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Original Research

Optimization of Dynamic Diaphragm System by Response Surface Methodology for Synergistic Electrochemical Degradation of Typical PPCPs Wastewater

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Abstract

The treatment of PPCPs wastewater was studied in a self-made new dynamic diaphragm system electrochemical reactor. The single-factor experiment was optimized using response surface methodology, and the optimum reaction conditions were as follows: electrolysis voltage 16.2V, electrode plate spacing 4.76 cm, NaCl concentration 0.08 mg/L. The experimental results show that the dynamic diaphragm system cathode and anode co-electrochemical method can effectively treat PPCPs wastewater. Under optimal conditions, the pollutant removal rate reaches 96.27%. The order of influence on the removal rate of PPCPs is DC voltage>electrolyte concentration>electrode plate spacing. The results provide an experimental basis for the electrochemical removal of PPCPs wastewater by the diaphragm system.

Keywords: cathode and anode, PPCPs removal rate,response surface methodology, the diaphragm system

Introduction

Pharmaceutical and Personal Care Products (PPCPs) are a new type of aquatic pollutants, including antibiotics, hair dye, synthetic musk, painkillers, and so on. PPCPs wastewater cannot be effectively removed by conventional methods, and some organic matter in the treated sewage is often found in higher concentrations than the original sewage [1]. This has become a major social concern, PPCPs wastewater is continuously used in life and discharged into the water system [2, 3].

Due to the production of hydroxyl radicals (·OH), electrocatalytic oxidation technology is expected to be used for the degradation of refractory organics, electrocatalytic technology has a high potential for the treatment of refractory wastewater by combining electric and catalytic processes. Treatment of PPCPs wastewater by electrochemical oxidation has attracted much attention [4, 5]. Researchers mostly use electrocatalytically active electrodes (DSA) as anode materials. And through the catalytic process to produce H_2O_2 and hydroxyl radicals (·OH) to degrade

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pollutants， and this method has been applied to some refractory organic wastewater. However, due to the difference between cathodic reduction and anodic oxidation products, it is difficult for the cathode to generate active substances with strong oxidation. Based on this, many scholars devoted themselves to the study of the electrolytic reactor, which mainly changes the degradation rate of pollutants by changing the mass transfer effect of the electrolytic cell [6]. Electrochemical reactor configuration can be divided into a diaphragm (double chamber) electrolytic cell and a non-diaphragm (single chamber) electrolytic cell, porous diaphragm is usually used to separate the cathode chamber and the anode chamber in a diaphragm electrolyzer. This diaphragm has a significant effect on the degradation rate. Most of the reported electrochemical removal of PPCPs is carried out in a single-chamber cell [7].

Given this, Ibuprofen (IBU) is a typical PPCPs wastewater as the research object, using a self-made electrochemical reactor diaphragm device for experiments. Electrochemical reaction in order to avoid the reaction of anode and cathode and the mutual influence of products, most of them use a proton exchange diaphragm to separate anode and cathode, to prevent the side reaction formed in the oxidation-reduction process affects the main electrochemical reaction process. The diaphragm material not only blocks the mutual interference of REDOX reactions in the anode and cathode but also plays a role in strengthening the ion transfer in the electrolytic cell [8]. As shown in Table 1, The research group screened out the common experimental schemes in the electrochemical experiment of the diaphragm system and optimized the experimental conditions. The experiment selected Ti plate as the cathode, Ti/RuO_2/ IrO_2 as the anode, Nafion117 was used as diaphragm material, The degradation of IBU was investigated by anode and cathode circulation flow.

Material and Methods

Materials and Reagents

As shown in Fig. 1, the reactor device is mainly composed of an electrochemical reaction tank, electrode plate, diaphragm device and DC-regulated power supply. The reactor specifications are: 100 MM × 100 MM × 100 MM, the actual effective volume is 800 mL, 400 mL for each anode and cathode chamber; The size of the electrode plate material is 100 MM × 100 MM, the effective size of the plate in the test is 100 MM × 40 MM. The power supply is transistor adjustable DC voltage regulated power supply (Type of YJ34), purchased from Great Wall Electric Instrument Factory (China), the adjustment range is 0~30 V; The cell material is plexiglass, the card slot is arranged on the edge of the container, and the spacing of the plate can be adjusted according to the demand. The adjustable range is 20~60 MM. Detachable diaphragm tank is arranged in the middle of the electrolytic cell, and the effective contact size between the diaphragm and the electrolyte is 50 MM × 50 MM. The anode uses Ti/RuO_2/IrO_2 plate, the cathode uses Ti plate, the dimensions were 10 cm × 10 cm, 1 mm × 1 mm, Purchased from Suzhou Shultai Industrial Technology Co., LTD; Digital distribution peristaltic pump (Type of YZ1515X), Purchased from Baoding Chuangrui Pump Industry Co., LTD (China); Air compressor (Type of ACO-318), Purchased from Guangdong Haili Group Co. LTD (China); Proton exchange diaphragm was used for diaphragm, and Nafion117 was used after optimization, with the size of 50 MM × 50 MM. Purchased from DuPont (America); NaCl as the electrolyte, all chemical samples are analytically pure and are used as is without further purification, were purchased from Tianjin Kemeio Chemical Reagent Development Center (China).

Preparation of Solution and Experimental Material

Configuration of Simulated Water Samples

IBU was selected as a typical PPCPs wastewater for the experiment. Firstly, 1 g IBU powder was weighed and dissolved in distilled water, and the powder was fixed to 1000 mL in a brown volumetric bottle and stored in a refrigerator at 2ºC as a reserve liquid. Before the experiment, a certain volume of the reserve solution was weighed and diluted to 10 times with distilled water to obtain IBU solution with a mass concentration of 100 mg/L.

Preparation of Plates and Diaphragm

All the plates were immersed in dilute sulfuric acid for 24 h. Deionized water was used to wash organic matter and impurities on the surface, then they were immersed in deionized water for 12 h. The diaphragm was treated with 5% H_2O_2 at 80ºC for 60 min and then treated with deionized water for 30 min, followed by soaking in sulfuric acid with a mass ratio of 10% for about 20 min, and finally boiled in deionized water at 80ºC for 30 min.

Analytical Methods

All valves in the electrolytic cell were pre-closed, and 800 mL of PPCPs simulated wastewater sample with an initial concentration of 100 mg/L was prepared in the electrolytic cell. The electrolyte was added and stirred until it was completely dissolved. The pretreated cathode and anode plates were placed in the electrolytic cell, and a rubber tube was used to connect the electrolytic cell, peristaltic pump, and reservoir. After the power supply parameters are pre-adjusted according to the test conditions, After the preparation is completed, the electrolyte is added to the electrolytic cell, and the peristaltic pump is started to run at a rate

