

Original Research

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

Nana Wu^{1*}, Chenguang Wei¹, Xinyu Zhou¹, Yuying Pi¹, Licheng Zhang¹,
Yusi Wang², Yifei Wei¹

¹School of Municipal and Environmental Engineering, Shenyang Jianzhu University, Shenyang 110168, China

²China Energy Engineering Corporation Limited Liaoning Institute, Shenyang 110179, China

Received: 19 March 2022

Accepted: 20 June 2022

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_{cr} removal efficiency. Afterwards, a multiphase Fenton/ultrasonic system was used for advanced treatment. By comparing the SEM results, BET results, XRD results and COD_{cr} removal efficiency of the catalysts prepared by different supports and methods, CuO/CeO₂ catalyst prepared by the deposition precipitation method was used in this experiment. The dissolution rate of copper in the catalyst CuO/CeO₂ 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_{cr} was 29.8%. It proved that the catalyst CuO/CeO₂ 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_{cr} removal efficiency. This study found that electro-flocculation-multiphase Fenton/ultrasonic system could finally achieve 99.09% COD_{cr} removal efficiency.

Keywords: high concentration cutting fluid wastewater, electro-flocculation, catalyst CuO/CeO₂, multiphase Fenton/ultrasonic system

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 flocs, 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 ($\cdot\text{OH}$) 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_2 , H_2O 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_{cr} 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_2

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 $18\text{ M}\Omega\cdot\text{cm}$. 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 2θ 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_{cr} 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_{cr} 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 $0.22\ \mu\text{m}$ organic pinhole filter membrane. Finally, measured the COD_{cr} 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_2O_2 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 $0.22\ \mu\text{m}$ organic pinhole filter membrane. Finally, measured COD_{cr} value and compared the degradation effect of multiphase Fenton/ultrasonic system.

The COD_{cr} 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 pre-treat cutting fluid wastewater. Anode aluminum-cathode 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_{cr} removal efficiency as the experimental evaluation standard, the $L_{16}(3^4)$ orthogonal experiment with 3 levels and 4 factors was carried out. The best experimental parameters were obtained: the current density was 20 mA/cm^2 ; the plate spacing was 4 cm; the reaction time was 70 min; and the initial pH was 8. Under these conditions, the COD_{cr} 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_{cr} 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_{cr} Degradation Efficiency

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

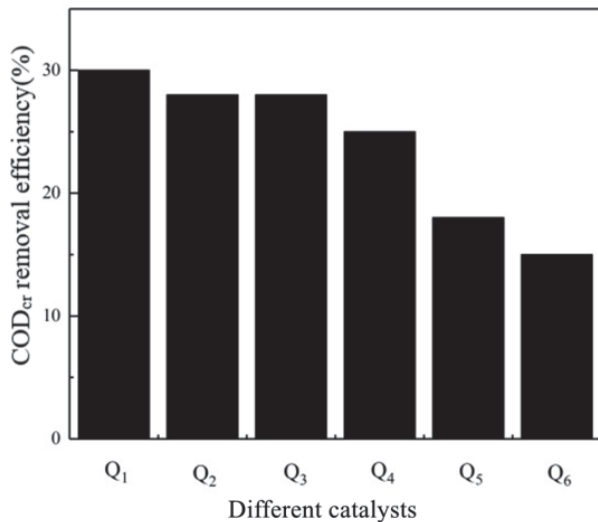


Fig. 1. Degradation of COD_{cr} over catalysts prepared with different supports.

(Q₁:CuO/CeO₂ catalyst prepared by the deposition precipitation method; Q₂:CuO/CeO₂ catalyst prepared by the co-precipitation method; Q₃:CuO/Al₂O₃ catalysts prepared by the deposition precipitation method; Q₄:CuO/Al₂O₃ catalysts prepared by the co-precipitation method. Q₅:CuO/activated carbon catalysts prepared by the deposition precipitation method; Q₆: 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 H₂O₂ was 0.3 mol/L. The reaction time was 120 min. The effect of the catalyst on the degradation of COD_{cr} was studied, and the experimental results were shown in Fig. 1. It could be seen from Fig. 1

that, in general, the six supported catalysts had a certain effect on the removal efficiency of COD_{cr}, but they were generally not high. From the removal efficiency of COD_{cr}, it could be concluded that the removal ability of the supported catalyst was: Q₁>Q₂>Q₃>Q₄>Q₅>Q₆. The catalyst with CeO₂ as the carrier (Q₁, Q₂) had significantly better degradation effect on COD_{cr} than that with Al₂O₃ (Q₃, Q₄) and activated carbon (Q₅, Q₆) as the carrier, while the catalyst with activated carbon as carrier COD_{cr} 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 (Q₁>Q₂, Q₃>Q₄, Q₅>Q₆). But the difference was not very large. The removal efficiency of COD_{cr} differed by more than 2%~3% .

