COD_{er}$  value. Then cleaned the electrode plate. After drying, inserted the electrode plate into the reaction tank and connected it to the DC stabilized power supply to ensure that the connection is in good contact. Then turned on the power and adjusted the range. Adjusted the current to the preset value. After the reaction was over, turned off the power and used a pipette to take the clear liquid to determine the  $COD_{er}$  value. The steps

of the multiphase Fenton experiment were as follows. First of all, took 200 ml of electro-flocculated effluent in a beaker. Added catalyst and stirred at a constant speed. Then turned on the peristaltic pump and added  $H_2O_2$  to the beaker at a uniform rate. Turned on the timer and used a pipette to aspirate the supernatant after a period of time. Then filtered with 0.22  $\mu m$ organic pinhole filter membrane. Finally, measured the COD value and compared the degradation effect of the multiphase Fenton system. The multiphase Fenton/ultrasound experiment steps were as follows. Took 200 ml of electro-flocculation effluent into the ultrasonic reactor and add catalyst. Then activated the ultrasound device. Turned on the peristaltic pump and added H<sub>2</sub>O<sub>2</sub> to the ultrasonic reactor at a uniform rate. Then turned on the timer and used the pipette to suck up the liquid after a period of time. Filtered with 0.22 µm organic pinhole filter membrane. Finally, measured COD<sub>ar</sub> value and compared the degradation effect of multiphase Fenton/ultrasonic system.

The COD<sub>cr</sub> value was determined by the rapid digestion method. The concentration of copper ions was determined by flame-atomic absorption spectrophotometry, and the dissolution of copper ions was analyzed.

#### **Results and Discussion**

#### **Electric Flocculation Pretreatment**

In this study, electro-flocculation was used to pretreat cutting fluid wastewater. Anode aluminumcathode 316 stainless steel was used as the electrode plate material. The effects of current density, plate spacing, reaction time and initial pH on the effect of demulsification pretreatment were studied. Taking the above factors as the factors of the orthogonal experiment and the COD<sub>cr</sub> removal efficiency as the experimental evaluation standard, the  $L_{16}$  (3<sup>4</sup>) orthogonal experiment with 3 levels and 4 factors was carried out. The best experimental parameters were obtained: the current density was 20 mA/cm<sup>2</sup>; the plate spacing was 4 cm; the reaction time was 70 min; and the initial pH was 8. Under these conditions, the COD<sub>cr</sub> removal efficiency could reach 97.4%. When electrocoagulation was used to treat high-concentration cutting fluid wastewater, the effects of various factors on the removal efficiency of COD<sub>er</sub> were as follows: current density>plate spacing>pH>reaction time. In the following experiment, the wastewater was pretreated by electro-flocculation under optimal conditions.

# Effects of Different Preparation Methods and Supports on Catalyst Activity and COD<sub>cr</sub> Degradation Efficiency

Under the condition of unadjusted temperature, light and initial pH value, 1 g/L catalysts prepared

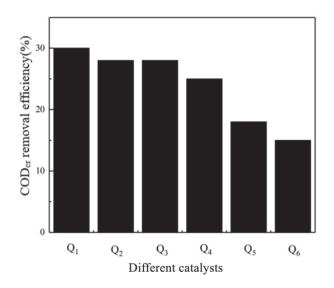


Fig. 1. Degradation of  $\mathrm{COD}_{\mathrm{cr}}$  over catalysts prepared with different supports.

 $(Q_1:CuO/CeO_2 \text{ catalyst prepared by the deposition precipitation method; Q_2:CuO/CeO_2 \text{ catalyst prepared by the co-precipitation method; Q_3:CuO/Al_2O_3 \text{ catalysts prepared by the deposition precipitation method; Q_4:CuO/Al_2O_3 \text{ catalysts prepared by the co-precipitation method.} Q_5:CuO/activated carbon catalysts prepared by the deposition precipitation method; Q_6: CuO/activated carbon catalysts prepared by the impregnation method.)$ 

with different supports and different methods were added with CuO loading amount of 5% respectively. The dosage of  $H_2O_2$  was 0.3 mol/L. The reaction time was 120 min. The effect of the catalyst on the degradation of COD<sub>er</sub> was studied, and the experimental results were shown in Fig. 1. It could be seen from Fig. 1

Table 1. Results of BET characterization of different catalysts.

that, in general, the six supported catalysts had a certain effect on the removal efficiency of COD<sub>cr</sub>, but they were generally not high. From the removal efficiency of COD<sub>cr</sub>, it could be concluded that the removal ability of the supported catalyst was:  $Q_1 > Q_2 > Q_3 > Q_4 > Q_5 > Q_6$ . The catalyst with  $CeO_2$  as the carrier  $(Q_1, Q_2)$  had significantly better degradation effect on COD<sub>cr</sub> than that with Al<sub>2</sub>O<sub>2</sub> (Q<sub>2</sub>, Q<sub>4</sub>) and activated carbon (Q<sub>5</sub>, Q<sub>6</sub>) as the carrier, while the catalyst with activated carbon as carrier COD, had the worst degradation effect. According to the analysis of the preparation method, it could be found that the catalyst prepared by the deposition precipitation method was better than the immersion method  $(Q_1>Q_2, Q_3>Q_4, Q_5>Q_6)$ .But the difference was not very large. The removal efficiency of  $COD_{r}$  differed by more than  $2\% \sim 3\%$ .

