Optimization of microelectrolysis process for treatment of PNP wastewater by response surface methodology

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Abstract. The simulated p-nitrophenol (PNP) wastewater was treated by micro-electrolysis. The Box-Behnken experimental design model in response surface method was adopted with iron-carbon as a micro-electrolytic filler. Factors such as iron chip dosage, initial pH value of solution and reaction time were used as investigation indexes to study the influence of single factors and their interactions on the PNP wastewater removal rate. The final optimization results show that the experiment has a good removal rate of PNP, with only a small difference from the predicted value. It can be seen that the response surface method is feasible and suitable for the process optimization of p-nitrophenol wastewater treatment by micro-electrolysis, which can be applied to engineering practice through further research and improvement.

1. Introduction
In recent years, organic wastewater has been widely involved in many industries such as medicine, printing and dyeing, pesticide, chemical industry[1]. As a result, the wastewater has the characteristics of concentration of organic matter, large odor, long residual time, poor biodegradability, etc[2]. Traditional water treatment methods are difficult to effectively treat, while micro-electrolysis technology [3] is a comprehensive water treatment technology with simple operation, low cost, improvement of biodegradability, resource utilization of waste and other characteristics. Zhang M.H., et al.[4] pretreated TNT wastewater by iron-carbon micro-electrolysis. After testing, most of the large molecular organic matter was decomposed and transformed to different degrees. Yang L., et al.[5] pretreated denim printing and dyeing wastewater with iron-carbon micro-electrolysis method, and obtained a removal rate of 49.2% and chroma removal rate of 80% by controlling initial reaction conditions.

In addition, response surface methodology (RSM) is introduced, which is a statistical method to solve multivariate problems. The purpose of this experiment is to provide the necessary basic data and theoretical guidance to improving the effectiveness, environmental friendliness, and application of this technology in the industrial treatment of refractory organic pollutants.

2. Methods
The simulated p-nitrophenol wastewater with a mass concentration of about 200 mg/L was prepared in 200mL, and the initial pH was adjusted. The pretreatment activated carbon and iron scrap were added into the simulated p-nitrophenol wastewater in a certain proportion, and the mixture was continuously stirred on the coagulation test mixer. At the end of the experiment, sodium hydroxide solution was added to precipitate the Fe³⁺ in the wastewater. After the precipitation, water samples were absorbed into the colorimetric tube with a syringe equipped with a 0.45 micron needle filter. Two drops of
NaOH solution were added and the pH was adjusted by shaking. The absorbance of the water sample was detected by UV spectrophotometer, and the corresponding removal rate was calculated.

3. Results and Discussion

3.1 Experimental design and result

Experiments of 3 factors and 3 levels were designed (coded as -1, 0, 1).

Table 1. Experimental factors and levels of response surface design

| Level | Factor A (g·L⁻¹) | Factor B | Factor C (min) |
|-------|-----------------|----------|----------------|
| -1    | 40              | 2.0      | 100            |
| 0     | 50              | 3.0      | 120            |
| 1     | 60              | 4.0      | 140            |

Table 2. Experimental design results of Box-Behnken

| No. | A  | B  | C   | Removal rate/% |
|-----|----|----|-----|----------------|
| 1   | -1 | -1 | 0   | 81.92          |
| 2   | 1  | -1 | 0   | 91.17          |
| 3   | -1 | 1  | 0   | 80.80          |
| 4   | 1  | 1  | 0   | 90.09          |
| 5   | -1 | 0  | -1  | 80.91          |
| 6   | 1  | 0  | -1  | 90.44          |
| 7   | -1 | 0  | 1   | 82.16          |
| 8   | 1  | 0  | 1   | 94.10          |
| 9   | 0  | -1 | -1  | 90.57          |
| 10  | 0  | 1  | -1  | 86.81          |
| 11  | 0  | -1 | 1   | 94.38          |
| 12  | 0  | 1  | 1   | 93.95          |
| 13  | 0  | 0  | 0   | 93.55          |
| 14  | 0  | 0  | 0   | 93.55          |
| 15  | 0  | 0  | 0   | 93.55          |
| 16  | 0  | 0  | 0   | 93.55          |
| 17  | 0  | 0  | 0   | 93.55          |

