



Optimization of an Electrocatalytic Membrane Reactor for Phenolic Wastewater Treatment by Response Surface Methodology

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ABSTRACT

A TiO₂ loading carbon membrane called TiO₂/carbon electrocatalytic membrane as anode and a stainless steel mesh as cathode constituted an electrocatalytic membrane reactor (ECMR) to treat phenolic wastewater. A synthetic phenol wastewater as the feed was prepared by mixing 10.0 mM phenol and electrolyte (Na₂SO₄) with the concentration of 15 g/L. A systematic experimental design based on the response surface methodology was used to optimize the operating conditions of ECMR. The effects of three-level-four-factors including current density, residence time, pH and temperature and their mutual interactions on the removal rate of COD were investigated. The results showed that two variables of residence time and current density have significant effect on the COD removal rate of phenolic wastewater. The removal rate of COD obtained by the model would be 82.23% at the optimized conditions: current density of 0.33 mA/cm², residence time of 4.77 min, pH of 5.56, temperature of 36.65 °C. The COD removal rate obtained by the experiment was 82.31%. The experimental results were in good agreement on the predicted value obtained. The energy consumption of ECMR was 0.32 kWh/kgCOD during the treatment of 10.0 mM phenolic wastewater at the optimal parameter conditions.

Keywords: Electrocatalytic membrane reactor; phenolic wastewater; response surface methodology; TiO₂/carbon membrane; chemical oxygen demand (COD)

1. INTRODUCTION

In recent decades, phenolic wastewater has been introduced to the environment from a variety of sources such as synthetic chemical plants, petroleum refineries, plastics, textiles, detergent, pesticide and pharmaceutical factories (Qu et al., 2010; Zhu et al, 2007). As a kind of typical phenolic compound, phenol is widely found in many kinds of industrial wastewater. It is harmful to ocean life, live stock, and human beings (Gattrell and Krik, 1990). The treatment of phenolic wastewater has received considerable attention as a result

of the increasingly stringent environmental legislation. Consequently, different treatment techniques such as solvent extraction (Yoon et al., 2011), adsorption (Ma et al., 2013), catalytic wet peroxide oxidation and biological methods (Dosta et al., 2011; Massa et al., 2011), have been employed to treat the wastewater. These technologies, however, have still some disadvantages such as the generation of secondary pollution, high cost, serious corrosion and low efficiency etc.

During the past decades, electrocatalytic oxidation with low toxicity and automatic control has been considered a competitive candidate for industrial wastewater treatment

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(Hsiao and Nobe, 1993). The inherent advantages of the electrocatalytic oxidation are the use of a clean reagent-the electron without the secondary pollution generation. A number of studies on the electro-oxidation of phenol and its derivatives have been carried out. For example, Wei et al. (2011) reported a boron-doped diamond anode (BDD) system for electrochemical oxidation of 2.0 mM phenolic wastewater with a current density of 22 mA/cm². It was found that the removal rate of COD was 70.7% and the energy consumption (EC) was 110 kWh/kg COD with a reaction time of 45 min. Yavuz and Koparal (2006) carried out the electro-oxidation of 1.88 mM phenolic wastewater in a parallel plate reactor using ruthenium mixed metal oxide anode. The removal efficiency of COD obtained in this reactor under a current density of 15 mA/cm² was 85.4% and the EC was 25.9-76.4 kWh/kg COD in 50 min of electrolysis time. Similar results were obtained by Weiss et al. (2007), where a compartment flow reactor with BDD anode was applied to the treatment of 20.0 mM phenolic wastewater. Under a current density of 47 mA/cm², 70.2% of COD was removed with a reaction time of 240 min. And the EC was more than 15.5 kWh/kg COD. In summary, the performances of these electrocatalytic reactors are not so satisfactory on phenolic wastewater treatment due to the low efficiency and high EC (Fockedey and Lierde, 2002). These disadvantages also hinder the extensive application of electrocatalytic oxidation technology.