After comprehensive consideration, the catalyst  $CuO/CeO_2$  (Q<sub>1</sub>) prepared by the deposition precipitation method with  $CeO_2$  as the carrier had the highest removal efficiency of  $COD_{cr}$  and the best degradation effect, which could reach 30%. In order to study the reasons for the difference in degradation effects of catalysts prepared by different methods and different supports, a series of characterizations were carried out on the catalysts.

Through BET characterization analysis, the specific surface area and pore volume of the catalyst could be measured. According to the results, the relationship between the specific surface area and pore volume and the degradation effect of  $COD_{cr}$  could be inferred. The characterization results of BET were shown in Table 1 and Table 2.

It could be seen from Table 1. that the specific surface area of the CuO/CeO<sub>2</sub> catalyst with CeO<sub>2</sub> as the carrier was the smallest, about 120 m<sup>2</sup>/g $\sim$ 150 m<sup>2</sup>/g.

Comula	Specific surface area	Pore volume	Pore size	
Sample	(m²/g)	(cm <sup>3</sup> /g)	(nm)	
CuO/CeO <sub>2</sub> (Q <sub>1</sub> )	150	0.18	4.40	
CuO/CeO <sub>2</sub> (Q <sub>2</sub> )	120	0.10	2.54	
CuO/Al <sub>2</sub> O <sub>3</sub> (Q <sub>3</sub> )	320	0.22	2.66	
CuO/Al <sub>2</sub> O <sub>3</sub> (Q <sub>4</sub> )	201	0.31	4.99	
CuO/Activated carbon $(Q_s)$	507	0.22	2.70	
CuO/Activated carbon (Q <sub>6</sub> )	498	0.23	2.44	

Table 2. BET characterization of CuO/CeO, and CeO,

Comula	Specific surface area	Pore volume	Pore size	
Sample	(m²/g)	(cm <sup>3</sup> /g)	(nm)	
CeO <sub>2</sub>	161	0.23	5.10	
CuO/CeO <sub>2</sub>	150	0.18	4.40	

The specific surface area of the CuO/Al<sub>2</sub>O<sub>3</sub> catalyst with Al<sub>2</sub>O<sub>2</sub> as the carrier was between 200 m<sup>2</sup>/g $\sim$ 300 m<sup>2</sup>/g. CuO/activated carbon catalyst with activated carbon as the carrier had the largest specific surface area, about 500 m<sup>2</sup>/g. After comparing the overall results in Table 1 with the results in Fig. 1, it could be found that the CuO/CeO<sub>2</sub> catalyst with CeO<sub>2</sub> as the carrier had the smallest specific surface area, but the degradation effect of COD, was the best and the removal efficiency was high. The CuO/activated carbon catalyst with activated carbon as the carrier had the largest specific surface area, but the removal efficiency of COD<sub>cr</sub> was low and the degradation effect was the worst. It was not that the larger the specific surface area, the better the degradation effect of the catalyst on COD<sub>cr</sub>. In other words, the specific surface area could not be the only factor that determines the degradation efficiency of the catalyst, which was consistent with the research results of Liu [29] and others.

From the above analysis results, it could be seen that the structure of the catalyst only provided a platform. The excellent performance of the catalyst was mainly determined by the interaction between the active components and the carrier, rather than physical factors such as specific surface area.

Table 2 was a separate comparison of the catalyst  $CuO/CeO_2$  and the carrier  $CeO_2$ . It could be seen from the results that after loading CuO, the specific surface area and pore volume of the carrier decreased. This showed that the enhancement of the removal efficiency of  $COD_{cr}$  by the catalyst  $CuO/CeO_2$  was not caused by the change of specific surface area and pore volume after loading. It further verified the viewpoints mentioned in the above analysis that the catalytic performance of

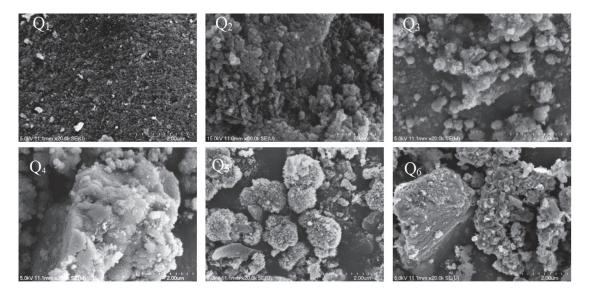
the catalyst was mainly determined by the interaction between the active components and the carrier, and the specific surface area and pore volume were not the decisive factors. In addition, it could be seen from Table 2. that the comparative surface area and pore volume were affected during the loading process, so appropriate loading conditions should be selected during loading to prepare the optimal supported catalyst.

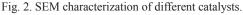
In this experiment, scouldning electron microscope was used to perform SEM scouldning characterization of 6 kinds of catalysts. The effect on COD<sub>er</sub> removal efficiency was verified according to the results. The experimental results were shown in Fig. 2. Detection conditions: acceleration voltage was 20 KV; working distance was 10 mm; magnification was 2000 times.

According to Fig. 2, it could be seen that the catalyst  $CuO/CeO_2$  ( $Q_1$  and  $Q_2$ ) with  $CeO_2$  as the carrier had a relatively uniform distribution of oxides on its surface, small oxide particle size, high regularity, and loose structure. The catalyst CuO/Al<sub>2</sub>O<sub>3</sub> ( $Q_3$  and  $Q_4$ ) supported by Al<sub>2</sub>O<sub>3</sub> and the catalyst CuO/activated carbon ( $Q_5$  and  $Q_6$ ) supported by activated carbon had larger surface oxide particles, uneven dispersion and irregular shapes.