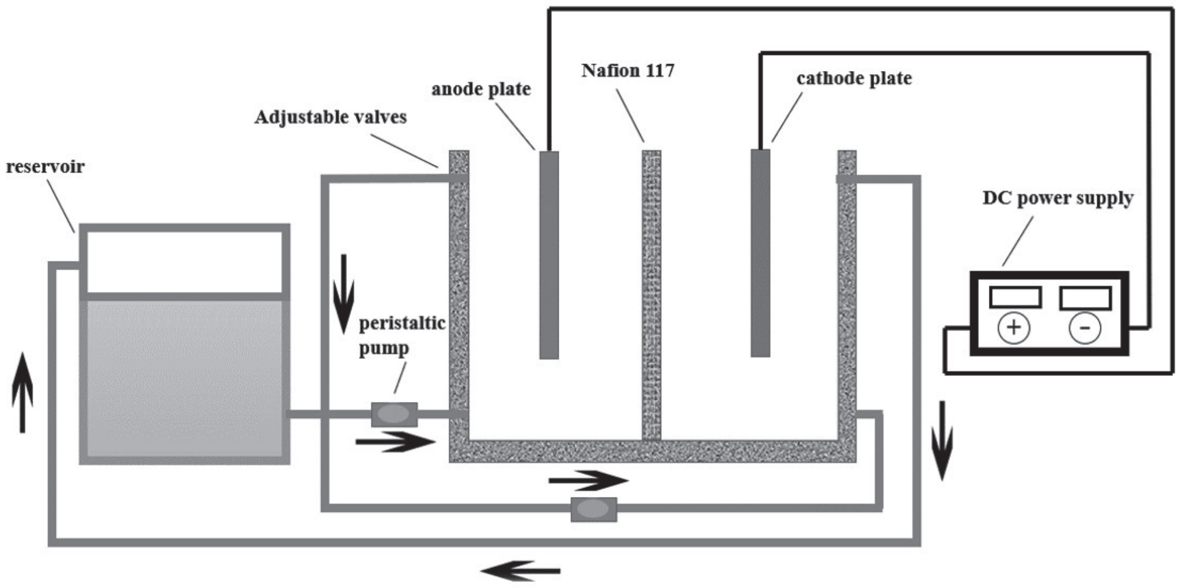
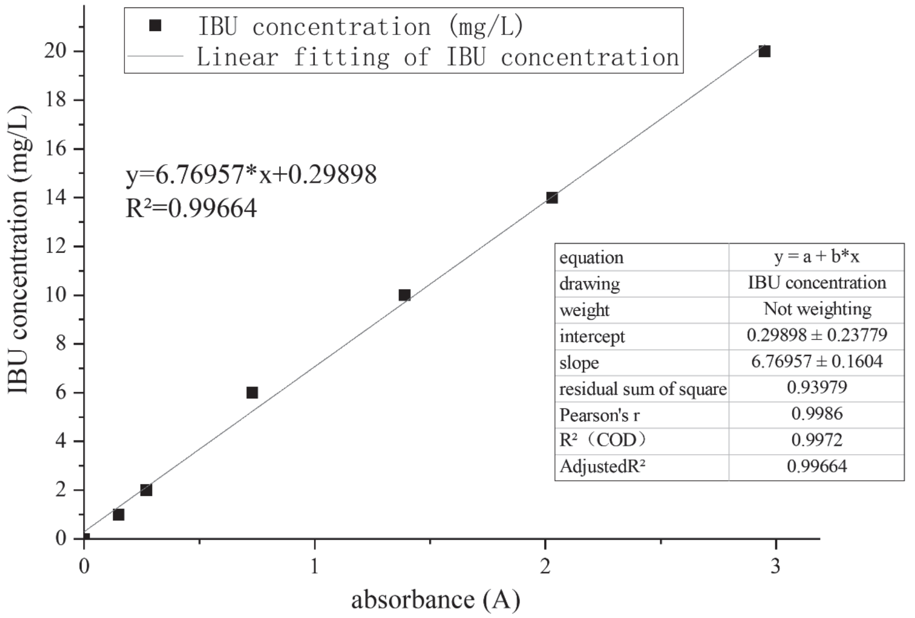


Fig. 1. Diagram of Dynamic Diaphragm Reactor Experimental Device.

of 60 rpm, all valves are adjusted to the open state, As shown in Fig. 1. The channel above the cathode chamber will slowly transport the liquid in the electrolytic cell to the storage tank, and the channel below the storage tank will transport the liquid to the bottom of the anode chamber through the peristaltic pump. When there is a uniform and stable bubble flow in the hose connected to the peristaltic pump, the dynamic aeration cycle is completed, and then IBU simulated wastewater is added to the electrolytic cell, and the DC power supply is connected to start the experiment. This experiment collects wastewater from the anode chamber for analysis. Sampling was performed once every 10 min in the reservoir, and then drugs were added for testing, and data were recorded. Determination of IBU concentration by ultraviolet spectrophotometry. Firstly, 0, 0.5, 1, 3, 5, 7, and 10 ml IBU solution and distilled water were added to 50 ml in 7 test tubes, respectively. After standing for 15 min, a colorimetric dish with an optical path of 10 nm was used with distilled water as a reference. Determination of IBU wastewater concentration with a UV-Vis spectrophotometer (Shimadzu UV3600IPLUS, Japan) with a wavelength of 210 nm [9]. IBU content-absorbance curve was shown in Fig. 2. The IBU removal rate is calculated as follows:



equation	y = a + b*x
drawing	IBU concentration
weight	Not weighting
intercept	0.29898 ± 0.23779
slope	6.76957 ± 0.1604
residual sum of square	0.93979
Pearson's r	0.9986
R²（COD）	0.9972
AdjustedR²	0.99664

Fig. 2. IBU standard absorption curve.

$$\eta=\frac{A_0-A_t}{A_0}\times 100\% \tag{2-1}$$

η is the removal rate of IBU; A_0 is the IBU absorbance at time 0; A_t is the IBU absorbance at time t.

COD was determined by the rapid closed catalytic digestion method. Digestion solution configuration: 8.8 g potassium dichromate, 25.0 g potassium aluminum sulfate, 5.0 g ammonium molybdate, dissolved in 250 ml water, added 100ml concentrated sulfuric acid, cooled, transferred to a 500ml volumetric flask, diluted with water to the line. The concentration of potassium dichromate in the solution was about 0.4 mol/L; catalyst configuration: 4.4 g analytical pure Ag_2SO_4 was dissolved in 500 ml concentrated sulfuric acid. Masking agent configuration: 10.0 g analytically pure $HgSO_4$ was weighed and dissolved in 100 ml 10% sulfuric acid. Seven concentration gradients of COD standard solution (50, 100, 200, 400, 600, 800, 1000 mg/L, purchased from Cono Reagent Company, China) were configured, and 3 ml of standard solution was accurately weighed and placed in 7 digestion tubes. After adding 1ml masking agent to each digestion tube, it was fully shaken, and then 3 ml digestion solution and 5 ml catalyst were added to fully shake. After the rubber plug was tightly covered, it was placed in the digester and digested at 165ºC for about 15 min. After sufficient cooling, the absorbance was measured under the wavelength 600 nm ultraviolet spectrophotometer and the COD standard absorption curve was drawn. The above-mentioned unannotated pharmaceutical chemical samples were all analytically pure and purchased from Tianjin Comio Chemical Reagent Development Center (China). The removal rate of COD was calculated as follows:

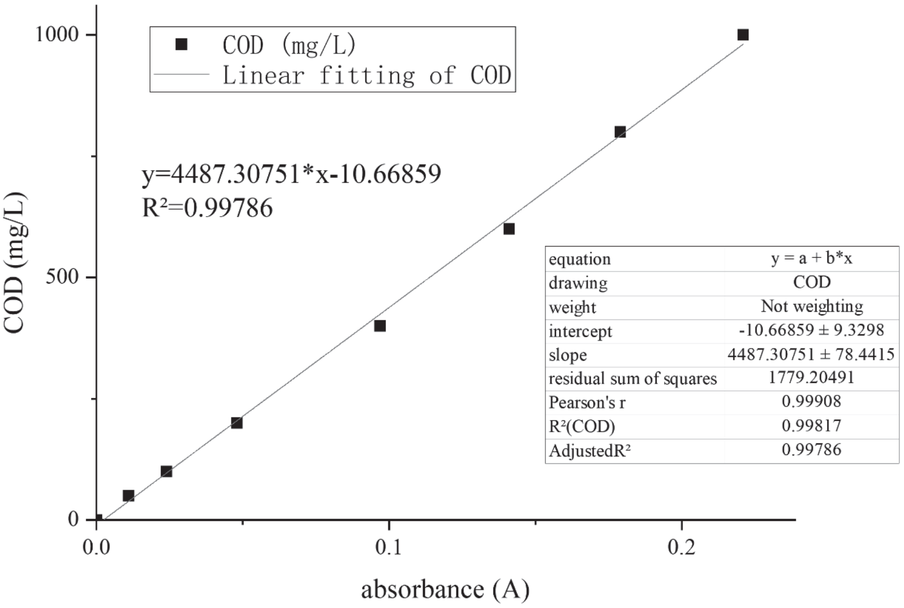
$$\eta=\frac{C_0-C_t}{C_0}\times 100\% \tag{2-2}$$

η is the removal rate of COD; C_0 is the measured value of COD at time 0 of degradation (mg/L); C_t is the measured value of COD at time t of degradation (mg/L).

The experimental results were designed by Box-Behnken Design (BBD) response surface method. The interaction experiments were carried out on the three factors of DC voltage, electrolyte concentration, and plate spacing. After establishing the mathematical model and obtaining the objective function, the optimal value was taken for experimental verification.