To solve these challenging problems, a simple strategy of an electrocatalytic membrane (ECMR) reactor was designed for industrial wastewater treatment in our previous work (Yang et al., 2011). Membrane filtration and electrocatalytic oxidation were integrated for wastewater purification. A TiO₂/carbon membrane in ECMR, namely the electrocatalytic membrane, functions both as electrocatalytic anode and filter during the treatment.

The TiO₂/carbon membrane can react with H₂O and O₂ to generate strong oxidizing intermediates (such as ·OH, O₂⁻, HO₂·), to decompose the organic pollutants into CO₂ and H₂O as well as the biodegradable products. Furthermore, Zhang et al. (2012) optimized the operating parameters of ECMR for the treatment of 200 mg/L oily wastewater by response surface methodology (RSM). It was found that the COD removal rate was 97.5% at current density of 0.31 mA/cm² and residence time of 3.8 min. And the energy consumption was 3.30 kWh/kg COD.

As a useful statistical technique, response surface methodology (RSM) is employed to evaluate the relative significance of several affecting factors and complex interactions during many variable optimization processes. RSM is also used for multiple regression and correlation analyses. Its principal advantage is the reduced number of experimental runs required to generate sufficient information for a statistically acceptable result (Jeong et al., 2009). RSM has been widely applied to the optimization of wastewater treatment such as Fenton peroxidation, coagulation-flocculation, electrocatalytic oxidation (Ahmadi et al., 2005; Körbahti et al., 2007; Wang et al., 2007b).

The aim of the present study is to employ the existing ECMR to treat phenolic wastewater and optimize a suitable ECMR design by RSM. The effects of three-level-four-factors such as current density, residence time, pH and temperature etc. and their mutual interactions on the COD removal rate of phenolic wastewater were also investigated.

2. MATERIALS AND METHODS

2.1 Materials and chemicals

The tubular carbon membrane with electrical resistivity of $1.1 \times 10^{-3} \Omega \cdot \text{m}$, an average pore size of 0.41 μm , a porosity of 32.6 %, 8.8 mm

in outer diameter, 5.0 mm in inner diameter was made in our laboratory. All the reagents were of AR and purchased from Kermel (Tianjin Kermel chemical reagent Co., Ltd. China) and used without further purification.

2.2 Preparation of TiO₂/carbon membrane

The tubular carbon membrane was used as the substrate. The membrane was first pretreated in 65 wt. % HNO₃ solution for 30 min, cleaned and dried. The activated carbon membrane was dipped into tetrabutoxide sol for 20 min, then removed from the solution at a certain speed and dried at normal temperature. Finally, the treated membrane was placed in a muffle furnace to sinter at 400 °C for 120 min to prepare the TiO₂/carbon membrane (Yang et al., 2012).

2.3 Electrochemical degradation and analysis of phenolic wastewater

TiO₂/carbon membrane obtained as an anode and a stainless steel mesh surrounding the membrane as a cathode were connected by a DC regulated power supply (M8811, Maynuo Electronics) to constitute an electrocatalytic membrane reactor (ECMR) for the phenol wastewater treatment (Figure 1). The ECMR was operated under current supply of 0.2 mA/cm²-0.4 mA/cm². During the treatment, the wastewater permeated through the membrane from the outside in by means of a suction pump (BT100L, Leadfluid) operating in a dead-end filtration manner and the "clean" water was obtained from the inside.

A parameter termed residence time (RT) was used to describe the relationship between oxidation time of phenol in ECMR and the COD removal rate. RT is the ratio of catalyst volume to the volumetric feed rate per minute. Herein, RT (min) was defined as the ratio of the volume of membrane reactor (cm³) to the

minutely volume of permeate (cm³/min). The RT of phenol in the membrane reactor was controlled by the permeate flux.