After comprehensive consideration, the catalyst CuO/CeO₂ (Q₁) prepared by the deposition precipitation method with CeO₂ 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/CeO₂ catalyst with CeO₂ as the carrier was the smallest, about 120 m²/g~150 m²/g.

Table 1. Results of BET characterization of different catalysts.

Sample	Specific surface area	Pore volume	Pore size
	(m ² /g)	(cm ³ /g)	(nm)
CuO/CeO ₂ (Q ₁)	150	0.18	4.40
CuO/CeO ₂ (Q ₂)	120	0.10	2.54
CuO/Al ₂ O ₃ (Q ₃)	320	0.22	2.66
CuO/Al ₂ O ₃ (Q ₄)	201	0.31	4.99
CuO/Activated carbon (Q ₅)	507	0.22	2.70
CuO/Activated carbon (Q ₆)	498	0.23	2.44

Table 2. BET characterization of CuO/CeO₂ and CeO₂

Sample	Specific surface area	Pore volume	Pore size
	(m ² /g)	(cm ³ /g)	(nm)
CeO ₂	161	0.23	5.10
CuO/CeO ₂	150	0.18	4.40

The specific surface area of the CuO/Al₂O₃ catalyst with Al₂O₃ as the carrier was between 200 m²/g~300 m²/g. CuO/activated carbon catalyst with activated carbon as the carrier had the largest specific surface area, about 500 m²/g. After comparing the overall results in Table 1 with the results in Fig. 1, it could be found that the CuO/CeO₂ catalyst with CeO₂ as the carrier had the smallest specific surface area, but the degradation effect of COD_{cr} 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_{cr} 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_{cr}. 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/CeO₂ and the carrier CeO₂. 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/CeO₂ 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, scanning electron microscope was used to perform SEM scanning characterization of 6 kinds of catalysts. The effect on COD_{cr} 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/CeO₂ (Q₁ and Q₂) with CeO₂ 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/Al₂O₃ (Q₃ and Q₄) supported by Al₂O₃ and the catalyst CuO/activated carbon (Q₅ and Q₆) 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/CeO₂ had a good surface morphology and could better catalyze and degrade COD_{cr} 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

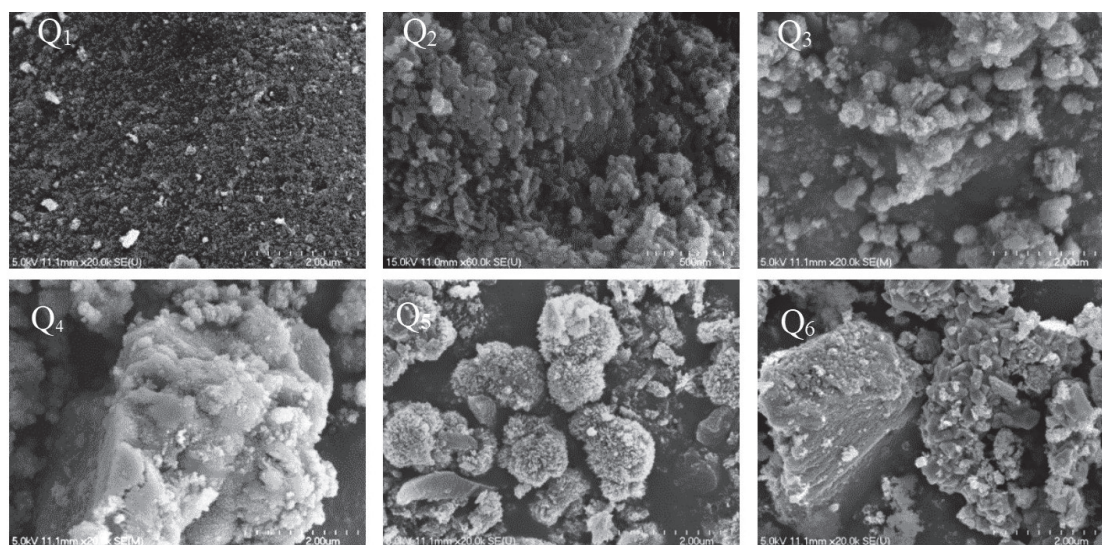


Fig. 2. SEM characterization of different catalysts.