Response Surface Analysis

Response surface analysis (RSM) is a statistical method that uses a reasonable experimental design method to obtain certain data through experiments, uses a multivariate quadratic regression equation to fit the functional relationship between factors and response values, and seeks optimal process parameters through the analysis of regression equations. In this experiment, Design-Expert (version 10.0.1.0 64-bit) was used for response surface analysis. The software, developed by Stat-Ease, can screen the key factors and components in the experiment, characterize the interaction, and finally achieve the best process settings and product formulations. Design-Expert has mathematical statistics functions such as Box-Behnken Design (BBD) and Central Composite Design (CCD), Historical Data Designed. The software allows interactive 2D maps to set markers and explore contours, and then visualize the response surface from all angles with a rotatable 3D map. In this experiment,



equation	y = a + b*x
drawing	COD
weight	Not weighting
intercept	-10.66859 ± 9.3298
slope	4487.30751 ± 78.4415
residual sum of squares	1779.20491
Pearson's r	0.99908
R^2(COD)	0.99817
AdjustedR^2	0.99786

Fig. 3. COD standard absorption curve.

Box-Behnken Design was used to optimize the response surface design of the experiment, and the specific details were given below.

Result and Discussion

Research on the Influencing Factors of IBU Degradation by Electrochemical Method in Dynamic Diaphragm System

Based on the preliminary experiment of electrochemical degradation of IBU in the diaphragm system, the main factors affecting the removal of IBU in the electrochemical system were studied. In this experiment, a dynamic circulating diaphragm system was used. At the beginning of the reaction, the pH in the anode chamber was 2~3, and the pH in the cathode chamber was 11~12. After the cycle is opened, the solution in the chamber is fully exchanged. In order to prevent excessive energy loss, the rate of the peristaltic pump is adjusted at 60 rpm. After 5 minutes of the reaction, the pH of the reaction in the cathode and anode chambers was maintained at about 5~6, and other experiments showed that PH = 5 was the more suitable PH value for the electrochemical degradation of IBU [10]. The initial pH of the test was between 8 and 9; the test temperature was the indoor temperature of the laboratory (about 18ºC), and the solution temperature slightly increased to about 22ºC during the reaction. In this experiment, the effects of operating parameters such as initial concentration of pollutants, concentration of NaCl, electrolytic voltage and plate spacing on pollutant removal were investigated.

Electrochemical Degradation Mechanism

In recent decades, with the in-depth study of electrochemistry by scholars, the research on electrode materials has been developed rapidly, especially the application of metal oxide electrode materials, which makes the research of electrochemical advanced oxidation process for sewage treatment develop rapidly [11, 12]. The electrochemical method of the diaphragm system is to provide an energy source for the system through an applied electric field in the chamber separated by the diaphragm, so that the solution can produce strong oxidizing substances, such as hydroxyl radicals, active chlorine, etc. Different from the traditional double-chamber electrocatalytic reaction, the dynamic diaphragm system in this experiment can interact with the active substances in the double-chamber. The mechanism of IBU removal by producing active substances is shown in Fig. 4.

Hydroxyl Radical

There are two main sources of hydroxyl radicals in the separator system. One is the discharge of H_2O in the anode chamber. The other is that O_2 reacts with the metal oxide coating of the anode under acidic conditions to form H_2O_2, which is then anodized to form hydroxyl radicals. The reaction is as follows:

$$H_2O \rightarrow \cdot OH + H^+ + e^- \tag{3-1}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \rightarrow \cdot OH \tag{3-2}$$

$$IBU + \cdot OH \rightarrow \ldots \rightarrow CO_2 + H_2O + H^+ + e^- \tag{3-3}$$

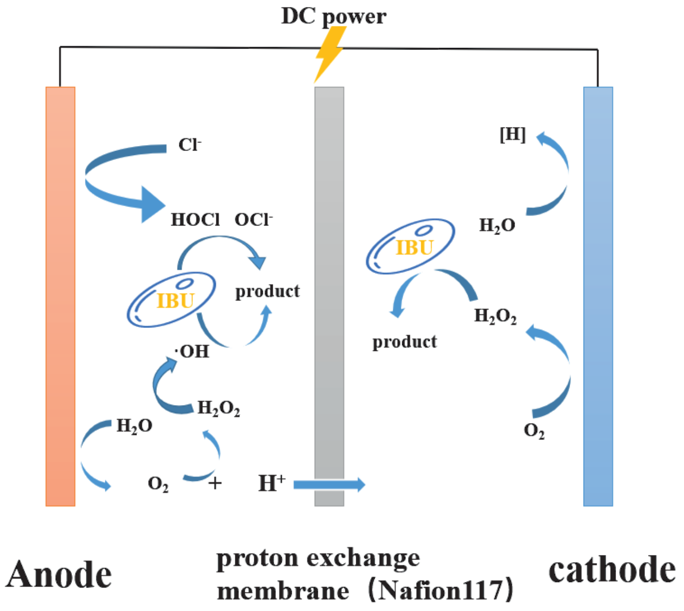


Fig. 4. Electrochemical degradation mechanism diagram of diaphragm system.

Among them, H_2O_2 can also be generated by a reduction reaction in the cathode chamber. The generation process is to obtain electrons through O_2 on the surface of the catalyst in the cathode chamber, and then form peroxyl ions, and then obtain hydroxyl radicals through a series of reactions. The reaction is as follows:

$$O_2 + e^- \rightarrow O_2^- \quad (3\text{-}4)$$

$$O_2^- + H^+ + e^- \rightarrow HO_2^- \quad (3\text{-}5)$$

$$2HO_2^- \rightarrow H_2O_2 + O_2 \quad (3\text{-}6)$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \quad (3\text{-}7)$$

Active Chlorine

The Cl^- in the separator system mainly comes from the electrolyte NaCl. Under acidic conditions, Cl^- is easily oxidized by DSA to form Cl_2, which reacts with water to form hypochlorous acid, and then the organic pollutants can be decomposed into small molecular intermediates until completely removed. In the cathode chamber, chemically adsorbed hydrogen atoms are formed on the cathode surface, and then the C-Cl bond is hydrogenated, which can accelerate the degradation of pollutants by reduction reaction. The reaction process is as follows:

$$2Cl^- \rightarrow Cl_2(aq) + 2e^- \quad (3\text{-}8)$$

$$Cl_2(aq) + H_2O \rightarrow HOCl + H^+ + e^- \quad (3\text{-}9)$$

$$R + HOCl \rightarrow \ldots \rightarrow CO_2 + H_2O \quad (3\text{-}10)$$

$$H_2O_2 + e^- \rightarrow [H] + \text{hydroxide} \quad (3\text{-}11)$$

$$[H] + RCl \rightarrow RH + Cl^- \quad (3\text{-}12)$$

Single Factors Analysis

Effect of Ibuprofen Concentration

As shown in Fig. 5, the substrate concentration has a certain effect on the electrochemical mass transfer rate and the electrode surface control steps. In order to explore the optimum concentration of IBU degradation in this system and investigate the electrochemical reaction ability, the effects of IBU concentration (50, 100, 150, and 200 mg/L) on IBU degradation were studied in this section. When the NaCl concentration increased from 50 mg/L to 100 mg/L, the IBU removal rate gradually increased and finally reached 90.3%, and the COD removal rate also increased, reaching 56.8%. However, when the substrate concentration reached 150 mg/L and 200 mg/L, the removal efficiency of IBU and COD was not as good as before. The removal rate of IBU was only 87.0%, and the removal rate of COD was only 22.0%. With the increase of substrate concentration, the contact area between pollutants and active groups can be effectively improved, which is conducive to the degradation of pollutants. However, many references [13] consistently conclude that: The higher initial concentration requires longer electrolysis time to achieve the same decoloring or mineralization effect, because when the substrate concentration increases, the active group cannot fully reflect the organic matter near the electrode surface in a short time. Wang et al. [14] found that the oxidation rate of IBU decreased with increasing IBU concentration. The reason for this observation may be due to the increase in the ratio of hydroxyl radicals to IBU and the increased possibility of these radicals attacking IBU freely at lower initial concentrations. Therefore, the initial concentration of IBU was set to 100 mg/L in this experiment.