The synthetic phenol wastewater chosen for the study could represent the composition of some specific industrial wastewater, especially in chemical synthesis industry. For example, the synthesis process of tribromophenol produced a large number of wastewater containing phenol and inorganic salts. And the synthetic phenol wastewater was considered as the most typical representative of the phenolic wastewater in some literature (Chen et al., 2005; Zhou et al., 2005). The synthetic phenol wastewater was prepared by mixing 10.0 mM phenol and electrolyte (Na₂SO₄) with the concentration of 15 g/L. The pH of the solutions was adjusted by means of H₂SO₄ and NaOH solution. The chemical oxygen demand (COD) of feed and permeate were measured by a portable spectrophotometer (DR2800, Hach). The COD removal rate was calculated by Eq. (1):

$$R = \frac{\text{COD}_f - \text{COD}_p}{\text{COD}_f} \times 100\% \quad (1)$$

where R is the COD removal rate (%), COD_f and COD_p are the COD (g/L) of feed and permeate solution.

The energy consumption (EC) was calculated by Eq. (2) (Wang et al., 2007a):

$$\text{EC} = \frac{UIt}{3.6(\text{COD}_f - \text{COD}_p)V} \times 100\% \quad (2)$$

where U is the voltage applied (V), I is the current intensity (A), V is the volume of the permeate (L), t is the time (s).

2.4 Experimental design

During the treatment, the main parameters of ECMR including current density, RT, pH and temperature were selected as the most influential parameters on the basis of a single-factor experiment (Guan et al., 2013). A four

-level-three-factors Box-Behnken factorial design was adopted to optimize the results and analyze the interaction between these parameters. A summary of the variables and their variation levels was given in Table 1.

3. RESULTS AND DISCUSSION

3.1 Model fitting

In order to study the optimized reaction condition of phenol degradation, a Box-Behnken factorial design with four factors and three levels, including three replicates at the centre point, was used for fitting a second-order response surface. Table 2 showed the factor settings and results according to the Box-Behnken factorial design.

On the basis of the experimental data in Table 2, a second order response surface model fitting in the form of ANOVA was given in Table 3. In general, the values of "P>F" with less than 0.0500 is preferable. It can be seen from Table 3 that the P-value (P>F) obtained by the model was less than 0.0001. It indicated

the model terms are statistically signifi-

cant. The P-values of the coefficients for linear and quadratic effect of RT and current density were all less than 0.0001. It suggested that these two variables have significant influence on the COD removal rate of phenolic wastewater.

The co-efficient (R^2) is measure of goodness of fit. Its value varies from 0.0 to 1.0, with higher values being preferable. In this case, the value of R^2 obtained is 0.9910 as shown in Table 3. This result indicates that the fitted model could explain 99.10% of the variability. The accuracy and general ability of the polynomial model were reliable (Cui et al., 2006). In addition, "Adeq Precision" measures the signal to noise ratio and a ratio is greater than 4.0 being desirable in a model. The ratio obtained was 33.974 as shown in Table 3. It indicated that an adequate signal was proved in this model. It also revealed that this model could be used to navigate the design space (Senthilkumar et al., 2008). In summary, the ANOVA analysis demonstrated that the quadratic regression model could effectively predict the degradation process of phenolic wastewater in ECMR.

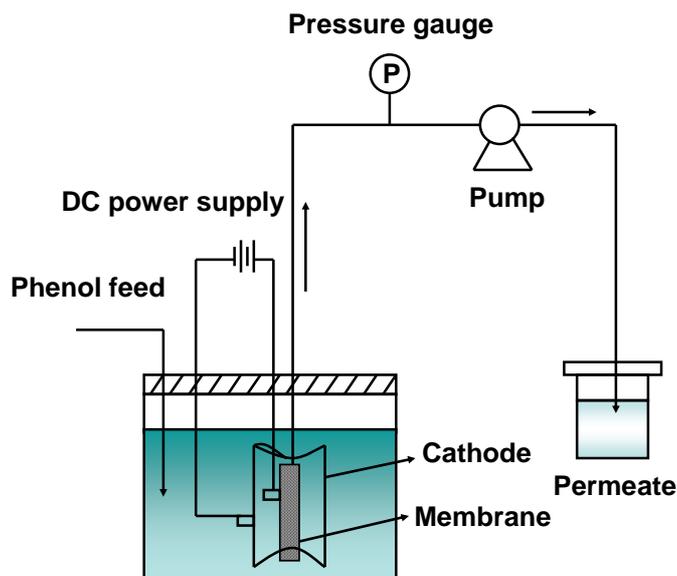


Figure 1 Electrocatalytic membrane reactor

Table 1 Experimental range and levels of the independent variables

Variables	Symbol coded	Range and levels		
		-1	0	1
Current density (mA/cm ²)	X ₁	0.2	0.3	0.4
RT (min)	X ₂	2.6	3.9	5.2
pH	X ₃	4	6	8
Temperature (°C)	X ₄	30	35	40

