

Studies on the preparation of Caro's acid by ultrasonic enhanced electrochemistry

Linbo Li, Zeli Yu*, Tao Hong, Zhao Fang, Jishi Peng and Zhao Yang

Xi'an University of Architecture and Technology, Xi'an 710055, P. R. China

*Corresponding author e-mail: 1206764982@qq.com

Abstract. Ultrasonic cavitation effects can generate hydroxyl radicals and high energy, which is widely applied in the field of oxidation currently. Ultrasound-enhanced electrochemical is used to prepare Caro's acid, which improves the generate rate of Caro's acid. In this article, the influences of ultrasonic frequency and ultrasonic power on the electrolysis voltage, electrolyte temperature, electrolyte concentration and the concentration of additive in the process of electrochemical preparation of Caro's acid was studied. And the optimal production conditions were determined. The research results showed that ultrasonic can significantly improve the production of Caro's acid and the product can increase by about 20 g/L under the best condition.

1. Introduction

The study on ultrasonic-induced electrochemical reactions has developed rapidly, which was widely used in water treatment [1-2], ore decomposition [3], electroplating [4] and preparation of nano-materials [5-8] and other fields currently. Zhuping [9] and her co-workers had studied treatment of non-leaching refractory gold ores with electrochemical antioxidant under two conditions including ultrasonic and ultrasonic condition. The results showed that ultrasound can reduce the reaction time and increase leaching rate by 35.84%.

Electrolytic oxidation technology [10-11], which is a green and efficient chemical process, is widely used in wastewater treatment [12].with the aid of ultrasonic; the electrochemical process can enhance the mass transfer process, reduce the electrolytic voltage and reduce the energy consumption in ultrasonic environment. Moreover, ultrasonic cavitation can produce a micro environment of high temperature and high pressure, which can produce a lot of hydroxyl radicals with high oxidizing ability and improve oxidation efficiency. Domestic and foreign scholars mainly applied ultrasonic electrochemical oxidation to wastewater treatment. For example, Zhao Guohua [13] from Tongji University combined boron doped electrode with ultrasound to treat phenol and phthalic acid. The results showed that hydroxyl radical produced during electrolytic process under ultrasonic environment. Furthermore, the oxidation capacity increased and the oxidation peak increased by 32%, the degradation efficiency was significantly improved. Meanwhile the energy consumption was greatly reduced.

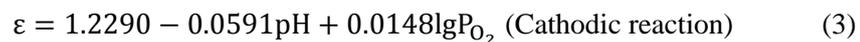
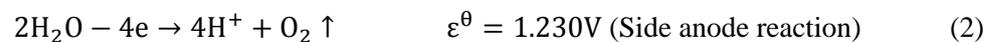
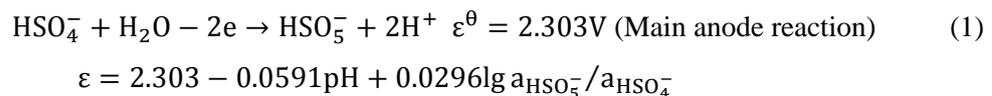
In this study, ultrasonic chemical and electrochemical were combined together for the preparation of Caro's acid in a low concentration of sulfuric acid. The results indicated that the anode oxidation rate, current efficiency and mass transfer rate were improved greatly with a reduced energy consumption. The problems existing in the preparation of Caro's acid by electrolysis have been solved fundamentally, which lays the foundation for industrial production.



2. Experimental part

2.1. Experimental principle

2.1.1. Electrolysis principle. Under the action of electric field force, the anions and cations move to cathode and anode respectively in electrolyte solution. Finally, the hydrogen sulfate is oxidized to Caro's acid at the anode and the hydrogen ion is reduced to hydrogen in the cathode. The main reaction and side reaction were as following:



2.1.2. Principle of Ultrasonic Enhanced Electrochemistry. When electrolysis process was carried out under ultrasonic environment, ultrasonic cavitation can make electrolyte solution generate hydroxyl, hydrogen peroxide and hydrogen free radicals as shown in formula (4) ~ (8)[14]. When the cavitation bubble is been compressed, the vapor in the bubble is decomposed into hydroxyl and hydrogen free radicals. In the absence of oxidized objects, H₂O₂ is the main product of ultrasonic decomposition. When the air is involved in the reaction, hydrogen free radicals and oxygen were combined rapidly to form hydrogen peroxide free radicals. Hydrogen peroxide produced by ultrasonic cavitation reacted with HSO₄⁻ in solution to form Caro's acid, which was shown as formula (9).