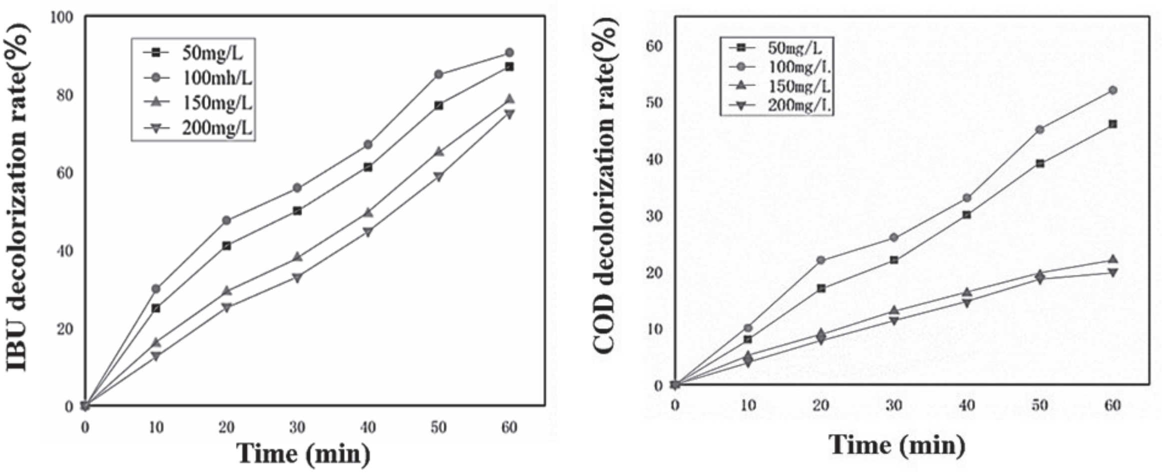


Fig. 5. Results of electrolysis for 60 min in 100 mg / L simulated PPCPs (electrolysis voltage 15 V, electrode plate spacing 4 cm, NaCl concentration 0.06 mol / L, initial pH = 8, circulating current 60 rpm).

Effect of Electrolyte Concentration

In the electrochemical degradation test, it is often necessary to add a certain amount of electrolyte to the reactor. The electrolyte dissolves in water and dissociates free-moving anions and cations. Under the action of an external electric field, the anions and cations will move directionally to form an internal circuit, so that the entire circuit constitutes a closed loop. Some research results and theoretical models suggest that changes in electrolyte composition can be considered as an additional degree of freedom in designing efficient electrocatalytic systems [15, 16]. A variety of electrolyte types can be divided into three categories: salt, alkali, acid. With the further development of experimental methods and the basic understanding of electrocatalytic processes, the influence of alkali metal cations has once again attracted great attention from the environment [17]. Many researchers used NaCl and Na_2SO_4 as the electrolyte in the process of electrocatalysis of organic pollutants, but compared with Na_2SO_4, the presence of NaCl as supporting electrolyte greatly enhanced the oxidation of PPCPs wastewater [18, 19]. Since the sulfate ions in Na_2SO_4 solution only play a conductive role, and did not produce other substances involved in the degradation of pollutants, part of the H-O bond of water molecules in the solution will be broken under the action of external electric field, resulting in H_2O_2, superoxide radicals and other active particles with direct oxidation. NaCl is usually used to increase the conductivity of wastewater to be treated, the study of Luo et al. [20] showed that chloride ions can significantly weaken the adverse effects of other anions on electrochemical reactions, such as HCO_3^-, sulfate, etc. Since the addition of sodium chloride increases the conductivity, the resulting indirect oxidation reaction can assist the degradation process and reduce the power consumption of the diaphragm electrocatalytic system. In addition, in the actual chemical wastewater treatment, electrochemically generated chloride ions can also play a role in disinfection. Therefore, the experimental group selected NaCl as the electrolyte.

As shown in Fig. 6., in order to explore the NaCl concentration suitable for the reaction system, different concentrations of electrolyte NaCl were added to the electrolytic cell and dissolved in the simulated PPCPs wastewater by controlling the variables. The initial concentrations of NaCl were 0.04 mol/L, 0.06 mol/L, 0.08 mol/L and 0.10 mol/L, respectively. The other test conditions are the same as before. Through observation, it can be seen that the electrochemical degradation effect of the chlorine-containing system on IBU is obvious. At the end of the reaction, the removal rate of IBU was as high as 92.6%, and the removal effect of COD became better. This is because, in addition to the direct oxidation of hydrogen peroxide and hydroxyl radicals produced by water electrolysis in the reaction system, the active chlorine produced by Cl^- in anodic oxidation also has a strong indirect oxidation effect.

Many scholars found in the experiment that the removal rate increased slowly after one hour of the experiment. Similar to the results obtained in this experiment, researchers generally believe that it is caused by the side reaction of OCl^- at the cathode and anode:

$$2OCl^- + 4H_2O \rightarrow ClO_3^- + ClO^- + 8H^+ + O_2^- + 7e^- \tag{3-13}$$

$$2OCl^- \rightarrow 2Cl^- + O_2 \tag{3-14}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{3-15}$$

Therefore, the test condition of the electrolyte is 0.08 mol/L.

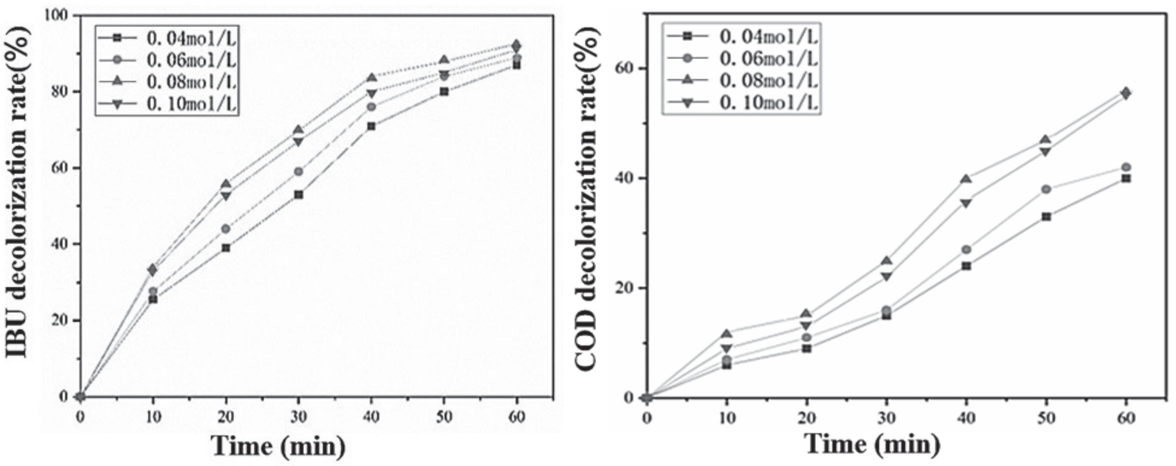


Fig. 6. In simulated PPCPs, NaCl was added as the electrolyte, and the results of electrolysis for 60 min (initial substrate concentration 100 mg/L, initial solution pH 8, electrolysis voltage 15 V, circulation 60 rpm, electrode plate spacing 4 cm).