Table 2 Experimental design and results of the Box-Behnken factorial design

Run	Current density (mA/cm ²)	RT (min)	pH	Temperature (°C)	COD removal rate (%)
1	0	1	-1	0	75.6
2	0	-1	0	1	56.4
3	0	-1	-1	0	51.6
4	0	0	0	0	77.1
5	0	0	0	0	77.3
6	0	0	-1	-1	72.8
7	-1	-1	0	0	46.6
8	-1	0	1	0	57.4
9	0	1	0	-1	76.1
10	1	0	-1	0	72.3
11	-1	0	0	-1	60.3
12	0	1	0	1	81.1
13	0	0	1	1	71.8
14	1	0	1	0	67.5
15	0	-1	0	-1	54.5
16	0	0	1	-1	66.9
17	0	0	0	0	77.4
18	0	0	-1	1	73.3
19	1	0	0	-1	74.1
20	-1	1	0	0	69.2
21	1	0	0	1	72.1
22	1	1	0	0	78.1
23	-1	0	-1	0	63.1
24	-1	0	0	1	64.4
25	1	-1	0	0	54.3
26	0	1	1	0	70.2
27	0	-1	1	0	50.8

Table 3 ANOVA for the quadratic model

	SS	DF	MS	F-value	P>F
Model	2493.02	14	178.07	94.87	< 0.0001
X ₁	274.56	1	274.56	146.28	< 0.0001
X ₂	1543.60	1	1543.60	822.43	< 0.0001
X ₃	48.40	1	48.40	25.78	0.0003
X ₄	17.28	1	17.28	9.20	0.0104
X ₁ X ₂	0.36	1	0.36	0.19	0.6692
X ₁ X ₃	0.20	1	0.2025	0.10	0.7482
X ₁ X ₄	9.30	1	9.3025	4.95	0.0459
X ₂ X ₃	5.29	1	5.29	2.81	0.1190
X ₂ X ₄	2.40	1	2.4025	1.28	0.2800
X ₃ X ₄	4.84	1	4.84	2.57	0.1343
X ₁ ²	266.02	1	266.02	141.73	< 0.0001
X ₂ ²	424.83	1	424.83	226.34	< 0.0001
X ₃ ²	151.23	1	151.23	80.57	< 0.0001
X ₄ ²	12.20	1	12.20	6.50	0.0255
Residual (error)	22.52	12	1.87		
Lack of fit	22.47	10	2.24	96.32	0.0103
Pure error	0.04	2	0.02		
Total	2515.54	26			

Note: SS, sum of squares; DF, degrees of freedom; MS, mean square. CV = 2.04%, R² = 0.9910, Adj R² = 0.9806, Adeq Precision=33.974

Using the designed experimental data (Table 2), the polynomial model was regressed and was shown as below (Eq. 3):

$$Y = 77.26 + 4.78X_1 + 11.34X_2 - 2.00X_3 + 1.2X_4 + 0.3X_1X_2 + 0.22X_1X_3 - 1.52X_1X_4 - 1.15X_2X_3 + 0.77X_2X_4 + 1.1X_3X_4 - 7.06X_1^2 - 8.92X_2^2 - 5.32X_3^2 - 1.51X_4^2 \quad (3)$$

where Y is the response (COD removal rate), and X₁, X₂, X₃ and X₄ are the coded values of current density (mA/cm²), RT (min), pH and temperature (°C), respectively.

3.2 Effect of operation parameters

Regression equation of the model was analyzed using 3D response surface and 2D contour plots. The 3D response surface plots were obtained by plotting the response (COD

removal rate) on the Z-axis against any two variables while the other variables were kept at zero level. Thus three independent response surface plots and their respective contour plots were obtained using Design Expert as shown in Figures 2-4. In order to explore the interaction of RT and temperature on the COD removal rate of phenolic wastewater, the 3D response surface and 2D contour plots of these two variables were presented in Figure 2.