(Q₁:CuO/CeO₂ catalyst prepared by the deposition precipitation method; Q₂:CuO/CeO₂ catalyst prepared by the co-precipitation method; Q₃:CuO/Al₂O₃ catalysts prepared by the deposition precipitation method; Q₄:CuO/Al₂O₃ catalysts prepared by the co-precipitation method. Q₅:CuO/activated carbon catalysts prepared by the deposition precipitation method; Q₆: 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 K α ; 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/CeO₂ (Q₁ and Q₂) prepared by different methods with CeO₂ as the carrier both had the main phase of CeO₂ 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 CeO₂. It could be seen from the diagram (b) in Fig. 3 that the catalyst CuO/Al₂O₃ (Q₃ and Q₄) prepared by different methods with Al₂O₃ 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 Al₂O₃, indicating that the main oxidation state and reduction state were still Al₂O₃. It could be seen from the diagram (c) in Fig. 3 that the catalyst CuO/activated carbon (Q₅ and Q₆) prepared by different methods with activated carbon as the carrier, Q₅ and Q₆ 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/CeO₂ (Q₁) 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 CeO₂ supported catalyst CuO/CeO₂ was used as the catalyst in the heterogeneous Fenton experiment.

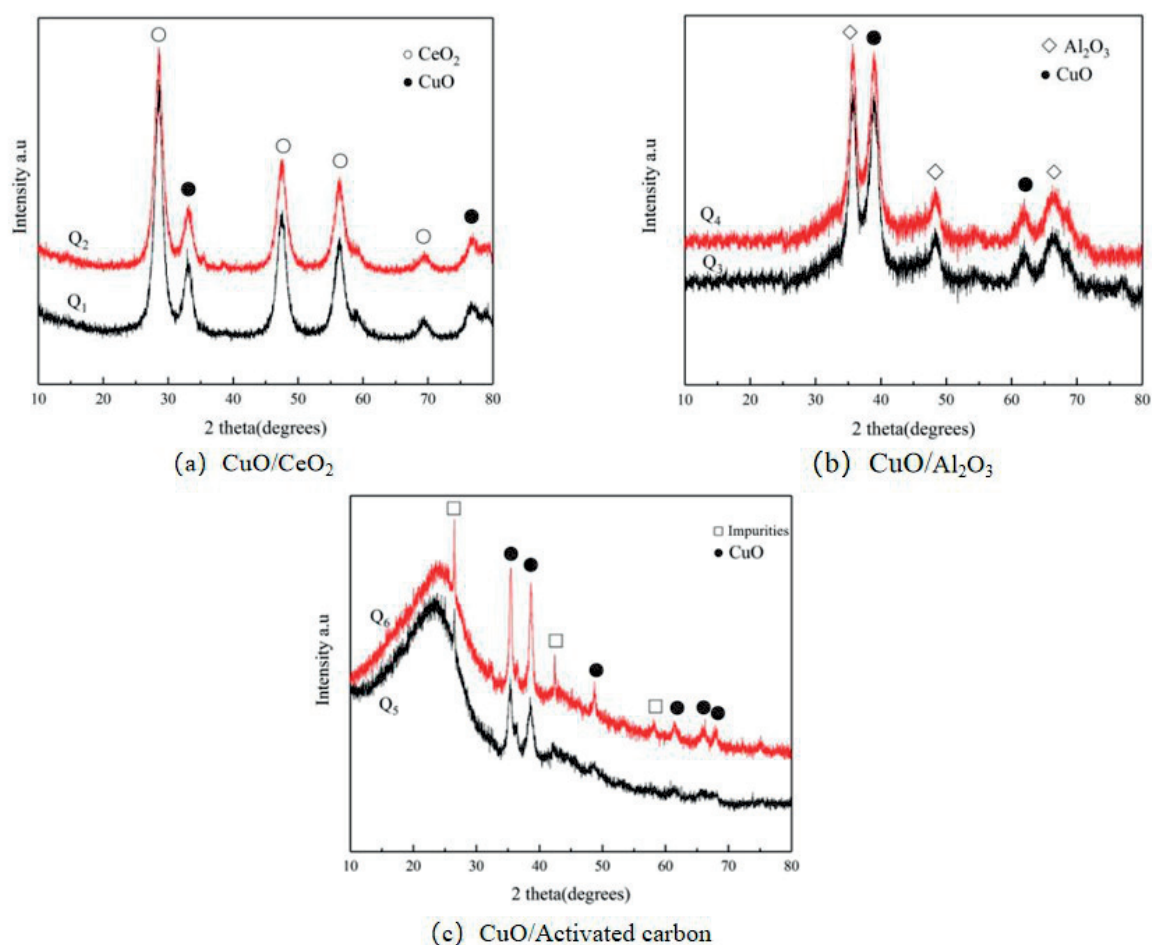


Fig. 3. XRD characterization of different catalysts.