Effect of Voltage

As shown in Fig. 7., the removal rates of IBU and COD in the system changed with time under the conditions of 10 V, 15 V, 20 V, and 25 V, respectively. Among the factors affecting the electrochemical degradation of IBU, electrolytic voltage plays a decisive role. The DC voltage applied on the two plates directly affects the electron transfer rate, especially the COD removal efficiency, because the application of anode bias can not only effectively improve the oxidation efficiency by minimizing the recombination of electron-hole pairs, but also provide an energy source for direct or indirect electrochemical oxidation of organic pollutants [21]. Both IBU removal rate and COD removal rate increased obviously in electrolysis process. At the same time, when the voltage increased from 10 V to 15 V, the removal rate increased significantly from 88.0% to 92.8%. When the voltage reached 20 V and 25 V, the IBU removal rate was 90.0% and 85.0%, respectively. The essence of the electrochemical reaction process is the transfer and transfer of electrons. Keeping the plate spacing unchanged is equivalent to keeping the internal resistance unchanged. When the voltage applied to the plate increases, the current of the system will also increase according to Ohm ‘s law. The electron transfer rate is accelerated, and the degradation efficiency is also increased. However, when the electrolysis voltage increases from 10 V to 25 V, the removal effect is getting smaller and smaller. Anodic current density increases with the increase of voltage, and then water can be discharged from the surface of the electrode, resulting in the precipitation of O_2 [22]. The excessive DC voltage causes the polarization effect of the plate. These processes are essentially caused by the decomposition of peroxides at the electrolyte interface. The evolution of excess oxygen is likely to be due to the simultaneous reaction of H_2O_2 and OH^- ions. The increase in heat released during electrolysis directly leads to an increase in heat loss, and the decrease in catalytic rate affects the degradation efficiency of IBU [23]. And the author observed the COD degradation and IBU degradation curve is different, at the moment the presence of organic matter is small molecules. Considering the removal effect and practical application, the electrolysis voltage is 15 V in this experiment.

Effect of Electrode Plate Spacing

In the electrochemical reaction of the diaphragm system, the existence of the diaphragm device makes the system resistance become the equivalent resistance of the electrode resistance and the electrolyte resistance in series. The overall resistance relationship of the electrolyte is usually positively correlated with the electrode plate spacing. The distance between the electrodes determines the size of the resistance in the electrolytic cell, the electron transfer distance and the material transfer speed, and affects the energy consumption in the reaction process. As shown in Fig. 8, the research group adjusted the plate spacing to 3, 4, 5, 6 cm respectively, and the other test conditions were the same, and the IBU degradation test was carried out.

When the distance between the anode and cathode is 5 cm, the electrochemical reaction can degrade 96.0% of IBU after 60 min, and the COD removal rate can reach 62.0%. When the plate spacing is too small, due to the narrow reaction space, the pollutant content per unit volume in the efficient degradation area becomes less, and the electric field strength is too large, which will lead to the instantaneous discharge of the plate and the decrease of the regional flow. Too short mass transfer distance will promote the occurrence of anodic passivation reaction and affect the IBU removal efficiency. When the plate spacing is 5 cm, the mass transfer capacity of the solution is improved. However, when the plate spacing is increased to 6 cm,

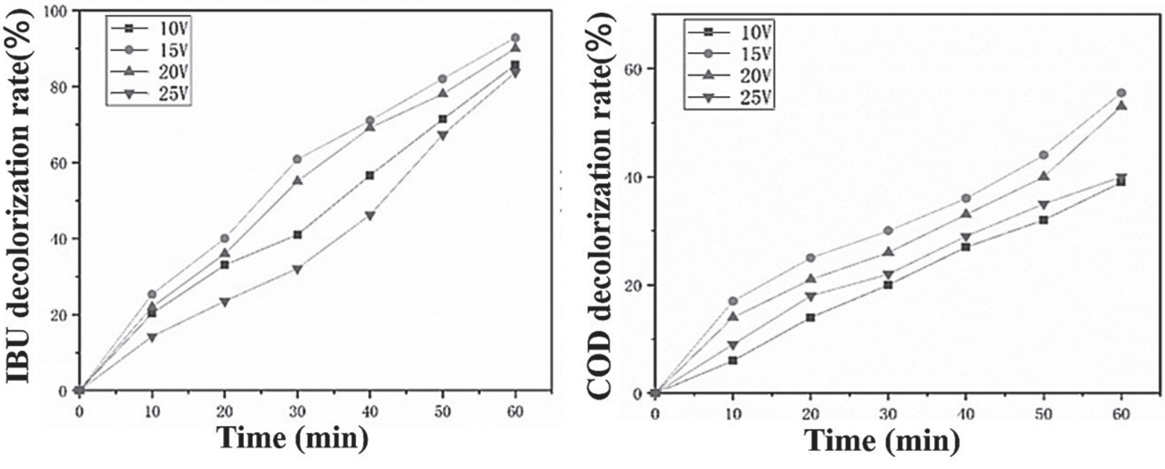


Fig. 7. Results of electrolysis in simulated PPCPs for 60 min (initial substrate concentration 100 mg/L, initial solution pH 8, NaCl concentration 0.08 mol/L, circulation 60 rpm, electrode plate spacing 4 cm).

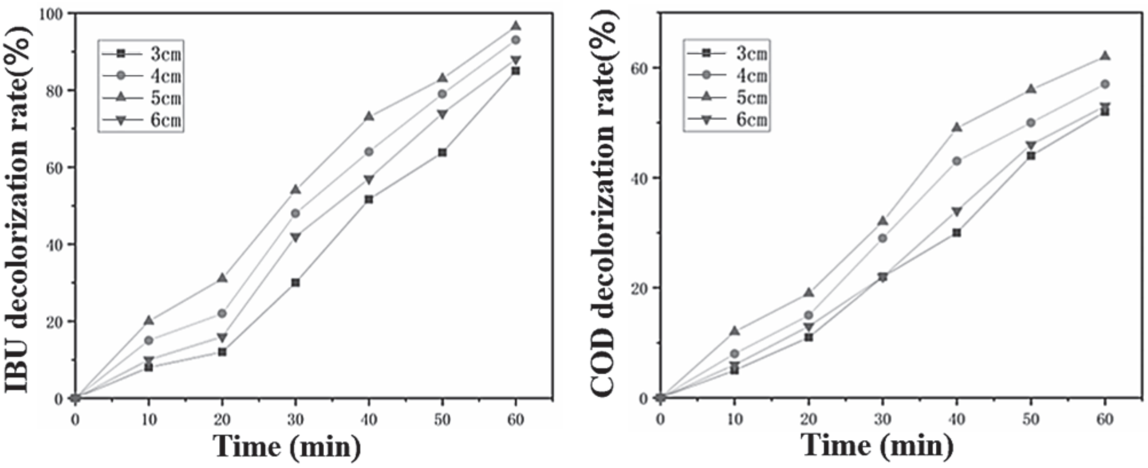


Fig. 8. Results of 60 min electrolysis in simulated PPCP wastewater (initial substrate concentration 100 mg/L, NaCl concentration 0.08 mol/L, initial pH = 8, circulation 60 rpm, electrolysis voltage 15V).

increasing the electrode spacing will inevitably lead to an increase in the resistance of the entire system, thereby reducing the electric field strength of the reactor and indirectly increasing the mass transfer distance. The diffusion path of the active substance is extended, and the migration rate of the organic molecule is slowed down. The electrolysis treatment time also increases accordingly. At this time, the number of active groups effectively participating in the reaction per unit volume will decrease [24]. Therefore, too small or too large plate spacing is not conducive to the degradation of IBU. Therefore, the plate spacing used in the test is 5 cm.

Box-Behnken Design Response Rurface Analysis

In many practical applications, the analysis of experimental data involves the use of numerical programs such as finite element analysis, where performance functions may not be available in explicit form. In these cases, RSM can be used to approximate the implicit performance function. The basic concept of RSM is to fit the actual performance function g(x) in a closed form polynomial function [25], In this study, the research data were analyzed according to DESIGN EXPERT version 10. From the results of the above single factor analysis, it can be seen that the electrode plate distance, electrolysis voltage and electrolyte concentration have a great influence on the degradation effect. Therefore, we selected three factors that affect the degradation rate, namely, the electrolysis voltage, the electrode plate distance and the electrolyte concentration as variables A, B, and C, respectively. The response value is the IBU removal rate Y, where the electrolysis voltage is 15V, the electrode plate spacing is 5 cm, and the electrolyte concentration is 0.08 mol/L. Under this condition, the maximum removal rate was obtained. Under this condition, 5 experiments were repeated to verify the reliability of the regression model. The number of runs for each experiment is: $N = 2^k + 2k + C0$, Substituting $k = 3$, $N = 17$ times. Statistical significance of model equations and parameters was assessed by analysis of variance (ANOVA) and P values (significance level). Table 2 and Table 3 listed the coding level of design factors, response surface design and results respectively.

Table 1. Pre-experimental electrode working conditions.