It can be seen in Figure 2 that the COD removal rate increased rapidly from 56.7% to 79.8% with the increase of RT from 2.6 min to 5.2 min. The longer the RT the reaction was carried out in the ECMR, the longer the oxidation process by reactive intermediates was. It showed that the RT was a key factor in the ECMR operation. Simultaneously, only a marginal change of COD removal rate with the variation of reaction temperature from 30

to 40 °C could be observed in Figure 2. The maximum removal rate of COD was observed only at 36.5 °C. This result implied that the temperature exhibits a less significant influence on the COD removal rate. There are two reasons. On the one hand, a higher reaction temperature promoted the collision between reactants and catalyst, resulting in the increase of the reaction rate (Parka et al., 2010). On the

other hand, a higher reaction temperature also leads to the acceleration of oxygen evolution on membrane surface, which further hindered the interfacial oxidation between pollutants and catalyst (Ma et al., 2007). Furthermore, the parallel contour plots of the two axes suggest that the two parameters of RT and temperature were quite independent of each-other.

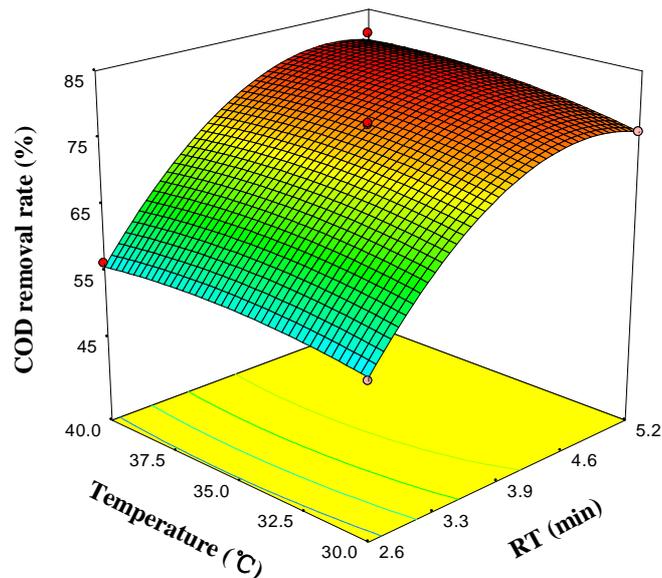


Figure 2 Response surface plot of the relationship between COD removal rate, RT and temperature during the ECMR operation.

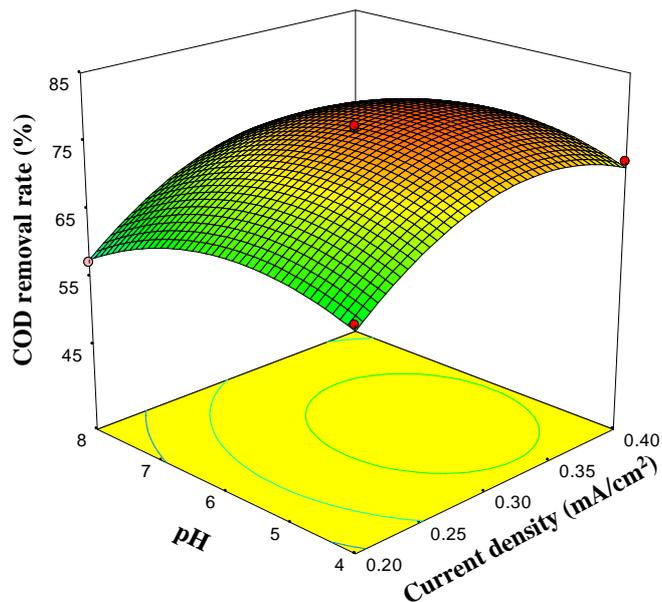
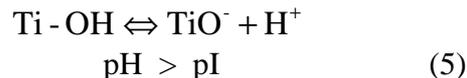
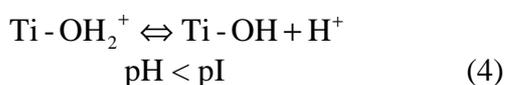


Figure 3 Response surface plot of the relationship between COD removal rate, current density and pH during the ECMR operation.