Stability of the CuO/CeO₂ 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_{cr} removal efficiency of the catalysts prepared by different supports and different methods, it was determined that the CuO/CeO₂ catalyst prepared by the deposition precipitation method with CeO₂ 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_{cr} 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_{cr} 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 H₂O₂ 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_{cr} from cutting fluid wastewater could reach 65%. Using electro-flocculation-multiphase Fenton/ultrasonic system to treat high-concentration cutting fluid wastewater, the final COD_{cr} 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/CeO₂ was the fastest, and the dissolution ratio of Cu²⁺ 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.

Table 3. Copper ion dissolution.

Reaction time (min)	0	60	120	180	240
Dissolved amount of copper ion (mg)	0	0.921	1.154	1.183	1.212
Cu ²⁺ 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

When the reaction reached 240 min, the dissolution amount of copper ions was 1.212 mg, which was only 1.29% dissolution ratio. According to the results, it could be seen that the amount of copper dissolved out of the catalyst CuO/CeO₂ after a period of time was very small, and the homogeneous reaction was less, so it had good stability.

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/CeO₂ (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/CeO₂ 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/CeO₂ 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 COD_{cr} decreased to a certain extent. In the first 30 min of the reaction, the removal efficiency of COD_{cr} 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 COD_{cr} removal efficiency basically reached a stable state. Even if the reaction continued for 30 min, it did not increase

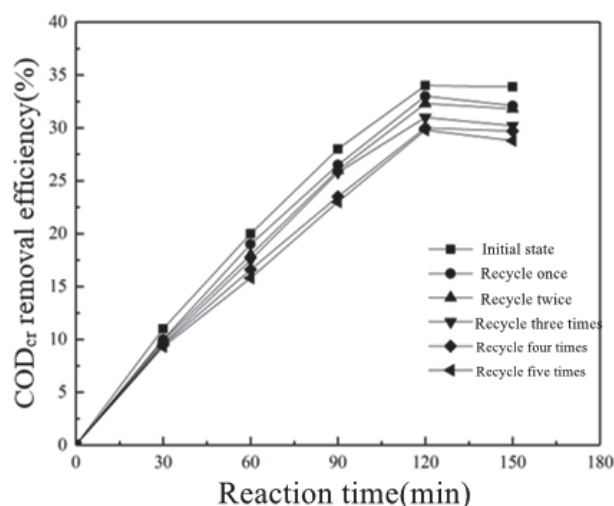


Fig. 4. Effect of recovery and reuse times of catalyst at different reaction times on COD_{cr} removal efficiency.

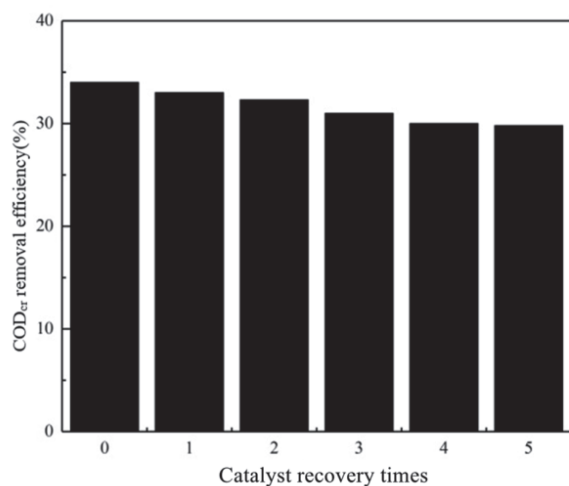


Fig. 5. Effect of catalyst recovery and reuse times on COD_{cr} removal efficiency when reaction time was 120 min.

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_{cr} removal efficiency also showed the same trend.

In summary, it could be further confirmed that the catalyst CuO/CeO₂ had good stability, high catalytic activity, and still had high catalytic degradation performance after multiple recycling and reuse.