Combining the results of Fig. 2 and Fig. 1, it could be seen that the CuO was uniformly dispersed and had a relatively regular shape, which was more conducive to the activity of the catalyst and increased the effective contact area between the catalyst and the pollutants. Taken together, the catalyst CuO/CeO<sub>2</sub> had a good surface morphology and could better catalyze and degrade COD<sub>cr</sub> in wastewater.

The crystal structure and phase composition could be detected by X-ray diffraction. In this experiment, the XRD method was used to detect and characterize





 $(Q_1:CuO/CeO_2 \text{ catalyst prepared by the deposition precipitation method; Q_2:CuO/CeO_2 \text{ catalyst prepared by the co-precipitation method; Q_3:CuO/Al_2O_3 \text{ catalysts prepared by the deposition precipitation method; Q_4:CuO/Al_2O_3 \text{ catalysts prepared by the co-precipitation method; Q_6:CuO/activated carbon catalysts prepared by the deposition precipitation method; Q_6:CuO/activated carbon catalysts prepared by the impregnation method.)$ 

the six catalysts. The experiment was carried out on the X'pert Pro X-ray diffractometer produced by PANalytical Corporation in the Netherlands. Detection parameters: X-ray adopts Cu Ka; target voltage was 40 kV; target current was 40 mA; diffraction angle was scanned between 2 Theta 10° and 80°. The test result was shown in Fig. 3.

According to Fig. 3, it could be seen that the characteristic peaks of the X-ray diffraction patterns of the six catalysts were relatively clear. It could be seen from the diagram (a) in Fig. 3 that the catalyst  $CuO/CeO_2$  (Q<sub>1</sub> and Q<sub>2</sub>) prepared by different methods with CeO<sub>2</sub> as the carrier both had the main phase of CeO<sub>2</sub> in its reduced and oxidized states. The characteristic peaks of CuO could not be clearly observed in the XRD pattern, which indicated that the active component of the catalyst CuO was distributed more uniformly on the surface of the carrier CeO<sub>2</sub>. It could be seen from the diagram (b) in Fig. 3 that the catalyst CuO/Al<sub>2</sub>O<sub>2</sub> (Q<sub>2</sub> and Q<sub>4</sub>) prepared by different methods with Al<sub>2</sub>O<sub>3</sub> as the carrier had a relatively sharp characteristic diffraction peak. This might be because during the loading process, a certain part of the load was uneven, and some CuO aggregated. But as a whole, it could be seen that the main phase detected in the

figure was Al<sub>2</sub>O<sub>3</sub>, indicating that the main oxidation state and reduction state were still Al<sub>2</sub>O<sub>3</sub>. It could be seen from the diagram (c) in Fig. 3 that the catalyst CuO/activated carbon ( $Q_5$  and  $Q_6$ ) prepared by different methods with activated carbon as the carrier,  $Q_5$  and  $Q_6$ had extremely sharp characteristic peaks. This might be because there were still some impurities that had not been removed during the catalyst calcination process. It could also be seen from the figure that there were many CuO diffraction peaks, which indicated that there were a lot of CuO diffraction peaks in the catalyst. The free CuO crystal phase exists, or a large amount of CuO was not loaded on the activated carbon. For the six catalysts, no new characteristic diffraction peaks appeared in the XRD spectra, which indicated that no new phases were formed during the preparation of the catalysts. Based on Fig. 1, Fig. 2, Fig. 3 and Table 1, the catalyst CuO/CeO<sub>2</sub> (Q<sub>1</sub>) prepared by the deposition precipitation method had good degradation efficiency, high specific surface area, regular structure and uniform active components (CuO) distribution. Therefore, a self-made CeO<sub>2</sub> supported catalyst CuO/CeO<sub>2</sub> was used as the catalyst in the heterogeneous Fenton experiment.

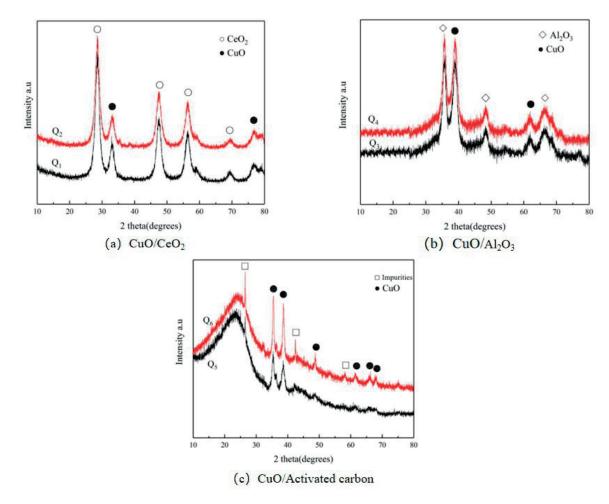


Fig. 3. XRD characterization of different catalysts.