2.2. Experimental Method

2.2.1. *Experimental Device.* Diagram of ultrasonic enhanced electrolytic equipment, as shown in Figure 1.

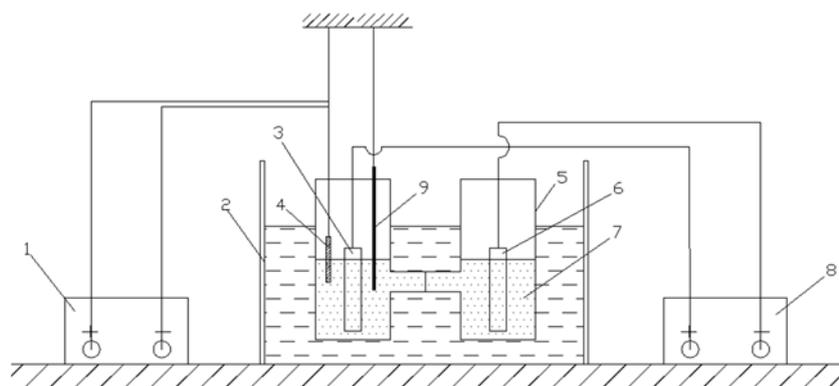


Figure 1. Diagram of ultrasonic enhanced electrolytic equipment.

(1-the ultrasonic generator, 2-low temperature thermostatic bath, 3-platinum plated titanium anode, 4-transducer probe, 5- electrolytic tank, 6- Graphite cathode, 7- electrolyte, 8- DC power supply, 9- thermometer.)

2.2.2. *Analysis Method.* The potassium dichromate to oxidation-reduction titration. Due to the strong oxidation of persulfate, ferrous ions can be oxidized to ferric ions. So excessive ferrous sulfate solution can be added to the solution, in which part of ferrous ions were oxidized by per sulfate and residual ferrous ions were oxidized by potassium dichromate. According to the amount of ferrous ions oxidized by potassium dichromate oxidation, the amount of ferrous ions oxidized by persulfate ions was calculated. So as the concentration of sulfuric was obtained in the solution.

2.2.3. *Experimental reagents.* 98% concentrated sulfuric acid, phosphoric acid, potassium dichromate, ammonium ferrous sulfate, sodium diphenylamine sulfonate, ammonium thiocyanate, etc.

3. Results and Discussion

3.1. The Influences of Ultrasonic Frequency and Time on Electro oxidation

In ultrasonic environment, the hydrogen free radicals and hydrogen peroxide free radicals can be generated owing to the cavitation effect in water solution, which can enhance the oxidation of the solution and increase the synthesis rate of Caro's acid. Ultrasonic can also improve the ion activity in solution, accelerate ion migration rate and reduce concentration polarization. Therefore, the effects of ultrasonic and ultrasonic time on the electrochemical oxidation process should be investigated.

Experimental conditions: the voltage of electrolysis is 6.0V, the concentration of electrolyte is 400g/L, the concentration of ammonium thiocyanate is 0.5g/L, the ultrasonic power is 150W, the temperature of reaction is 15°C and the proper reaction time is 4 hours while a sample was taken every 15 min for testing. The influences on three conditions for electrolysis process were investigated and the three conditions included absence of ultrasonic, different ultrasonic frequency including 20 kHz and 40 kHz as well as ultrasonic time. The results are shown in Fig. 2.

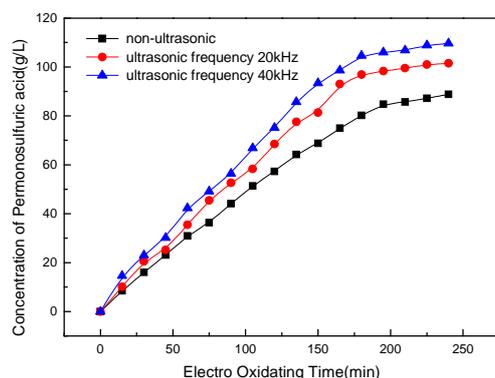


Figure 2. The influences of ultrasound frequency and time on the concentration of Caro's acid generation in the process of electrolysis