Effects of Different Systems on COD_{cr} Removal Efficiency

In order to study the degradation effect of COD_{cr} by the heterogeneous Fenton system composed of catalyst CuO/CeO₂ and H₂O₂, a comparative experiment on the degradation effect of different reaction systems on COD_{cr} was carried out. The experimental conditions were controlled as follows: reaction time was 300 min; catalyst dosage was 2 g/L; H₂O₂ dosage was 0.6 mol/L; H₂O₂ 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_{cr} from cutting fluid wastewater was studied and the experimental results were shown in Fig 6a). In order to study the COD_{cr} degradation effect of the multiphase Fenton/ultrasonic system, a comparative experiment of the degradation effects of different reaction systems on COD_{cr} was carried out first. The experimental conditions were controlled as follows: reaction time was 180 min; catalyst dosage was 1.6 g/L; H₂O₂ dosage was 0.5 mol/L; H₂O₂ 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_{cr} 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_{cr}, and the order of degradation effect was: CuO/CeO₂/H₂O₂>CeO₂/H₂O₂>H₂O₂. When the reaction system contains only H₂O₂, the strong oxidizing property of H₂O₂ could have a certain degradation effect on COD_{cr}, but the removal effect was poor and the process was slow. After the reaction was carried out for 300 min, COD_{cr} was only about 10% removal efficiency. In the CeO₂/H₂O₂ system, because CeO₂ itself had a certain adsorption capacity, compared to the system containing only H₂O₂, the COD_{cr} removal efficiency was slightly improved, reaching about 17%. In the CuO/CeO₂/H₂O₂ system, the removal efficiency of COD_{cr} 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/CeO₂ 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_{cr} removal efficiency. According to Fig. 6b), it could be seen that the three systems CuO/CeO₂-US-H₂O₂ (multiphase Fenton/ultrasonic system), CuO/CeO₂-H₂O₂ (multiphase Fenton system) and US-H₂O₂ all have some degradation effects on COD_{cr}. The US-H₂O₂ system had the lowest removal efficiency of COD_{cr}, only about 10%, while the multiphase Fenton/ultrasonic system had the best removal efficiency that the COD_{cr} removal efficiency

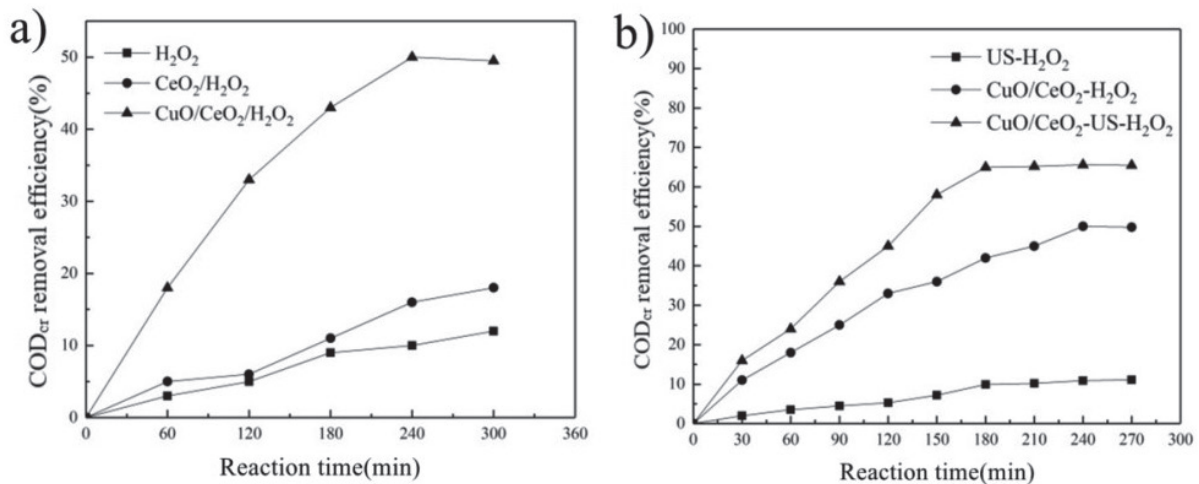
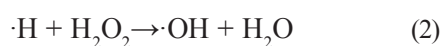
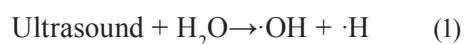


Fig. 6. Effects of different systems on COD_{cr} removal efficiency.

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/CeO₂ itself had a certain adsorption capacity, which could adsorb pollutants to the surface. The active material CuO on the catalyst reacts with H₂O₂ to produce a large amount of ·OH, which then degraded organic matter. After the addition of ultrasound, the pore structure of the catalyst CuO/CeO₂ improved the cavitation effect. The local high temperature and high pressure were generated. Then the following reaction occurred, as shown in equations (1) ~ (3):



It could be seen from the above reaction that the addition of ultrasound could not only produce ·OH with strong oxidizing ability to oxidize and degrade pollutants, but also produce ·H which could react with H₂O₂ to generate more ·OH, improving the oxidative degradation ability of the reaction system.

