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# Optimization of Fenton Process for Treatment of Landfill Leachate Using Response Surface Methodology

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In the paper, the treatment of the landfill leachate from Chongqing landfill by Fenton process was studied. Response surface methodology (RSM) and Box-Behnken central design had been applied to describe and optimize chemical oxygen demand (COD) removal efficiency of landfill leachate treatment using pH value, $H_2O_2$ dosage and $FeSO_4·7H_2O$ dosage by Fenton process. The mutual interactions between three independent variables, *viz*. pH value, $H_2O_2$ dosage and $FeSO_4·7H_2O$ dosage were obtained. The results revealed that the most influential variable under selected reaction conditions were pH value. The optimized conditions for landfill leachate treatment were as follows: pH value of 3.2, $H_2O_2$ dosage of 1.1 % and $FeSO_4·7H_2O$ dosage of 0.4 %. Under these conditions, the maximum chemical oxygen demand removal efficiency of 59.1 % was achieved. This experimental value was in a good agreement with predicted one, which proved the validity of the model. Chemical oxygen demand analysis showed the landfill leachate could be effectively chemical oxygen demand removal by Fenton process.

**Keywords: Landfill leachate, Treatment, Fenton process, Response surface methodology.**

## INTRODUCTION

Landfill leachate is formed when the refuse moisture content exceed its field capacity, which is defined as the maximum moisture that can be retained in a porous medium without downward percolation[1]. Landfill leachate is a complex and high strength wastewater, characteristically rich in organic matter, ammonia, heavy metals and toxic materials such as xenobiotic organic compounds. Also, waste type and compaction, landfill hydrology, climate and particularly, landfill age have an influence to the amount and composition of landfill leachate[2,3]. According to the survey[4,5], three types of leachate can be classified by landfill age *i.e.*, young, intermediate and stabilized (Table-1). In general, young leachate is highly contaminated with organic compounds, ammonia, halogenated hydrocarbons and heavy metals. Nevertheless, with increasing landfill age, the produced leachates are characterized by the presence of substantial quantities of recalcitrant, difficult-to-treat, hard chemical oxygen demand compounds. There are various treatments for reducing the contents of organic matter such as leachate transfer, chemical and physical methods[6], membrane processes[7] and biodegradation. Physical and chemical processes include reduction of suspended solids, colloidal particles, floating material, color and toxic compounds by either coagulation-flocculation, adsorption, advanced oxidation, *etc*. Physico-chemical treatments for the landfill leachate are used in addition at the treatment line (pre-treatment or last purification) or to treat a specific pollutant[3]. Particularly, advanced oxidation processes, namely photo-Fenton, Fenton-like, Fenton and UV/$H_2O_2$, have been reported as powerful technologies capable of degrading a wide variety of refractory compounds from landfill leachate[8].

TABLE1
CLASSIFICATION AND COMPOSITION OF LANDFILL LEACHATE WITH AGE

| Leachate type | Young | Intermediate | Stabilized |
|---|---|---|---|
| Age (years) | < 5 | 5-10 | > 10 |
| pH | < 6.5 | 6.5-7.5 | > 7.5 |
| BOD/COD | 0.5-1 | 0.1-0.5 | < 0.1 |
| COD(mg·$L^{-1}$) | > 10,000 | 4000-10,000 | < 4000 |
| $NH_3$-N(mg·$L^{-1}$) | < 400 | N.A. | > 400 |
| Heavy metals | Low-medium | Low | Low |
| Biodegradability | High | Medium | Low |

N.A.-Not applicable

While, the Fenton method is more efficient and implies a lower capital cost than other advanced oxidation processes. The Fenton process is based on the electron transfer between

$H_2O_2$ and ferrous ion ($Fe^{2+}$), which acts as a homogenous catalyst, yielding hydroxyl radicals ($^{\bullet}OH$) that can degrade organic compounds[9]. Generally, Fenton process is composed of following stages: pH adjustment, oxidation reaction, neutralization, coagulation and solid-liquid separation[10]. Both oxidation and coagulation played important roles in the removal of organics. It is important to understand the mutual relationships between reaction parameters in terms of hydroxyl radical production and consumption, in order to understand better and improve Fenton reaction.

The statistical method of response surface methodology has been proposed to include the influences of individual factors as well as their interactive influences[11]. Response surface methodology is very useful for designing experiments, building models, evaluating the effects of the several independent variables and searching optimum conditions for desirable responses. The main advantage of RSM is the reduced number of experimental trials needed to find optimum conditions for desirable responses[12,13]. It has been reported that RSM has been applied to optimize and evaluate the interactive effects of independent factors in Fenton's and Fenton-like processes for wastewater treatment such as humic acid (HA), herbicides aqueous or laboratory wastewaters[14]. Zheng *et al.*[15] proposed that pH, initial chemical oxygen demand and their interaction gave negative effects whilst $Fe^{2+}$ dosage and $H_2O_2/Fe^{2+}$ mole ratio showed positive effect on chemical oxygen demand removal. Despite the existent several studies carried on the treatment of landfill leachate by the Fenton process, if it is applied as the only treatment process, it can be expensive. So, it is important to determine the best treatment option as well as the optimal operation conditions required to achieve the maximum removal of recalcitrant compounds.