# Stability of the CuO/CeO<sub>2</sub> Catalyst

The effect of electro-flocculation-multiphase Fenton/ ultrasonic system in synergistic degradation of cutting fluid wastewater produced in actual production of a precision instrument processing factory in Shenzhen was experimentally studied. By comparing the SEM results, BET results, XRD results and COD<sub>er</sub> removal efficiency of the catalysts prepared by different supports and different methods, it was determined that the CuO/CeO<sub>2</sub> catalyst prepared by the deposition precipitation method with CeO<sub>2</sub> as the support was used as the supported catalyst in the experiment. The recovery and reuse of the catalyst CuO/CeO2 and the dissolution rate of copper were investigated. It was proved that the dissolution rate of copper was extremely low after repeated recycling and reuse, and there was still a high COD<sub>er</sub> removal efficiency and good stability. By studying the removal effect of different systems on cutting fluid wastewater, it was found that the multiphase Fenton/ultrasonic system had a better COD<sub>cr</sub> removal efficiency than the single ultrasonic system and the multiphase Fenton system. Then, by studying the influence of the experimental conditions of the multiphase Fenton/ultrasonic system, it was found that the best experimental conditions were that the initial pH value was 8; the initial temperature was room temperature (25°C); the H<sub>2</sub>O<sub>2</sub> dosing method was uniform dosing; the H2O2 dosing amount was 0.5 mol/L; the catalyst dosing amount was 1.6 g/L; the reaction time was 180 min and the ultrasonic frequency was 800 KHz. Under the best experimental conditions, the removal efficiency of COD<sub>cr</sub> from cutting fluid wastewater could reach 65%. Using electroflocculation-multiphase Fenton/ultrasonic system to treat high-concentration cutting fluid wastewater, the final COD<sub>cr</sub> removal efficiency could reach 99.09%, and the treatment effect was better.

According to the results in Table 3, in the first 60 min, the dissolution rate of copper ions in the catalyst  $CuO/CeO_2$  was the fastest, and the dissolution ratio of  $Cu^{2+}$  was close to 1%. With the increase of time, the amount of dissolution of copper ions continued to increase, but the dissolution rate gradually decreased.

The repeated utilization of the catalyst was also an important manifestation of the stability of the catalyst. This experiment studied the changes in catalytic performance of the catalyst CuO/CeO<sub>2</sub> (prepared with 7% CuO content, calcination temperature of 400°C, and calcination time of 3 h) after zero, one, two, three, four and five times of recovery. The experimental condition was that the dosage of catalyst CuO/CeO<sub>2</sub> was 1 g/L and the dosage of hydrogen peroxide was 0.3 mol/L. The experimental results were shown in Table 4.

It could be seen from Table 4. that the main loss of the catalyst was concentrated in the first time, with a loss of about 3%. And then as the number of recycling increased, the amount of recycling was basically the same, and the loss was getting smaller and smaller. After five times of recycling, the recovery rate was still 95%, which showed that the stability of the catalyst was better.

It could be seen from the above results that the loss rate was still very low after multiple recovery, but the catalytic activity of the catalyst  $CuO/CeO_2$  after recovery and reuse needed to be further determined. Therefore, the degradation experiment was performed on each recovered catalyst. The experimental results were shown in Fig. 4 and Fig. 5.

According to Fig. 4 and Fig. 5, it could be seen that as the number of recovery increased, the removal efficiency of  $\text{COD}_{er}$  decreased to a certain extent. In the first 30 min of the reaction, the removal efficiency of  $\text{COD}_{er}$  did not change much, and it could be about 10%. With the increase of time, the difference in the degradation effect of the catalyst with different recycling times became more and more obvious. After the reaction time reached 120 min, the  $\text{COD}_{er}$  removal efficiency basically reached a stable state. Even if the reaction continued for 30 min, it did not increase

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Reaction time (min)	0	60	120	180	240
Dissolved amount of copper ion (mg)	0	0.921	1.154	1.183	1.212
Cu <sup>2+</sup> dissolution ratio (%)	0	0.98	1.23	1.26	1.29

Table 4.	Catalyst	recovery	and	reuse.

Recycling times	0	1	2	3	4	5
Recycling amount (g)	0.1	0.097	0.096	0.096	0.096	0.095
Recovery rate (%)	100	97	96	96	96	95

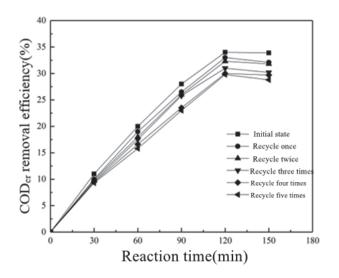


Fig. 4. Effect of recovery and reuse times of catalyst at different reaction times on COD<sub>er</sub> removal efficiency.

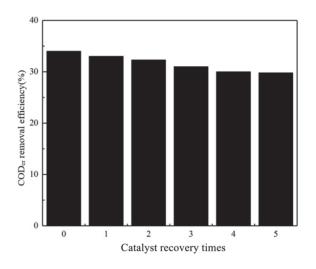


Fig. 5. Effect of catalyst recovery and reuse times on  $\text{COD}_{cr}$  removal efficiency when reaction time was 120 min.

the removal efficiency, indicating the degradation ability reached the limit. In the experiment, the catalyst was recovered 5 times in total. The removal efficiency of  $COD_{cr}$  by the catalyst after each recovery was 33%, 32.3%, 31%, 30%, 29.8%, and 34% of the initial use.

In general, it could be seen that there was a 4.2% difference in the degradation rate before and after the recovery. The degradation rate decreased less, and the downward trend became slower. This might be because as the number of recovery increased, the amount of the catalyst decreased more and more slowly, and the COD<sub>cr</sub> removal efficiency also showed the same trend.

In summary, it could be further confirmed that the catalyst  $CuO/CeO_2$  had good stability, high catalytic activity, and still had high catalytic degradation performance after multiple recycling and reuse.