In summary, the heterogeneous Fenton system composed of the catalyst CuO/CeO₂ catalyzed by H₂O₂ had the best effect in the oxidative degradation of COD_{cr} in wastewater. The oxidative degradation capacity of CuO/CeO₂/H₂O₂ system was significantly higher than that of H₂O₂ system and CeO₂/H₂O₂ system alone, and the degradation efficiency also had huge advantages. These results all indicated that the catalyst CuO/CeO₂ in the CuO/CeO₂/H₂O₂ system had very high catalytic activity, so the heterogeneous Fenton system composed of the catalyst CuO/CeO₂ and H₂O₂ 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_{cr} 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 H₂O₂ Dosage on COD_{cr} Removal Efficiency in the Multiphase Fenton/Ultrasonic System

According to Fig. 7a), as the ultrasonic frequency increased, the removal efficiency of COD_{cr} first increased and then decreased. At 800 KHz, the removal efficiency of 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/CeO₂ and H₂O₂, and the other part from the cavitation effect. The greater the ultrasonic frequency, the greater the ultrasonic power required,

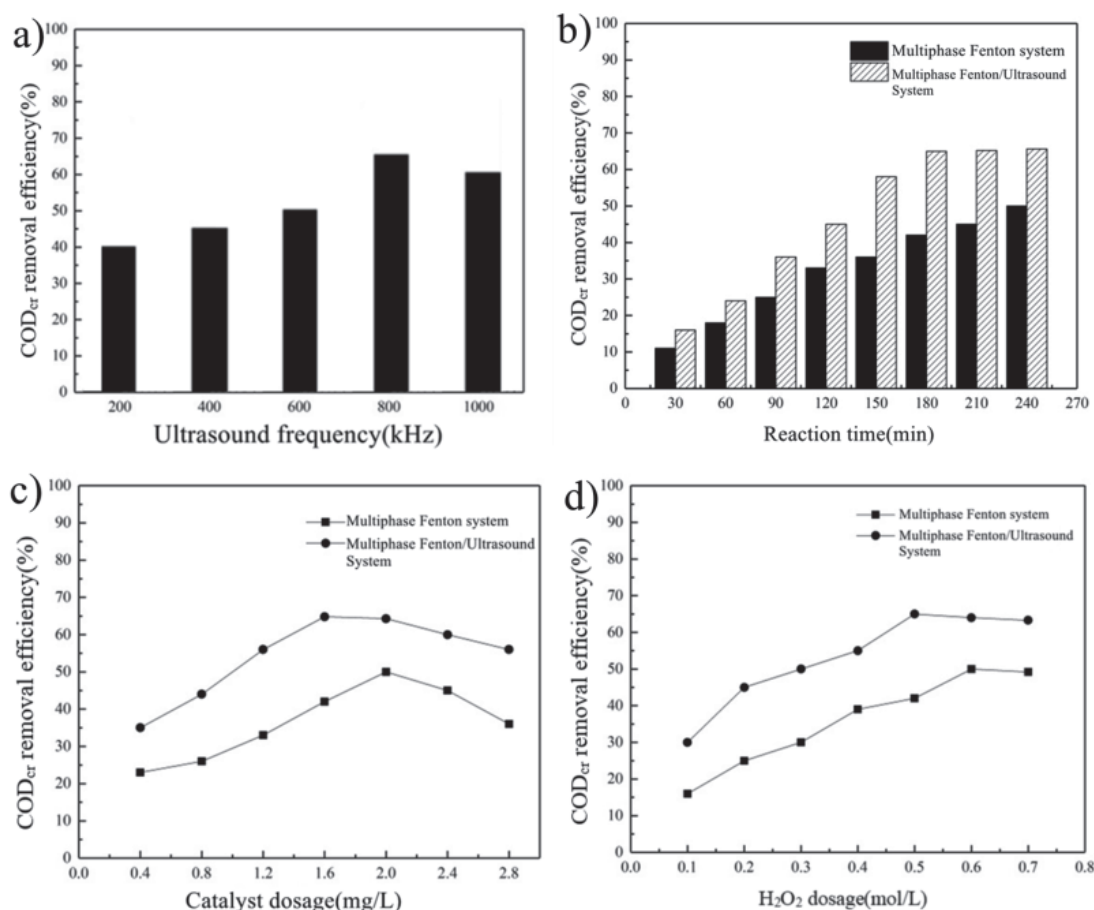


Fig. 7. Effect of ultrasonic frequency a), reaction time b), catalyst dosage c) and H₂O₂ dosage d) on COD_{cr} removal efficiency.