According to the data in Table 2, the regression equation between the variable and the removal rate of PNP was obtained, as shown in equations (1):

\[ Y_1 = 93.55 + 5.00A - 0.94B + 1.84C - 0.02AB + 0.60AC - 0.58BC - 5.33A^2 - 2.22B^2 - 1.31C^2 \] (1)

Table 3. PNP removal rate variance analysis table

| Source           | Sum of Squares | df | MeanSquare | FValue | p-value | p-value   |
|------------------|----------------|----|------------|--------|---------|-----------|
| Model            | 396.08         | 9  | 44.01      | 57.94  | <0.000  | Significant|
| Residual         | 5.32           | 7  | 0.76       |        |         |           |
| Lack of Fit      | 5.10           | 3  | 1.77       | 10.82  | 0.0151  | Significant|
| Pure Error       | 0.22           | 4  | 0.055      |        |         |           |
| Cor Total        | 401.40         | 16 |            |        |         |           |

C.V. = 0.98%; \( R^2 = 0.9868 \); \( \text{Radj}^2 = 0.9697 \); \( R^2\text{Pred} = 0.8881 \); Precision = 21.399

As shown in Table 3, the order of influence of each factor on the removal effect of PNP was obtained by F test: Adding amount of iron scrap > initial pH value > reaction time. F and P values show
that the regression model is very significant, which indicates that the model is reliable in predicting the removal rate of PNP. $R^2=0.9868; \text{Radj}^2=0.9697; R^2\text{Pred}=0.8881$, the difference between them is 0.0816 and the precision of the experiment was 21.399. It was generally considered that the better condition of the model was that the precision was greater than 4, which further indicated the model could well predict the experimental results.

The optimal predicted value obtained by response surface model optimization is: iron scrap dosage 50.58 g/L, pH value 2.52, reaction time 120 min. In PNP wastewater with a mass concentration of 200 mg/L under this condition, the removal rate of PNP reached 95.76%.

### 3.2 Response surface analysis and optimization

As shown in Figures 1, 2 and 3, the contour density moving to the peak along factor A is significantly higher than that of B, while B is higher than C. This indicates that the amount of iron filings contributes the most to the effect value. In Figure 1 and Figure 2, the contour line is obviously oval and the response surface has a steep slope. It can be seen that the iron chip addition has significant interaction with the initial pH value of the solution, the iron chip addition and the reaction time, which has a significant influence on the removal effect of PNP.

According to the analysis, the addition of iron chips can increase Fe$^{2+}$ and new ecology [H]. At the same time, the removal ability of PNP by micro-electrolysis was improved. Fe$^{2+}$ in water is easy to be
oxidized to form Fe(OH)$_3$ colloid, which can reduce PNP of wastewater to a certain extent. In the case of fewer iron filings, a small amount of Fe can have a certain removal effect on PNP. When the system is acidic and neutral, the removal rate of PNP will decrease with the increase of pH. But when the system is in alkaline condition, the removal rate of PNP decreases rapidly. Because the potential difference of galvanic cells is reduced, the reaction efficiency of the electrode is reduced. Meanwhile, Fe$^{2+}$ is easy to be consumed by OH$^-$ to generate a large amount of Fe(OH)$_2$ and Fe(OH)$_3$ precipitation, so the growth rate of removal of PNP decreased.

4. Conclusion
(1) The results obtained from the Box-Behnken model are highly reliable. The interaction between the amount of iron chip added and the initial pH value of the solution, the amount of iron chip added and the reaction time will significantly affect the removal rate of PNP, while the interaction between pH and the reaction time is relatively weak.

(2) The final optimization conditions were as follows: the iron scrap dosage was 50.58mg/L, the pH was 2.52, and the reaction time was 120min. Under this condition, the maximum removal rate of PNP is 95.76%. The results show that the process parameters of iron-carbon microelectrolysis technology are reliable.

Acknowledgments
I would like to thank the teachers in the school and laboratory for their help in my research and writing with my co-authors. We would also like to thank the postdoctoral fund of Shenyang Jianzhu University and the innovative talent support program of higher education institutions of Liaoning province in 2018 for their joint help in providing financial support for our research.

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