# Effects of Different Systems on COD<sub>cr</sub> Removal Efficiency

In order to study the degradation effect of COD<sub>cr</sub> by the heterogeneous Fenton system composed of catalyst CuO/CeO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>, a comparative experiment on the degradation effect of different reaction systems on COD<sub>cr</sub> was carried out. The experimental conditions were controlled as follows: reaction time was 300 min; catalyst dosage was 2 g/L; H<sub>2</sub>O<sub>2</sub> dosage was 0.6 mol/L; H<sub>2</sub>O<sub>2</sub> dosage method was uniform dosage; initial pH was 8; initial temperature was room temperature (25°C); and stirring speed was 400 r/min. The effect of different systems on the removal efficiency of COD<sub>cr</sub> from cutting fluid wastewater was studied and the experimental results were shown in Fig 6a). In order to study the COD<sub>cr</sub> degradation effect of the multiphase Fenton/ultrasonic system, a comparative experiment of the degradation effects of different reaction systems on COD<sub>er</sub> was carried out first. The experimental conditions were controlled as follows: reaction time was 180 min; catalyst dosage was 1.6 g/L; H<sub>2</sub>O<sub>2</sub> dosage was 0.5 mol/L; H<sub>2</sub>O<sub>2</sub> dosage was uniform speed; initial pH was 8; initial temperature was room temperature (25°C) and the ultrasonic frequency was 800 KHz. The effect of different systems on the removal efficiency of COD<sub>er</sub> from cutting fluid wastewater was studied and the experimental results were shown in Fig. 6b).

According to Fig. 6a), it could be seen that the three reaction systems had a certain degradation effect on cutting fluid wastewater COD, and the order of degradation effect was: CuO/CeO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>>CeO<sub>2</sub>/  $H_2O_2>H_2O_2$ . When the reaction system contains only H<sub>2</sub>O<sub>2</sub>, the strong oxidizing property of H<sub>2</sub>O<sub>2</sub> could have a certain degradation effect on COD<sub>er</sub>, but the removal effect was poor and the process was slow. After the reaction was carried out for 300 min, COD, was only about 10% removal efficiency. In the CeO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> system, because CeO, itself had a certain adsorption capacity, compared to the system containing only H<sub>2</sub>O<sub>2</sub>, the COD<sub>cr</sub> removal efficiency was slightly improved, reaching about 17%. In the CuO/CeO2/H2O2 system, the removal efficiency of COD<sub>cr</sub> was significantly better than that of the other two systems. It could reach about 50% after 240 min, which increased the removal efficiency by 30%. This is because, compared with the other two systems, the CuO/CeO, catalyst contained in this system had good catalytic activity, which could increase the utilization rate of H2O2, and catalyze it to produce a large amount of OH functional groups in a short time, and then improve COD<sub>ar</sub> removal efficiency. According to Fig. 6b), it could be seen that the three systems CuO/CeO2-US-H2O2 (multiphase Fenton/ultrasonic system), CuO/CeO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub> (multiphase Fenton system) and US-H<sub>2</sub>O<sub>2</sub> all have some degradation effects on COD<sub>er</sub>. The US-H<sub>2</sub>O<sub>2</sub> system had the lowest removal efficiency of COD<sub>cr</sub>, only about 10%, while the multiphase Fenton/ultrasonic system had the best removal efficiency that the COD<sub>cr</sub> removal efficiency

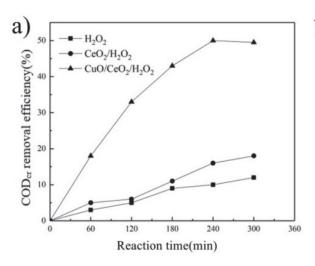


Fig. 6. Effects of different systems on COD<sub>er</sub> removal efficiency.

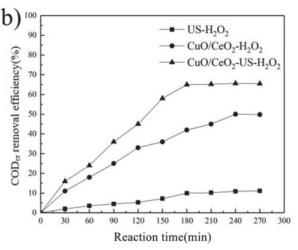
could reach 65%. At the same time, it could be seen that, compared with a single multiphase Fenton system, after adding ultrasound, the removal efficiency of  $COD_{cr}$  in each time period had been significantly improved. It could be seen that in the process of degrading cutting fluid wastewater, the combination of multiphase Fenton technology and ultrasound technology was not just a simple superposition of the two technologies, but also had a synergistic effect in the constructed multiphase Fenton/ultrasound system. This synergy was the key factor for the removal of pollutants in the multiphase Fenton/ultrasonic system.

The synergy in the multiphase Fenton/ultrasound system was mainly reflected in two aspects. On the one hand, ultrasound could enhance the dispersion of the catalyst in the system, playing a role in mechanical stirring. It avoided the deposition of the catalyst and increased the effective contact area between the catalyst and pollutants. So it promoted the efficient use of active substances, and accelerated the solid-liquid phase transfer rate and the conversion rate between ions. On the other hand, in the heterogeneous Fenton system, the catalyst CuO/CeO<sub>2</sub> itself had a certain adsorption capacity, which could adsorb pollutants to the surface. The active material CuO on the catalyst reacts with H<sub>2</sub>O<sub>2</sub> to produced a large amount of OH, which then degraded organic matter. After the addition of ultrasound, the pore structure of the catalyst CuO/ CeO<sub>2</sub> improved the cavitation effect. The local high temperature and high pressure were generated. Then the following reaction occured, as shown in equations  $(1) \sim (3)$ :

$$Ultrasound + H_2O \rightarrow OH + H$$
 (1)

$$H + H_2O_2 \rightarrow OH + H_2O$$
(2)

$$H \rightarrow 1/2 H_2 \tag{3}$$



It could be seen from the above reaction that the addition of ultrasound could not only produce  $\cdot$ OH with strong oxidizing ability to oxidize and degrade pollutants, but also produce  $\cdot$ H which could react with  $H_2O_2$  to generate more  $\cdot$ OH, improving the oxidative degradation ability of the reaction system.