As shown in Fig. 2, the concentration of Caro's acid showed a growing trend as time went on. While the generation rate of oxidant decreased when electrolyte time was longer than 3 h, this is because Caro's acid is not stable and hydrolyzed easily and produce sulphuric acid and hydrogen peroxide. While electrolysis process was an exothermic reaction. The longer the time, the higher the temperature, which led to decomposition of Caro's acid. As a result, the optimal time was 3 h. The presence of ultrasonic promoted the generation rate of oxidant. At the same time, oxidant concentration increased when the ultrasonic power was increased. This was mainly because the acoustic cavitation effect helped generate hydrogen free radicals and hydrogen peroxide free radicals, accelerated ion mobility, increased oxidant generation rate. Based on the experiment results, ultrasonic power should be 40 kHz.

3.2. The Influence of Ultrasonic Power on Electro oxidation Process

Ultrasonic power is one of the important factors that effect of cavitation effect, which directly affects the reaction temperature and reaction rate. It is very important to investigate the influence of ultrasonic power on electro oxidation process.

Experimental conditions: the voltage of electrolysis is 6.0V, the concentration of electrolyte is 400g/L, the concentration of ammonium thiocyanate is 0.5g/L, the temperature of reaction is 15°C and the optimal reaction time is 3hours. The experimental results are shown as Fig. 3.

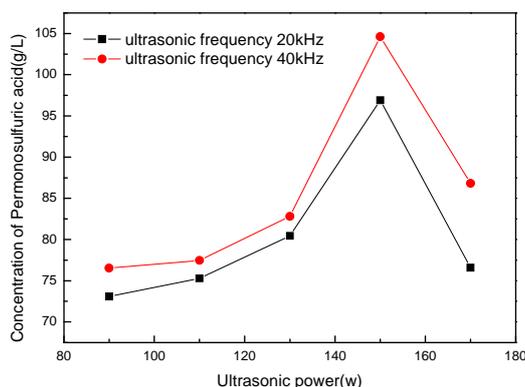


Figure 3. The influences of ultrasound power on the concentration of Caro's acid generation in the process of electrolysis

As shown in Fig. 3, when ultrasonic frequency was a constant, the generation rate of Caro's acid showed a trend of increasing firstly and then decreasing with the increasing of ultrasonic power. This is

because the increase of ultrasonic power to speed up the rate of the anodic reaction, but if the ultrasonic power was too large then most of the electrical energy was converted into heat, promoting the decomposition of Caro's acid and reducing the rate of oxidation. When the ultrasonic frequency was 20 kHz and 40 kHz, the generation rate of Caro's acid reached its peak value when ultrasonic power was 150W. Therefore, the appropriate ultrasonic power is 150W.

3.3. The Influences of Ultrasonic and Electrolysis Voltage

The electrolysis voltage is composed of theoretical voltage and over potential, and the over potential is caused by the polarization of the electrode. The presence of ultrasonic for electrolysis can help reduce concentration polarization and enhance the diffusion mass transfer so as to improve the anode electrode potential and anodic oxygen evolution over potential, inhibited side reactions and improve the formation rate of Caro's acid. The experimental results are shown in Table 1.

Table 1. The concentration of Caro's acid under different electrolysis voltage and ultrasonic frequency

decomposition voltage /V		5.0	5.5	6.0	6.5	7.0
The concentration of Caro's acid /g·L ⁻¹	non-ultrasonic	64.36	75.86	80.19	95.77	102.46
	20kHz	60.63	64.28	96.89	103.32	80.45
	40kHz	63.85	66.09	104.62	86.29	72.28

Experimental conditions: the concentration of electrolyte is 400g/L, the concentration of ammonium thiocyanate is 0.5g/L, the ultrasonic power is 150W, the temperature of reaction is 15°C and the optimal reaction time is 3 hours. The experimental results are shown in Figure 4.