and the stronger the cavitation effect. Then the more ·OH was produced and the removal efficiency of COD_{cr} 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_{cr}. 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_{cr} 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_{cr} removal efficiency gradually increased with the increase of time. The COD_{cr} removal efficiency reached the maximum at 180 min, reaching 65%. And then with the increase of time, the COD_{cr} 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_{cr} 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_{cr} 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_{cr} 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_{cr} 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/CeO₂ 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_{cr} . The reasons for the above results could be explained as follows. When the catalyst CuO/CeO_2 dosage was less than 1.6 g/L, in the same time, the catalyst dosage was proportional to the production of $\cdot\text{OH}$. And when the catalyst CuO/CeO_2 dosage was greater than 1.6 g/L, due to the excessive production of $\cdot\text{OH}$ in a short time, an accumulation reaction occurred. It caused a part of H_2O_2 to be wasted and the COD_{cr} 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_2 have a higher utilization rate and better catalytic activity. Therefore, the removal efficiency of COD_{cr} 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_2 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_2O_2 increased from 0.1 mol/L to 0.5 mol/L, the removal efficiency of COD_{cr} increased from 30% to 65%. Then, as the dosage of H_2O_2 continued to increase, COD_{cr} removal efficiency had a slower downward trend. The reason for the above results could be explained as follows. When the dosage of H_2O_2 was small, as the dosage of H_2O_2 increased, the more hydroxyl radicals were produced, the higher the removal efficiency of COD_{cr} . And when the dosage of H_2O_2 was too much, side reactions would occur due to the production of too many hydroxyl radicals, which reduced the removal efficiency of COD_{cr} . 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_{cr} . This was because the addition of ultrasound would produce a cavitation effect, forming high temperature and high pressure locally, then producing $\cdot\text{OH}$. And $\cdot\text{H}$ would also be produced during this process. It could react with H_2O_2 to produce more $\cdot\text{OH}$, leading to a reduction in H_2O_2 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_2O_2 was 0.5 mol/L.

Effects of H_2O_2 Dosing Method, Initial Temperature and Initial pH on COD_{cr} 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_{cr} was higher if H_2O_2 was added at one time; while after 105 min,

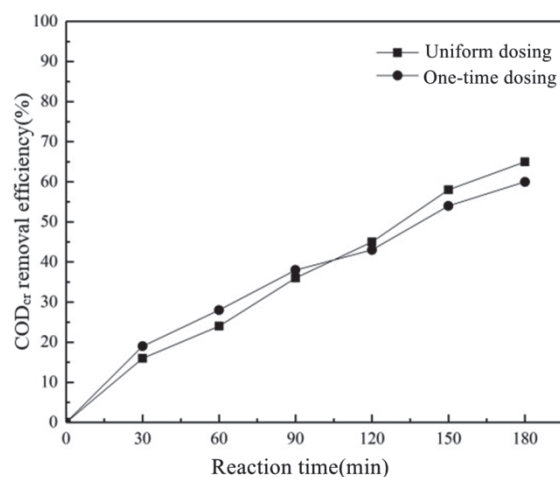


Fig. 8. Effect of H_2O_2 dosing method on COD_{cr} removal efficiency.

the removal efficiency of COD_{cr} was higher if H_2O_2 was added at a constant rate. Although the two dosing methods had different effects on the removal efficiency of COD_{cr} , at 180 min, the removal efficiency of COD_{cr} was 65% after H_2O_2 was added at a constant speed. And the removal efficiency of COD_{cr} was 60% after H_2O_2 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 $\cdot\text{OH}$ to be produced in a short time and accumulation reaction to occur, resulting in a certain amount of $\cdot\text{OH}$ waste, which made the removal efficiency of COD_{cr} 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

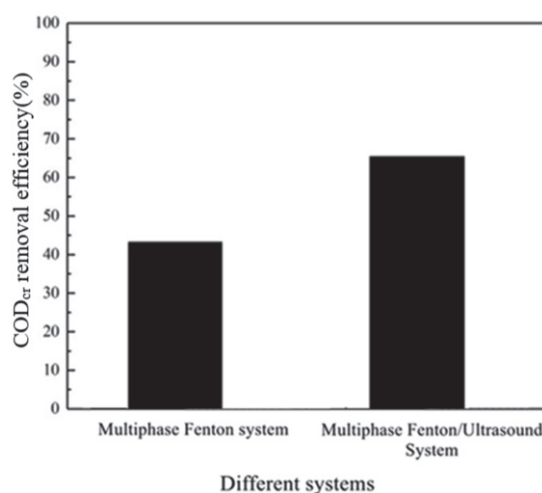


Fig. 9. Effects of different systems of uniform feeding on COD_{cr} removal efficiency.