In summary, the heterogeneous Fenton system composed of the catalyst CuO/CeO<sub>2</sub> catalyzed by H<sub>2</sub>O<sub>2</sub> had the best effect in the oxidative degradation of COD<sub>cr</sub> in wastewater. The oxidative degradation capacity of CuO/CeO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> system was significantly higher than that of H<sub>2</sub>O<sub>2</sub> system and CeO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> system alone, and the degradation efficiency also had huge advantages. These results all indicated that the catalyst CuO/CeO, in the CuO/CeO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> system had very high catalytic activity, so the heterogeneous Fenton system composed of the catalyst CuO/CeO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> was selected to treat the cutting fluid wastewater. The degradation effect of the multiphase Fenton or ultrasonic system alone was poor, while the multiphase Fenton/ultrasonic system had a good COD<sub>er</sub> removal efficiency. Therefore, this experiment would further study the optimization of the influencing factors of the system.

# Effects of Ultrasonic Frequency, Reaction Time, Catalyst Dosage, and H<sub>2</sub>O<sub>2</sub> Dosage on COD<sub>cr</sub> Removal Efficiency in the Multiphase Fenton/Ultrasonic System

According to Fig. 7a), as the ultrasonic frequency increased, the removal efficiency of  $\text{COD}_{cr}$  first increased and then decreased. At 800 KHz, the removal efficiency of  $\text{COD}_{cr}$  was the highest, which could reach 65%. The reason for the above changes was that, as the ultrasonic frequency increased, the content of OH in the water gradually increased, partly from the reaction of the catalyst CuO/CeO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>, and the other part from the cavitation effect. The greater the ultrasonic frequency, the greater the ultrasonic power required,

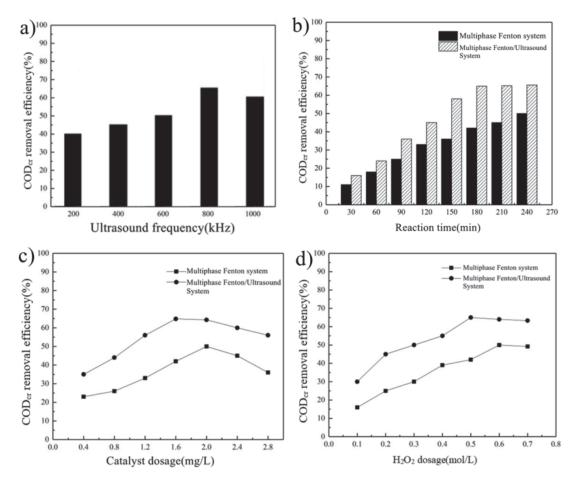


Fig. 7. Effect of ultrasonic frequency a), reaction time b), catalyst dosage c) and H<sub>2</sub>O<sub>2</sub> dosage d) on COD<sub>cr</sub> removal efficiency.

and the stronger the cavitation effect. Then the more OH was produced and the removal efficiency of  $COD_{er}$  would gradually increase. After the ultrasonic frequency reached 800 KHz, excessive OH was produced in a short time, and then an accumulation reaction occurred, resulting in a decrease in the effective OH content and the removal efficiency of  $COD_{er}$ . All in all, according to the experimental results, the final choice was to conduct the multiphase Fenton/ultrasonic experiment under the condition of an ultrasonic frequency of 800 KHz.

According to Fig. 7b), it could be seen that the removal efficiency of COD<sub>cr</sub> by the multiphase Fenton/ ultrasonic system was higher than that of the single multiphase Fenton system at all time points. In the multiphase Fenton/ultrasonic system, the COD<sub>ar</sub> removal efficiency gradually increased with the increase of time. The COD<sub>cr</sub> removal efficiency reached the maximum at 180 min, reaching 65%. And then with the increase of time, the COD<sub>cr</sub> removal efficiency did not change significantly. In addition, it could be seen that the optimal reaction time of the heterogeneous Fenton/ultrasonic system was 180 min, while the optimal reaction time of the heterogeneous Fenton system was 240 min. Therefore, the multiphase Fenton/ ultrasonic system could achieve a better removal effect in a shorter time. The reason for the above results was that as time increased, the generated OH gradually

increased, and then COD<sub>er</sub> removal efficiency gradually increased. When the time exceeded 180 min, since the oxidatively degradable organic matter in the water had reacted completely, even if there was still OH produced, the COD<sub>er</sub> removal efficiency remained unchanged. In addition, after adding ultrasound to the multiphase Fenton system, ultrasound could cause cavitation, which could produce more OH at the same time, so the earlier COD<sub>er</sub> removal efficiency were higher. However, the removal effect in the later stage was better than that of a separate multiphase Fenton system. This was because the thermal effect induced by ultrasound produced high-temperature pyrolysis and transient supercritical water. It could remove some refractory organic matter, so the final COD<sub>er</sub> removal efficiency was higher. All in all, according to the experimental results, it was finally determined that the reaction time of the multiphase Fenton/ultrasonic system to treat wastewater was 180 min.