Similarly, the relationship between the COD removal rate, current density and pH was depicted in Figure 3. As shown in Figure 3, the response showed a significant dependence on the current density. Firstly, the COD removal rate increased from 65.5% to 78.0% with the increase of current density from 0.2 mA/cm² to 0.33 mA/cm². After that, the COD removal rate slightly declined to 74.9% with the increase of current density to 0.4 mA/cm². Such the changes obtained could be explained by the competitive reaction between reactive intermediates generation and oxygen evolution on the TiO₂/carbon membrane (Zhou and He, 2008). The generation rate of reactive intermediates on TiO₂ catalyst increased with an increase in current density at the beginning, which eventually enhanced the phenol degradation. Further to increase the current density, the operation voltage also increased and led to an aggravation of oxygen evolution. The oxygen generated on the membrane would hinder the mass transfer of phenol molecule to the surface of TiO₂ catalyst, thereby resulting in a decline in the COD removal rate.

It also can be found from Figure 3 that the response showed a less significant dependence on pH by comparison with current density. The increase of COD removal rate was only marginal with the variation of pH. Firstly, the COD removal rate increased from 73.9% to 77.5% with the increase of pH from 4.0 to 5.6. After that, the COD removal rate slightly declined to 70.0% with the increase of pH to 8.0. This behavior was attributed to the amphoteric character of TiO₂ (Calza and Pelizzetti, 2001). In electrocatalysis, the adsorbed H₂O molecules on TiO₂ catalyst is dissociated to generate hydroxy radical, leading to the coverage of chemically equivalent metal hydroxyl groups (Ti-OH) on the surface of TiO₂ (Eq. 4-5).



The isoelectric point (pI) of common TiO₂ is 6.3 (Jaffeezia-renault and Pichat, 1986). When the pH was less than pI, there mainly existed TiOH₂⁺ on the surface of TiO₂. When the pH was higher than pI, there were more Ti-OH to be transformed into TiO⁻ on the surface of TiO₂. A variety of negatively charged intermediates including maleic acid, oxalic acid, etc. would be generated in the degradation process of phenol. Owing to the electrostatic interaction between the charged surface of TiO₂ and the protonated intermediates, the negatively charged intermediates were easily adsorbed by TiO₂ catalyst at pH < pI. So a relatively high removal rate of COD was achieved in acid condition. Furthermore, the response surface obtained was elliptical in the entire contour plot in Figure 3. It implied that there was a significant interaction between the two variables of current density and pH. Similarly, an elliptical contour was obtained in Figure 4. It demonstrated that a significant interaction also existed between current density and temperature.

3.3 Validation of the experimental model

The optimal natural values of the selected variables were obtained by solving the regression equation (Eq. 3). The optimal operating conditions of ECMR for phenolic degradation estimated by the model equation were current density of 0.33 mA/cm², residence time of 4.77 min, pH of 5.56 and temperature of 36.65 °C. The maximum COD removal rate obtained by the predict model under the above optimized conditions was 82.23%. In order to verify the prediction of the model, three independent tests for phenolic wastewater treatment were carried out with ECMR at the optimal reaction conditions. The average COD removal rate was 82.31±1.17%. The experi-

mental result was in agreement with that predicted by the model. This demonstrated that RSM can be effectively applied to the optimization of operation process in ECMR.

3.4 Electrocatalytic properties of ECMR

To investigate the electrocatalytic properties of ECMR, the phenolic wastewater with different concentrations were treated by ECMR at the optimal operating conditions obtained in Section 3.2. The relationship between the COD removal rates and EC and the concentration of phenol wastewater (2.0 mM, 5.0 mM and 10.0 mM) during the treatment by ECMR at a constant reaction time of 480 min was illustrated in Table 4.