In this study, chemical oxygen demand removal efficiency of landfill leachate treatment by Fenton process was investigated. The optimization of the reaction parameters for the Fenton process of landfill leachate was performed using response surface methodology and experimental design. The chemical oxygen demand removal efficiency was selected as the response for optimization and functional relationship between the response and the independent variables (pH value, $H_2O_2$ dosage and $FeSO_4{\cdot}7H_2O$ dosage) was established by means of experimental design.

## EXPERIMENTAL

All the reagents used in this study were analytical grade. The reagents include hydrogen peroxide solution, hydrochloric acid, sodium hydroxide and iron vitriol ($FeSO_4{\cdot}7H_2O$). All aqueous solutions and standard solutions were prepared with deionized water.

**Instruments used in the experimental setup were as follows:** ZR4-6 Jar Tester supplied by Zhongrun Water Industry Technology Development Co. Ltd., Shenzhen, China; pH meter: Delta 320 pH meter was supplied by Mettler Toledo Instruments Co., Ltd., Shanghai, China; chemical oxygen demand analyzer DR2800 was supplied by HACH, USA.

**Water sample:** The water samples were collected from Changshou Bridge landfill site in Chongqing, China. The wastewater was dark brown appearance and effluvium. The chemical analysis of the water samples showed the concentrations of turbidity, chemical oxygen demand, $NH_3^-$-N and pH value were 495-550 NTU, 3750, 2963 and 7.88 mg $L^{-1}$, respectively.

**Fenton process:** The Fenton process serves both oxidation and coagulation functions. In the oxidation step, 500 mL of landfill leachate was transferred into a beaker and the initial pH of the wastewater was adjusted to the set value using 0.5 N HCl and 0.5 N NaOH. A certain amount of $H_2O_2$ and $FeSO_4{\cdot}7H_2O$ were added to the water sample, at the same time, the water sample was mixed rapidly by a program controlled jar test apparatus (ZR4-6). In the coagulation step, the above oxidized water sample was slowly mixed at 50 rpm for 10 min and then allowed to stand still 60 min for sedimentation to take place. The supernatant sample was extracted from the beaker for measurement of chemical oxygen demand. The chemical oxygen demand was measured according to procedures described in standard methods (1995).

**Response surface methodology design:** Box-Behnken central design was chosen for finding out the relationship between the response function (Y) and variables (X)[16]. A 23 full factorial design is constructed in order to determine the effects of the main variables and the interactions between variables. A total of 15 experiments, including three replicates at the centre point and six star points were performed. For statistical calculations, the variables Xi were coded as xi according to the following relationship eqn. (1):

$$x_i = \frac{X_i - X_o}{\Delta x} \quad (1)$$

where $x_i$ is the dimensionless coded value of each independent variable, $X_0$ is the value of $X_i$ at the centre point and $\Delta x$ is the step change value[17]. pH value ($X_1$), $H_2O_2$ dosage ($X_2$) and $FeSO_4{\cdot}7H_2O$ dosage ($X_3$) were chosen as independent variables in this study. The response (Y) during all experimental design was chemical oxygen demand removal efficiency (%). Values of the independent variables and their variation limits were determined basing on the related scientific literature and previous experimental results 18 and are presented in Table-2. Low and high levels are denoted as (-1) and (+1), respectively.

TABLE-2
EXPERIMENTAL RANGES AND SIGNIFICANT LEVELS OF FACTORS

| Variables | Code | | Ranges and levels | | |
|---|---|---|---|---|---|
| | Coding | Non-coding | -1 | 0 | 1 |
| pH | $x_1$ | $X_1$ | 3 | 5 | 7 |
| $H_2O_2$ dosage (%) | $x_2$ | $X_2$ | 0.5 | 1 | 1.5 |
| $FeSO_4{\cdot}7H_2O$ dosage (%) | $x_3$ | $X_3$ | 0.2 | 0.4 | 0.6 |

The experimental result was analyzed using design expert 8 software and fitted by a polynomial response equation. Quadratic equation for the variables was as follow relationship eqn. (2):

$$Y = \beta_0 + \sum_{i=1}^{f} \alpha_i X_i + \sum_{i=1}^{f} \alpha_{ii} X_i^2 + \sum_{i=1}^{f} \sum_{j>1}^{f} \alpha_{ij} X_i X_j + \varepsilon \quad (2)$$

where Y is the predicted variable (chemical oxygen demand removal efficiency), $X_i$ and $X_j$ are the factors that influence the predicted response Y; $\beta_0$ is the constant coefficient, $\alpha_i$, $\alpha_{ii}$ and $\alpha_{ij}$ are the coefficient of linear, f is the number of independent test variables, ε is a random error. The feasibility of the quadratic equation model between the test and response variables were established using analysis of variance (ANOVA). The quality of the fit of polynomial model was expressed by the value of determination coefficient ($R^2$). The statistical significance was checked by F-test and P-values.