According to Fig. 7c), it could be seen that with the increase of the catalyst  $CuO/CeO_2$  dosage, the  $COD_{cr}$  removal efficiency showed a trend of first rising and then falling. In the heterogeneous Fenton/ultrasonic system, when the catalyst dosage was 1.6 g/L, the  $COD_{cr}$  removal efficiency was the highest, which could be about 65%. In the heterogeneous Fenton system, the catalyst dosage was more. The best removal efficiency

could reach at 2.0 g/L. In addition, when the catalyst dosage was the same, the heterogeneous Fenton/ ultrasonic system had a better removal effect on COD<sub>cr</sub>. The reasons for the above results could be explained as follows. When the catalyst CuO/CeO<sub>2</sub> dosage was less than 1.6 g/L, in the same time, the catalyst dosage was proportional to the production of OH. And when the catalyst CuO/CeO, dosage was greater than 1.6 g/L, due to the excessive production of OH in a short time, an accumulation reaction occured. It caused a part of H<sub>2</sub>O<sub>2</sub> to be wasted and the COD<sub>er</sub> removal efficiency to increase first and then decrease, which was in line with the discussion of Yin [30]. When the dosage of the catalyst was the same, the mechanical action of ultrasound could make the catalyst evenly distributed in the wastewater, increasing the central site of the active center and making the catalyst CuO/CeO<sub>2</sub> have a higher utilization rate and better catalytic activity. Therefore, the removal efficiency of COD<sub>cr</sub> by the multiphase Fenton/ultrasonic system was better than that of the multiphase Fenton system. Based on comprehensive considerations, it was finally determined that the dosage of the catalyst CuO/CeO, was 1.6 g/L when the multiphase Fenton/ultrasonic system was used to treat wastewater.

According to Fig. 7d), it could be seen that as the dosage of H<sub>2</sub>O<sub>2</sub> increased from 0.1 mol/L to 0.5 mol/L, the removal efficiency of COD<sub>cr</sub> increased from 30% to 65%. Then, as the dosage of H<sub>2</sub>O<sub>2</sub> continued to increase, COD<sub>er</sub> removal efficiency had a slower downward trend. The reason for the above results could be explained as follows. When the dosage of H<sub>2</sub>O<sub>2</sub> was small, as the dosage of H<sub>2</sub>O<sub>2</sub> increased, the more hydroxyl radicals were produced, the higher the removal efficiency of COD<sub>er</sub>. And when the dosage of H<sub>2</sub>O<sub>2</sub> was too much, side reactions would occur due to the production of too many hydroxyl radicals, which reduced the removal efficiency of COD<sub>cr</sub>. It could also be seen from Fig. 7d) that compared to the multiphase Fenton system, the multiphase Fenton/ultrasonic system had a higher removal efficiency of COD<sub>cr</sub>. This was because the addition of ultrasound would produce a cavitation effect, forming high temperature and high pressure locally, then producing OH. And H would also be produced during this process. It could react with H<sub>2</sub>O<sub>2</sub> to produce more  $\cdot$ OH, leading to a reduction in H<sub>2</sub>O<sub>2</sub> dosage. But the removal efficiency of the multiphase Fenton/ultrasonic system was higher. Therefore, it was finally determined that when the multiphase Fenton/ ultrasonic system was used to treat wastewater, the dosage of H<sub>2</sub>O<sub>2</sub> was 0.5 mol/L.

# Effects of H<sub>2</sub>O<sub>2</sub> Dosing Method, Initial Temperature and Initial pH on COD<sub>cr</sub> Removal Efficiency in the Multiphase Fenton/Ultrasonic System

According to Fig. 8, it could be seen that before 105 min, the removal efficiency of  $COD_{er}$  was higher if H<sub>2</sub>O<sub>2</sub> was added at one time; while after 105 min,

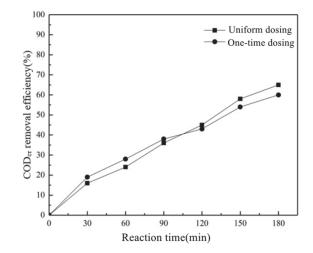


Fig. 8. Effect of  $H_2O_2$  dosing method on  $COD_{er}$  removal efficiency.

the removal efficiency of COD<sub>cr</sub> was higher if H<sub>2</sub>O<sub>2</sub> was added at a constant rate. Although the two dosing methods had different effects on the removal efficiency of COD<sub>cr</sub>, at 180 min, the removal efficiency of COD<sub>cr</sub> was 65% after H<sub>2</sub>O<sub>2</sub> was added at a constant speed. And the removal efficiency of COD<sub>cr</sub> was 60% after H<sub>2</sub>O<sub>2</sub> was added at a time. The reason for the above-mentioned changes could be explained as follows. Dosing too much  $H_2O_2$  at one time caused excessive OH to be produced in a short time and accumulation reaction to occur, resulting in a certain amount of OH waste, which made the removal efficiency of COD<sub>cr</sub> high in the early stage and low in the later stage. The uniform addition of  $H_2O_2$ avoided the occurrence of side reactions, and could also keep the entire system in a state of oxygen saturation, which was conducive to the formation of cavitation effects. It could be seen from Fig. 9 that under the conditions of uniform dosing, the removal efficiency

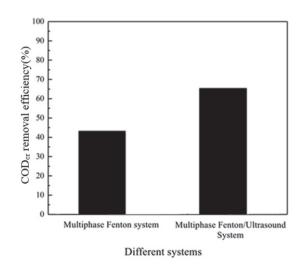


Fig. 9. Effects of different systems of uniform feeding on  $\text{COD}_{cr}$  removal efficiency.

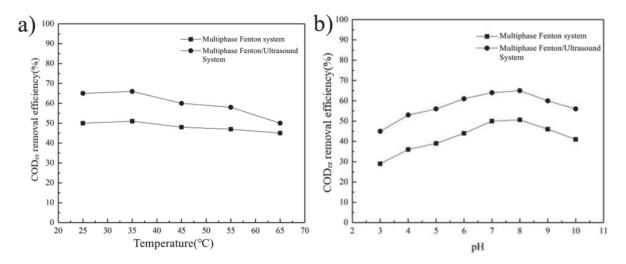


Fig. 10. Effect of initial temperature a) and initial pH b) on COD<sub>er</sub> removal efficiency.

of  $\text{COD}_{\text{cr}}$  of the multiphase Fenton system was lower than that of the multiphase Fenton/ultrasonic system, and there was a clear difference. This was because the addition of ultrasound created a synergistic effect between multiphase Fenton and ultrasound. It enhanced the ability of oxidative degradation, and removed pollutants in a larger range, thereby increasing the  $\text{COD}_{\text{cr}}$  removal efficiency. In summary, it was finally determined that when the multiphase Fenton/ultrasonic system was used to treat wastewater, the  $\text{H}_2\text{O}_2$  dosing method was uniform dosing.