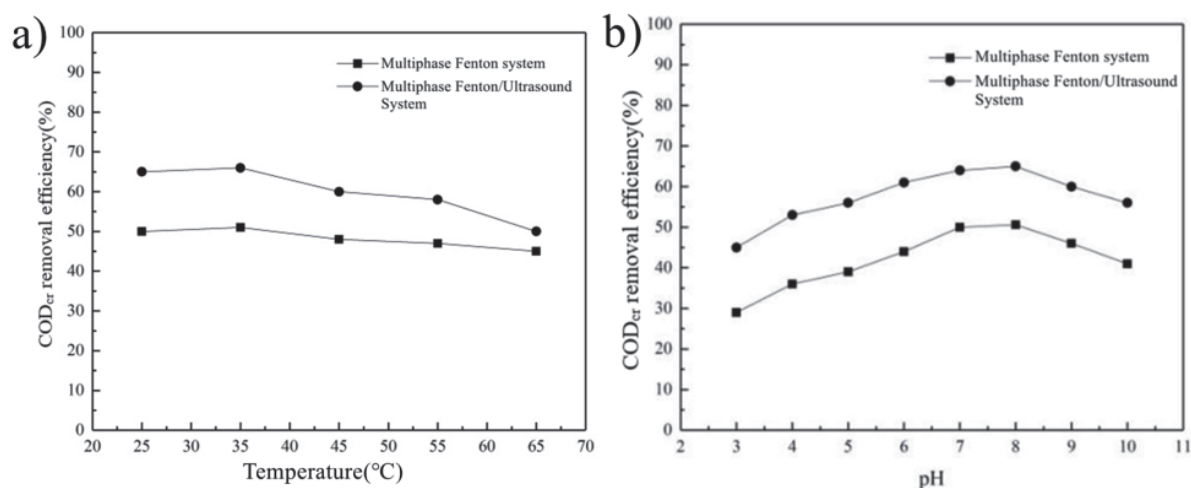


Fig. 10. Effect of initial temperature a) and initial pH b) on COD_{cr} removal efficiency.

of COD_{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 COD_{cr} removal efficiency. In summary, it was finally determined that when the multiphase Fenton/ultrasonic system was used to treat wastewater, the H₂O₂ dosing method was uniform dosing.

It could be seen from Fig. 10a) that as the initial temperature increased, the COD_{cr} removal efficiency first stabilized and then decreased. When the initial temperature increased from 25°C to 35°C, the COD_{cr} removal efficiency was maintained at about 65%. As the initial temperature further increased, the COD_{cr} 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_{cr}. 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_{cr} 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 H₂O₂, wasting a part of ·OH, and weakening the overall oxidative degradation ability, which was manifested as a reduction in the removal efficiency of COD_{cr}. 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_{cr} removal efficiency of the two systems had the same change trend. With the increase of the initial pH value, the COD_{cr} removal efficiency first increased and then decreased. The COD_{cr} removal efficiency reached the best when the initial pH value was 8, and at this time, the removal efficiency of COD_{cr} 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⁺ in the water reacted with CuO to form Cu²⁺, but the main catalytically active substance of the catalyst CuO/CeO₂ was CuO, not Cu²⁺, so the production of ·OH decreased, which was manifested by the lower removal efficiency of COD_{cr}. When the initial pH value was high, the solution was alkaline, and the ·OH contained in the water reacted with OH⁻, causing a part of ·OH loss, so the COD_{cr} 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/cm², the COD_{cr} removal efficiency of cutting fluid wastewater could reach 97.4%. By comparing the SEM results, BET results, XRD results and COD_{cr} removal efficiency of the catalysts prepared by different supports and methods, it was determined that the CuO/CeO₂ 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_{cr} 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_{cr} 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 H₂O₂ 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_{cr} from cutting fluid wastewater could reach 65%. Using electro-flocculation-multiphase Fenton/ultrasonic system to treat high-concentration cutting fluid wastewater, the final COD_{cr} removal efficiency could reach 99.09%. These results show that electro-flocculation-multiphase Fenton/ultrasonic system is an effective and environmental friendly method to treat high-concentration cutting fluid wastewater.

Acknowledgments

This work was supported as a National Natural Science Foundation of China (51778374) and a Department of Education Basic Scientific Research Project of Liaoning Province-Youth Project (LJKQZ2021058). The authors greatly thank the anonymous reviewers for their valuable comments and suggestions.

Conflict of Interest

The authors declare no conflict of interest.

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