Anode	Cathode	Diaphragm	Electrolytic voltage (V)	Electroplate spacing (cm)	Electrolyte (mol/L)	PPCPs (mg/L)
Ti	Graphite	None	15	4	0.8	100
Ti/RuO_2	Graphite	None	15	4	0.8	100
Ti/RuO_2/ IrO_2	Graphite	None	15	4	0.8	100
Ti/RuO_2/ IrO_2	Ti	None	15	4	0.8	100
Ti/RuO_2/ IrO_2	Ti	Polyester 739	15	4	0.8	100
Ti/RuO_2/ IrO_2	Ti	Nafion 110	15	4	0.8	100
Ti/RuO_2/ IrO_2	Ti	Nafion 117	15	4	0.8	100

Table 2. Design Factor Coding and Level Experimental design.

Factors	Variable	Level		
		-1	0	1
Electrolytic voltage (V)	A	10	15	20
Electroplate spacing (cm)	B	4	5	6
NaCl concentration (g/L)	C	0.06	0.08	0.10

Table 3. Experimental Design and Results of Response Surface.

Number	Electrolytic voltage (V)	Electroplate spacing (cm)	NaCl concentration (mol/L)	Ibuprofen removal rate (%)
1	10	4	0.08	89.8
2	20	4	0.08	94.2
3	10	6	0.08	90.3
4	20	6	0.08	92.6
5	10	5	0.06	88.4
6	20	5	0.06	92.4
7	10	5	0.10	88.4
8	20	5	0.10	90.3
9	15	4	0.06	93.1
10	15	6	0.06	93.1
11	15	4	0.10	92.9
12	15	6	0.10	91.8
13	15	5	0.08	95.9
14	15	5	0.08	96.4
15	15	5	0.08	96.0
16	15	5	0.08	96.2
17	15	5	0.08	96.2

Optimization Analysis of Removal Rate

The correlation coefficient of the model is $R^2 = 0.9977$, It can accurately fit 99.77 % of the response value change, and the experimental error is very small. The adjusted R_{adj}^2 and predicted R_{pred}^2 were 0.9947 and 0.9813, respectively. The difference between the correction coefficient and the prediction coefficient is only 1.3 %, less than 0.2, indicating that the model has reasonable consistency, and there is a good correlation between the predicted value and the measured value. Coefficient of dispersion CV = 0.2143%, he reliability of the experiment is high. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 51.878 indicates an adequate signal. Therefore, the model meets the requirements of prediction and optimization analysis of operating conditions. The F value of the model is 334.74, indicating that the model is significant. The p value (P) less than 0.05 indicates that it is statistically significant at the 95 % confidence level and has a high degree of significance. The mismatch error of the model is not significantly greater than the pure error, indicating that the model fitting is reliable. From the size of the F value, the order of the three factors affecting the IBU wastewater removal effect is: Electrolytic voltage>Electrolyte concentration>Electrode plate spacing. The IBU degradation efficiency formula generated after fitting is IBU removal rate = $96.14 + 1.57A - 0.28B - 0.45C - 0.53AB - 0.53AC - 0.28BC - 3.63A^2 - 0.78B^2 - 2.63C^2$.

As shown in Fig. 9 to Fig. 11, the contour plots representing the three factors affecting IBU degradation are shown in response. If the shape of the center of the contour map is elliptical, the interaction is significant, and the more round the shape is, the shallower the degree of mutual influence between the factors is. In the response surface diagram, the steep slope indicates that the more sensitive the reaction conditions change, and the color from blue to red indicates that the removal rate increases.

From Fig. 9, we can see that the contour map is elliptical, that is, the interaction between the electrolysis voltage and the electrode plate spacing is significant. The single factor analysis shows that the electrolysis voltage is closely related to the plate spacing, and the combination of high voltage and low plate spacing provides a good mass transfer environment for the system. Through the contour map, it can be seen that the best interval after the interaction of factors is in the electrolytic voltage of 14~16 V, the plate spacing of 4.5~5.5 cm, and the response value in this area is above 96 %. The analysis of the response surface shows that the influence of the electrode voltage on the system is significantly greater than that of the plate spacing. This is because the electrode voltage determines the energy of the system, and the appropriate plate spacing is adjusted to maximize the energy utilization.

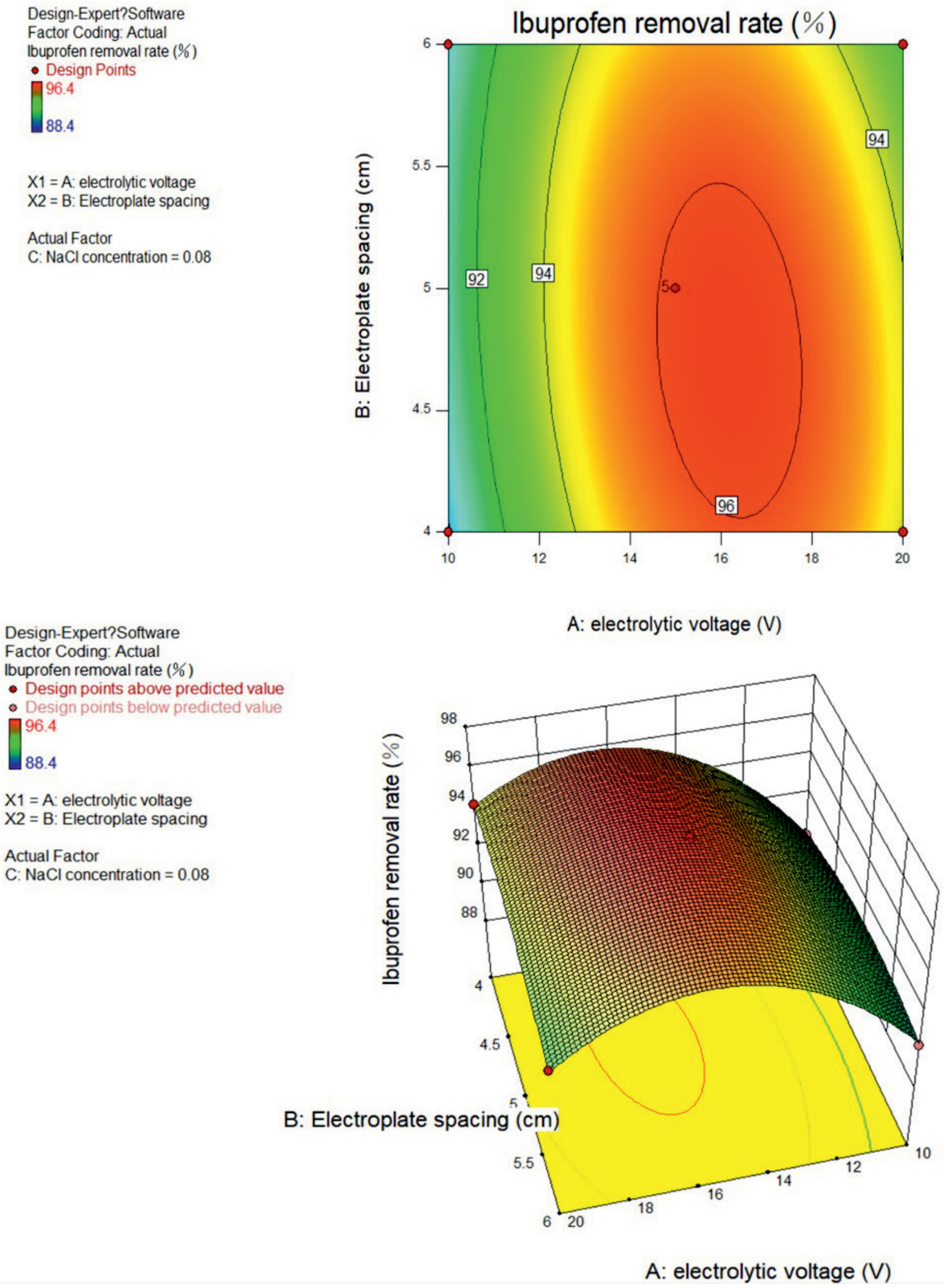


Fig. 9. Contour map of interaction between electrolytic voltage and electroplate spacing (up), response surface map (down).