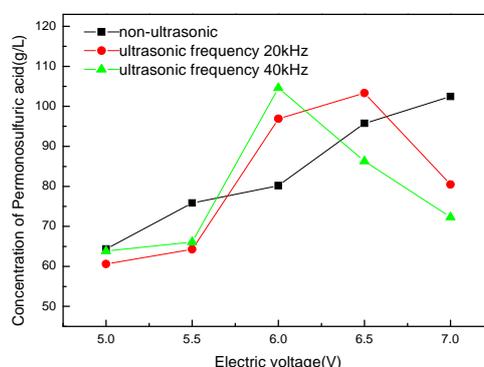


Figure 4. The influences of ultrasonic and voltage on the concentration of Caro's acid generation in the process of electrolysis

As shown in Fig. 4, the concentration of the Caro's acid was the highest when the ultrasonic voltage was 7.0V. When the ultrasonic frequency was increased, the peak value of the concentration Caro's acid shifted to the left, which indicated that the presence of ultrasound could reduce the voltage of the cell. After combining with ultrasound, the concentration of oxidant first increases and then decreases with the increase of electrolysis voltage. This is because the voltage is too high, which led to the increasing of anode over-potential and the energy consumption and the decomposition of Caro's acid was accelerated.

3.4. The Influences of Ultrasonic Frequency and Additive

After consulting the literature, [15-16] it is impossible to avoid the anode adverse reaction in electrolysis process. Therefore oxygen inhibitors must be added. In this study, ammonium thiocyanate was chosen

as the oxygen inhibitor and ultrasonic frequency as well as different concentration of oxygen inhibitors were investigated. The experimental results are shown in Table 2.

Table 2. The concentration of Caro's acid under different concentrations of additive and ultrasonic frequency

Additive concentration / g·L ⁻¹		0	0.1	0.3	0.5	0.7	0.9
The concentration of Caro's acid /g·L ⁻¹	non-ultrasonic	20.15	24.88	66.8	80.19	63.41	53.69
	20kHz	28.78	42.54	69.26	96.89	68.19	56.21
	40kHz	30.35	46.65	77.98	104.62	82.68	65.89

Experimental conditions: the concentration of electrolyte is 400g/L, the voltage of electrolysis is 6.0V, the temperature of reaction is 15°C, the ultrasonic power is 150W and the optimal reaction time is 3 hours. The experimental results are shown in Fig. 5.

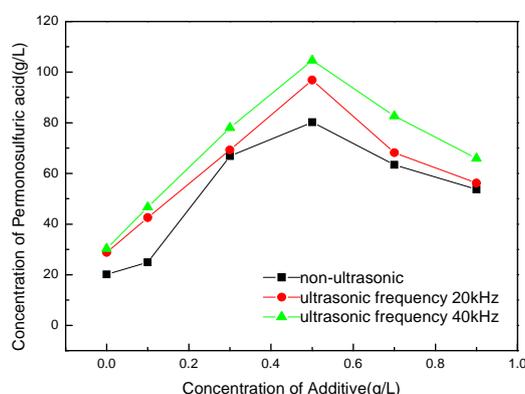


Figure 5. The influences of ultrasonic and additives on the concentration of a sulfuric acid generation in the process of electrolysis

As shown in Fig. 5 and Table 2, additives have great influence on the synthesis of Caro's acid for the reason that the addition of additives led to the formation of SCN⁻ adsorption layer on the anode surface, which greatly improved the oxygen precipitation over potential effectively and reduced electrolytic energy consumption [17]. What we can see from Fig.4 was that the formation rate of Caro's acid firstly increases and then decreases when the additive concentration increases. When the concentration of additive is 0.5g/L, the concentration of Caro's acid reached the maximum value. The concentration of additive shouldn't be too high. The result shows that the anode adsorption layer was too thick when the concentration of additives was too high, which hindered the oxidation of Caro's acid. Ultrasound can reduce the concentration gradient of the solution around the electrode and the concentration polarization of the solution so as to improve the yield of Caro's acid. The higher ultrasonic frequency leads to more Caro's acid, but the overall trend was unchanged. Accordingly, the optimal concentration of additive should be 0.5 g/L.

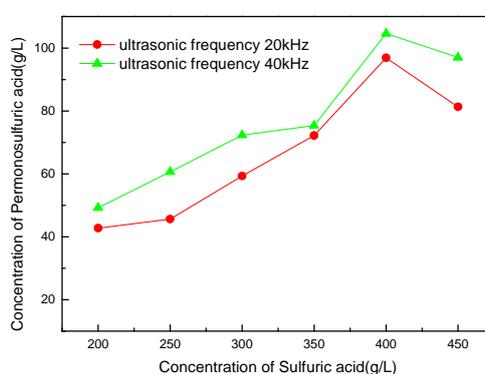
3.5. The Influence of Ultrasonic and Electrolyte Concentration

Ultrasound can enhance diffusion and mass transfer as well as decrease the concentration polarization of solution. Different concentration of Caro's acid solutions have different effects on the generation rate of Caro's acid in the presence of ultrasonic. The experiment results are shown in Table 3.