As shown in Table 4, the COD removal rate decreased from 92.12% to 82.31% with the increase of the phenol concentration in wastewater from 2.0 mM to 10.0 mM. This phenomenon is attributed to the utilization efficiency of reactive intermediates (Zhou and He, 2008). A certain amount of reactive intermediates was generated on TiO_2 catalyst with the same current supply of 0.33 mA/cm^2 .

Therefore, the ratio of reactive intermediates to phenol decreases with the increase of phenol concentration, resulting in the decline of COD removal rate during ECMR operating.

It also can be seen from Table 4 that the EC declined sharply from 1.45 kWh/kgCOD to 0.32 kWh/kgCOD with an increase in the phenol concentration from 2.0 mM to 10.0 mM. This phenomenon could also be explained by the utilization efficiency of reactive intermediates. A higher phenol concentration promotes the collision between reactive intermediates and reactants, leading to the increase of the electrocatalytic efficiency.

Furthermore, the COD removal rate and EC at RT of 0.0 min during the electrocatalytic oxidation of 10.0 mM phenol in ECMR was also shown in Table 4. With an operation time of 480 min, the COD removal rate and EC obtained were 6.12% and 4.35 kWh/kgCOD, respectively. In order to better understand the degradation process of phenolic wastewater, the next plan is to investigate the reaction-separation synergetic mechanism of ECMR.

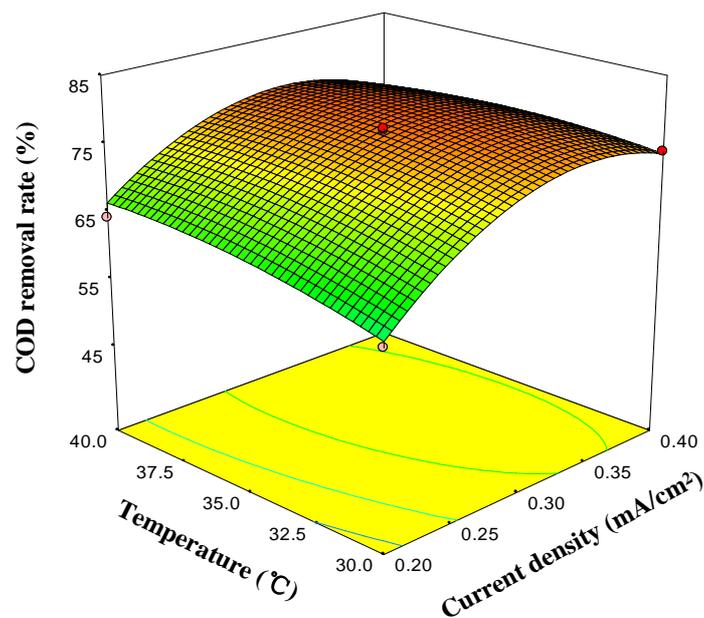


Figure 4 Response surface plot of the relationship between COD removal rate, current density and temperature during the ECMR operation.

Table 4 The COD removal rate and EC of ECMR for phenolic wastewater treatment

RT (min)	4.77			0.0
Phenol (mM)	2.0	5.0	10.0	10.0
COD of feed (mg/L)	482	1201	2406	2406
COD removal rate (%)	92.12	88.24	82.31	6.12
EC (kWh/kgCOD)	1.45	0.60	0.32	4.35

CONCLUSIONS

A systematic experimental design based on the RSM was used to determine the optimal reaction conditions during the phenolic wastewater treatment by ECMR. The optimal values of the variables were obtained as follows: current density of 0.33 mA/cm², residence time of 4.77 min, pH of 5.56 and temperature of 36.65 °C. The predicted COD removal rate was 82.23% during the ECMR operation at the optimum conditions, which was in agreement with the actual value (82.31%). The adjustment of RT and current density was found to have more significant influence on COD removal. The EC of ECMR was 0.32 kWh/kg COD during the treatment of 10.0 mM phenolic wastewater at the optimal parameter conditions.

ACKNOWLEDGEMENTS

This work was financially supported by National Science Foundation of China (Nos. 21076156 and 21206119) and National Program on Key Basic Research Project of China (973 Program) (no.2011CB612311).

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