Fig. 10 shows the interaction effect of electrolysis voltage and NaCl concentration on IBU removal rate. It can be seen from the contour map that the interaction between the factors is significant. When the electrolysis voltage increases from 14 V to 16 V and the NaCl concentration increases from 0.06 mol/L to 0.08 mol/L, the response value is getting closer to the highest domain (IBU removal rate >96%). This is because the conductivity of the solution increases while the number of active particles increases, and the synergistic effect of factors accelerates the degradation of IBU. It can be seen from the response surface diagram that the IBU removal rate is extremely sensitive to both changes, but the effect of electrode voltage is greater than that of electrolyte concentration. The explanation for this phenomenon is that the removal of IBU is restricted by side reactions and H^+ concentration, which are mostly due to the influence of electrolyte. The high concentration of sodium chloride in the solution will lead to the formation of a large number of organic chloride and polymer products, enhanced electrode passivation, current density decreases.

The contour graph in Fig. 11 is slightly rounded, indicating that the interaction between factors is not

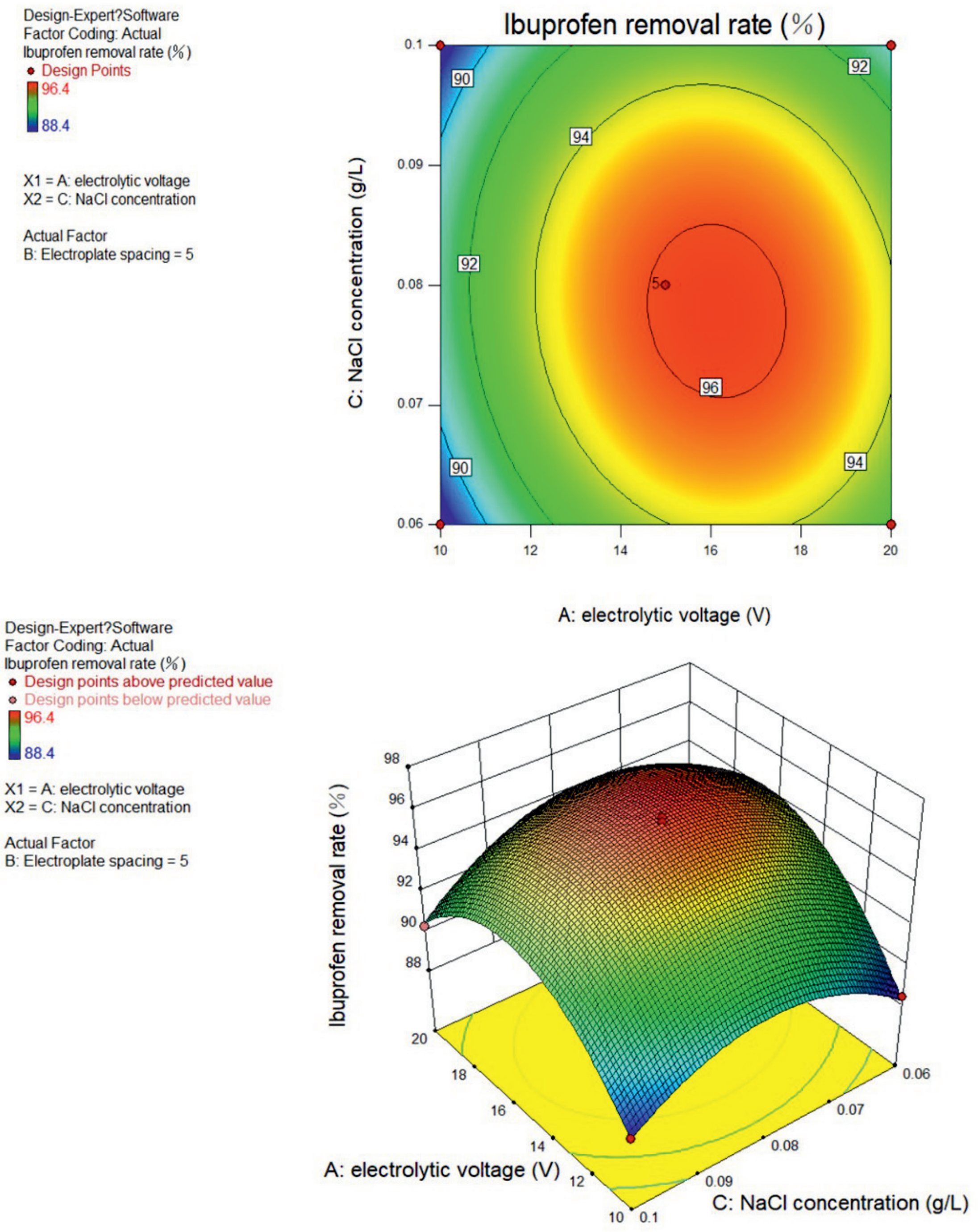


Fig. 10. Contour map of interaction between NaCl concentration and electrolytic voltage (up), response surface map (down).

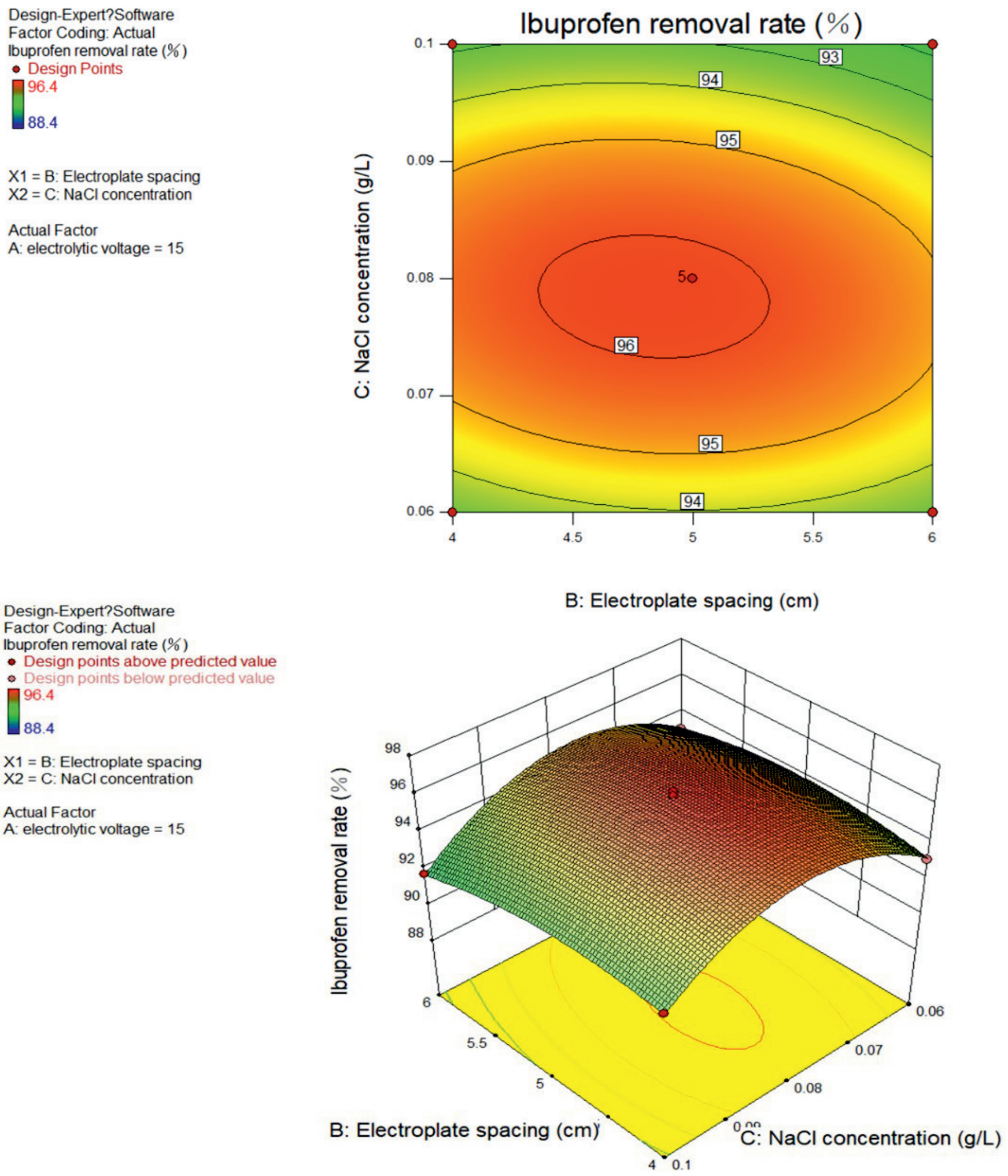


Fig. 11. Contour map of interaction between NaCl concentration and electroplate spacing (up), response surface map (down).

obvious. The information on the figure shows that the influence trend of plate spacing and NaCl concentration on the removal rate is typical first increase and then decrease. When the plate spacing is 4.5-5.5 cm and the electrolyte NaCl concentration is 0.07-0.09 mol/L, the removal of IBU in a large part of the region has a good effect. Although the response surface diagram is not obvious, it can be seen that the influence of NaCl concentration is slightly greater than the influence of plate spacing. This is because the generation of active particles (hypochlorite and hydroxyl radicals) in the system is affected by the electrolyte dosage, and then the mass transfer rate and the length of the mass transfer path. Therefore, the interaction between them is not so obvious, but dominated by electrolytic voltage, the absolute advantage.