Table 3. The concentration of Caro's acid under different concentration of sulfuric acid and ultrasonic frequency

Concentration of sulfuric acid / g·L ⁻¹		200	250	300	350	400	450
The concentration of Caro's acid /g·L ⁻¹	20kHz	42.75	45.61	59.34	72.19	96.89	81.34
	40kHz	49.25	60.65	72.3	75.38	104.62	97.01

Experimental conditions: the voltage of electrolysis is 6.0V, the concentration of ammonium thiocyanate is 0.5g/L, the temperature of reaction is about 15°C, the ultrasonic power is 150W and the optimal reaction time is 3 hours. The experimental results are shown in Fig. 6.

**Figure 6.** The influences of ultrasonic and concentration of electrolyte on the concentration of Caro's acid generation in the process of electrolysis

It can be seen that the concentration of Caro's acid firstly increases and then decreases with the increase of the concentration of sulfuric acid from Fig.6. When the concentration of sulfuric acid is 400g/L, the concentration of Caro's acid reached its maximum value. When the concentration of sulfuric acid was too low, HSO_4^- obtained from the decomposition of sulfuric acid was too little and the reaction intensity was low. When the concentration of sulfuric acid was high, the solution viscosity increased and it is not conducive to mass transfer. As a result, the ultrasonic cavitation will be weakened and ultimately lead to a low Caro's acid production rate. The higher the ultrasonic frequency was, the higher the formation rate of Caro's acid was.

3.6. The Effects of Ultrasound and Electrolyte Temperature

The addition of electrolytic process will produced a large number of cavitation bubble and cavitation bubble rupture will release heat, which led to the increasing of temperature for the solution. Thereby strengthening the ion transport and electrochemical reaction, but hydrolysis of Caro's acid was also accelerated. On the contrary, reducing temperature can inhibit hydrolysis of Caro's acid. Temperature should be reasonably control after adding ultrasound.

Experimental conditions: the voltage of electrolysis is 6.0V, the concentration of electrolyte is 400g/L, the concentration of ammonium thiocyanate is 0.5g/L, the ultrasonic power is 150W and the proper reaction time is 3 hours, the experimental results are shown in Fig. 7.

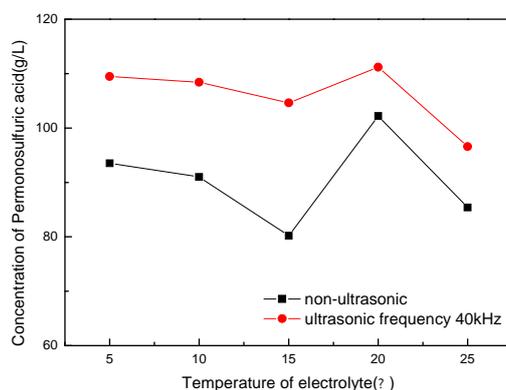


Figure 7. The influences of ultrasonic and temperature of electrolyte on the concentration of Caro's acid generation in the process of electrolysis

It can be seen that the temperature had a great influence on the rate of formation of the oxidant from Fig. 7. As the temperature of the electrolyte increases, the concentration of Caro's acid firstly decreased and then increased again and then decreases. This was mainly because the increasing temperature led to increasing hydrolysis of Caro's acid and the decreasing current efficiency. The concentration of Caro's acid increased about 20 g/L, but the overall trend was unchanged. Therefore, the temperature of electrolyte was chosen to be 20°C.

4. Conclusions

(1) In the process of preparing Caro's acid by electrolysis, adding additives can increase the over potential of oxygen precipitation and restrain the occurrence of oxygen evolution side reaction effectively.

(2) Electrolysis in ultrasonic environment can accelerate the ion migration rate, reduce the tank voltage, increase the anodic oxidation rate and promote the synthesis of over Caro's acid. Therefore the purpose of strengthening production could be achieved.

(3) The experiment results showed that maximum concentration of Caro's acid can reach 104.62g/L under the condition of using 400g/L sulfuric acid as electrolyte, electrolytic voltage control in 6.0V, ammonium thiocyanate concentration is 0.5g/L, the temperature controlled at 20°C, the ultrasonic frequency is 40kHz, ultrasonic power is 150W, optimal time is 3 h.

Acknowledgments

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