It could be seen from Fig. 10a) that as the initial temperature increased, the COD<sub>cr</sub> removal efficiency first stabilized and then decreased. When the initial temperature increased from 25°C to 35°C, the COD<sub>or</sub> removal efficiency was maintained at about 65%. As the initial temperature further increased, the COD<sub>er</sub> removal efficiency gradually decreased, and the rate of decrease was faster than that of the multiphase Fenton system. But overall, the multiphase Fenton/ ultrasonic system had a higher removal efficiency of COD<sub>er</sub>. The reason for the above results was that ultrasonic waves converted sound energy into heat energy during transmission. The manifestation was that the cavitation effect caused local high temperature and high pressure. When the initial temperature was not very high and was maintained at 25°C to 35°C, as the reaction progressed, the temperature of the reaction system gradually increased until it was relatively stable, reaching the equilibrium point of the system, and the removal efficiency of COD, was maintained at a stable level. When the initial temperature was too high, the ultrasound itself would further increase the temperature of the reaction system. Too high temperature would lead to instability and decomposition of H<sub>2</sub>O<sub>2</sub>, wasting a part of OH, and weakening the overall oxidative degradation ability, which was manifested as a reduction in the removal efficiency of COD<sub>ar</sub>. Based on comprehensive considerations, it was finally determined that when the multiphase Fenton/ultrasonic system was used to treat wastewater, the initial temperature was not adjusted, and room temperature was sufficient, which could simplify the operation and achieve a better removal effect.

It could be seen from Fig. 10b) that the multiphase Fenton/ultrasonic system was better than the separate multiphase Fenton system in degrading cutting fluid wastewater. The COD<sub>er</sub> removal efficiency of the two systems had the same change trend. With the increase of the initial pH value, the COD<sub>cr</sub> removal efficiency first increased and then decreased. The COD<sub>er</sub> removal efficiency reached the best when the initial pH value was 8, and at this time, the removal efficiency of COD by the multiphase Fenton/ultrasonic system could reach 65%. The reason for the above results could be explained as follows. When the initial pH value was low, the solution was acidic, and the H<sup>+</sup> in the water reacted with CuO to form Cu<sup>2+</sup>, but the main catalytically active substance of the catalyst CuO/CeO<sub>2</sub> was CuO, not Cu<sup>2+</sup>, so the production of OH decreased, which was manifested by the lower removal efficiency of COD<sub>cr</sub>. When the initial pH value was high, the solution was alkaline, and the OH contained in the water reacted with OH<sup>-</sup>, causing a part of OH loss, so the COD<sub>er</sub> removal efficiency was low. In summary, too high and too low initial pH values would have adverse effects. When it was selected as 8, the multiphase Fenton/ultrasonic system had the best effect on wastewater treatment. The pH of the effluent after electrocoagulation was 7.8, so the initial pH value during the experiment was not adjusted.

#### Conclusions

In this study, electro-flocculation-multiphase Fenton/ultrasound system was used to treat cutting fluid organic wastewater. The demulsification pretreatment was carried out by electroflocculation method to alleviate the degradation difficulty of the subsequent treatment process. Under the conditions of 316 stainless steel for the cathode, aluminum plate for the anode, a distance between the plates of 4 cm, an initial pH value of 8, a reaction time of 70 min, and a current density of 20 mA/cm<sup>2</sup>, the COD<sub>cr</sub> removal efficiency of cutting fluid wastewater could reach 97.4%. By comparing the SEM results, BET results, XRD results and COD<sub>ar</sub> removal efficiency of the catalysts prepared by different supports and methods, it was determined that the CuO/CeO<sub>2</sub> catalyst prepared by the deposition precipitation method was used as the supported catalyst in the experiment. It was proved that the dissolution rate of copper was extremely low after repeated recycling and reuse, and there was still a high COD<sub>cr</sub> removal efficiency and good stability. By studying the removal effect of different systems on cutting fluid wastewater, it was found that the multiphase Fenton/ultrasonic system had a better COD<sub>cr</sub> removal efficiency than the individual ultrasonic system and the multiphase Fenton system. Then, by studying the impact factors, it was found that the best experimental conditions were that the initial pH value was 8; the initial temperature was room temperature (25°C); the  $H_2O_2$  dosing method was uniform dosing; the H2O2 dosing amount was 0.5 mol/L; the catalyst dosing amount was 1.6 g/L; the reaction time was 180 min and the ultrasonic frequency was 800 KHz. Under the best experimental conditions, the removal efficiency of COD<sub>er</sub> from cutting fluid wastewater could reach 65%. Using electro-flocculation-multiphase Fenton/ultrasonic system to treat high-concentration cutting fluid wastewater, the final COD<sub>cr</sub> removal efficiency could reach 99.09%. These results show that electroflocculation-multiphase Fenton/ultrasonic system is an effective and environmental friendly method to treat high-concentration cutting fluid wastewater.

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## **Conflict of Interest**

The authors declare no conflict of interest.

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