Verification of Optimum Experimental Conditions

In order to verify the accuracy of the regression model, combined with the response surface prediction results and the actual situation, the test conditions were taken as follows: electrolysis voltage 16.2 V, NaCl concentration 0.08 mol/L, electrode plate spacing 4.76 cm, and the other conditions were the same. Three repeated tests were carried out to determine the IBU

Table 4. ANOVA results of variance analysis of regression model.

Std. Dev.	0.1989	R-Squared	0.9977
Mean	92.8235	Adj R-Squared	0.9947
C.V. %	0.2143	Pred R-Squared	0.9813
PRESS	2.2375	Adeq Precision	51.8782
-2 Log Likelihood	-21.7443	BIC	6.5879

Table 5. ANOVA Evaluation of regression model.

Project	Sum of	Degree of freedom	Mean	F	P-value	
Model	119.214	9	13.246	334.74	<0.0001	Significant
A-electrolytic voltage	19.845	1	19.845	501.50	<0.0001	
B-Electroplate spacing	0.605	1	0.605	15.29	0.00582	
C-NaCl concentration	1.62	1	1.62	40.94	0.00037	
AB	1.1025	1	1.1025	27.86	0.00115	
AC	1.1025	1	1.1025	27.86	0.00115	
BC	0.3025	1	0.3025	7.64	0.0279	
A^2	55.5581	1	55.5581	1404.00	<0.0001	
B^2	2.5781	1	2.5781	65.15	<0.0001	
C^2	29.1791	1	29.1792	737.38	<0.0001	
Residual	0.277	7	0.0396			
Lack of Fit	0.125	3	0.4167	1.10	0.44734	Not significant
Pure Error	0.152	4	0.038			
Cor Total	119.491	16				

Table 6. Verification of Optimal Test Conditions.

Project	Experimental times			Mean value	Relative error
	1	2	3		
IBU removal rate	95.9	96.5	96.4	96.27	1.14%

removal rate, and the results were shown in Table 6. The average IBU removal rate of three validation experiments was 96.27%, and the relative error was only 1.14% compared with the predicted value of quadratic regression equation. The above results show that the regression of the model is good and the significance is strong.

Analysis of IBU Removal Effect by Other Advanced Oxidation Methods

In order to more effectively analyze and compare the optimal process conditions, treatment effects and technical characteristics of typical PPCPs wastewater treatment by dynamic diaphragm system electrochemical technology, we summarized the research results of different advanced oxidation processes in related fields [26-31], as shown in Table 7. Some processes such as Fenton method still have some limitations such as insufficient reaction energy, which should be explored in combination with other processes to solve this problem. Compared with other processes, the dynamic diaphragm system technology has relatively low pollution and is more economical in terms of its experimental cost. In general, the rational use of advanced oxidation technology can often achieve good results, not only can alleviate the pollution of PPCPs refractory wastewater, but also can get better effluent quality.

Table 7. Verification of Optimal Test Conditions.

System	Experimental condition	Best result	REF
Heterogeneous Fenton-like method with copper/iron doped zirconia as catalyst	In pure water, 200ml of IBU with a concentration of 10 mg/L was added in batches, and H_2O_2 with a mass fraction of 3% was added. Different doped catalysts 250 mg/ L, pH = 5, and treated at 70ºC for 120 min.	ZrSrCu + H_2O_2 and ZrCu + H_2O_2 can achieve 100 % removal of IBU, and the salinity is 52% and 37%, respectively.	[26]
UV/$S_2O_8^{2-}$ and UV/ HSO_5 low pressure UVC were used to activate and degrade pharmaceutical wastewater.	Under the conditions of pH 7.8, UVC flux 4.17 mW/cm², dosage of 0.5~3.0 mM H_2O_2, treatment of 500 μg/L IBU in secondary effluent of WWTP for 30 min at 20ºC.	Under the condition of adding 0.5 mM oxidant, IBU degradation rate: 41 % (UV photolysis) < 86 % (UV/PMS) < 93 % (UV/H2O2) < 96 % (Uv/ Ps)	[27]
Based on Co-doped carbon matrix as persulfate activator, IBU degradation was assisted in a stirred tank reactor.	PH range is 5~7.5, 400 ml IBU concentration is 10 mg/L, 0.4 mM persulfate, 0.2 g/L co-doped carbon matrix in Co-P850/PMS system.	In the Co-P 850/PMS system, IBU can be completely removed within 60 min.	[28]
Different frequencies of ultrasonic activation of persulfate and persulfate degradation IBU	Under the condition of pH = 5,24ºC, 500 ml IBU with a concentration of 0.024 mM was degraded using ultrasonic frequency of 1000 kHz, power of 70 W, 0.03 mM PMS or PS.	The order of degradation rate was: US1000kHz-PDS>US1000kHz-PMS >US1000kHz-H_2O_2. The removal rates of TOC were 72.48%, 63.84 % and 55.97%, respectively. The activation energies of IBP decomposition by temperature were 14.64,10.03 and 18.61 k J/mol, respectively.	[29]
Membrane bioreactor-advanced oxidation process and moving bed biofilm reactor membrane bioreactor-advanced oxidation process combination treatment	A 72 L membrane bioreactor (MBR) at 20ºC was coupled to a photoreactor with a 150 W medium-pressure UV lamp. The 100 ug/L PPCPs wastewater containing IBU was operated in a wastewater treatment plant for 2 months, and 800 mL wastewater was treated in a 25 mg/L H_2O_2 UV/H_2O_2 photoreactor.	IBU was completely removed after MBR treatment, and only 28 μg/L carbamazepine and 0.61 μg/L ciprofloxacin were left in PPCPs wastewater.	[30]
Degradation of IBU by persulfate activated by graphite and SS electrode in a baffleless stirred tank reactor was investigated.	At pH = 7.25ºC, 2 μM IBU was dissolved in electrolyte, 30 mM $NaClO_4$ was added in batches, and 1.0mM persulfate was activated. The effective area of the electrode was 6.25 cm².	Within an hour, (AO, graphite/SS battery) and (SS/graphite battery) can reach 96 % and 68 % removal rate.	[31]

Conclusion

From the electrochemical system of the constructed dynamic diaphragm reaction system, the electrolysis voltage, NaCl concentration and electrode plate spacing have a great influence on the degradation of typical PPCPs. The experimental results proved the feasibility of using the response surface method to optimize the experimental results and the effectiveness of the dynamic diaphragm system electrochemical method for IBU degradation. Among the single factors, the electrolysis voltage, NaCl concentration and electrode plate spacing had the greatest influence on IBU degradation. The design response surface analysis showed that the order of influence on IBU removal rate was electrolysis voltage>NaCl concentration>electrode plate spacing. The optimal conditions were electrolysis voltage 16.2 V, NaCl concentration 0.08 mol /L, and electrode plate spacing 4.76 cm. The degradation rate of IBU can reach 96.27%. The experiment provides a reference for the treatment of PPCPs wastewater.

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Conflict of Interest

The authors declare no conflict of interest.

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