## RESULTS AND DISCUSSION

**Model fitting:** In the previous study[14], the influence of various parameters on chemical oxygen demand removal was investigated by classical univariate method using $H_2O_2$ and $FeSO_4{\cdot}7H_2O$. In order to overcome the disadvantages of single-factor methodology, the influence of selected parameters was investigated by means of experimental design methodology. The results from previous work showed that pH adjustment, $H_2O_2$ dosage and $FeSO_4{\cdot}7H_2O$ dosage have great effects on Fenton process and therefore these variables were selected for process optimization.

Table-3 describes the factorial design of experiments, including the codified experimental values and observed and predicted chemical oxygen demand removal efficiency. Central point experiments (denoted as 0) were repeated three times in order to check the reproducibility and obtain the standard deviation of the experimental response.

TABLE-3
BOX-BEHNKEN RESPONSE SURFACE EXPERIMENTAL DESIGN AND RESULTS

| No. | Factor 1 | Factor 2 | Factor 3 | Chemical oxygen demand removal efficiency (Y/%) | |
|---|---|---|---|---|---|
| | $X_1$ | $X_2$ | $X_3$ | Observed | Predicted |
| 1 | 5.0 | 1.5 | 0.6 | 47.0 | 48.0 |
| 2 | 5.0 | 1.5 | 0.2 | 42.8 | 43.0 |
| 3 | 5.0 | 1.0 | 0.4 | 50.4 | 50.4 |
| 4 | 3.0 | 1.0 | 0.2 | 47.3 | 48.0 |
| 5 | 7.0 | 1.0 | 0.6 | 38.3 | 37.6 |
| 6 | 7.0 | 0.5 | 0.4 | 33.6 | 34.5 |
| 7 | 3.0 | 1.0 | 0.6 | 48.8 | 48.7 |
| 8 | 5.0 | 1.0 | 0.4 | 50.4 | 50.4 |
| 9 | 3.0 | 0.5 | 0.4 | 47.8 | 48.1 |
| 10 | 3.0 | 1.5 | 0.4 | 51.5 | 50.6 |
| 11 | 5.0 | 0.5 | 0.6 | 41.8 | 41.6 |
| 12 | 7.0 | 1.5 | 0.4 | 39.2 | 39.0 |
| 13 | 5.0 | 1.0 | 0.4 | 50.4 | 50.4 |
| 14 | 7.0 | 1.0 | 0.2 | 33.8 | 33.9 |
| 15 | 5.0 | 0.5 | 0.2 | 43.2 | 42.2 |

The obtained results indicate that the experimental values of chemical oxygen demand removal efficiency are close to the predicted ones in all set of experiments. The highest efficiency of 51.5 % and the lowest efficiency of 33.6 % were observed. By using the obtained experimental results, a regression model relating the response to the variables for the chemical oxygen demand removal of Fenton process was developed. The relationship is given in the following polynomial equation, eqn. (3):

$$\text{COD removal rate} = 17.17813 + 6.90*pH + 18.45*H_2O_2 + 58.875*FeSO_4{\cdot}7H_2O + 0.475*pH*H_2O_2 + 1.875*pH*FeSO_4{\cdot}7H_2O + 14*H_2O_2*FeSO_4{\cdot}7H_2O - 1.12813*pH^2 - 11.45*H_2O_2^2 - 95.9375*FeSO_4{\cdot}7H_2O_2 \quad (3)$$

**Statistical analysis:** The significance and adequacy of the model was investigated using the analysis of variance (ANOVA) and the results are shown in Table-4. Considering only the first-order effect, the chemical oxygen demand removal efficiency was improved at low pH value ($X_1$), middle $H_2O_2$ dosage ($X_2$) and middle $FeSO_4{\cdot}7H_2O$ dosage ($X_3$) in the selected range of variables. According to parameter estimate and the corresponding *p*-values, the second one variety being pH produce the largest effects on chemical oxygen demand removal efficiency ($p < 0.0001$), while the effect of $FeSO_4{\cdot}7H_2O$ dosage is least significant ($p = 0.0228$) in tested range. The above analysis of variance shows that the model is significant effect was followed by pH adjustment, $H_2O_2$ dosage and $FeSO_4{\cdot}7H_2O$ dosage. Fig. 1 showed the relationship between predicted value and observed value, indicated that the prediction model is less deviation degree. In addition, high value for Fisher F test (F model = 60.96) and a very low probability value (P model > F = 0.0001) obtained in our study indicated that employed model is highly significant. Besides, the high value of the determination coefficient, $R^2 = 0.9910$, indicated a strong correlation between predicted and observed value. In order to increase the reliability of the model prediction, high value for adjusted determination coefficient (adjusted $R^2 = 0.9747$) indicating that 97.47 % of the result of the total variations can be explained by suggested model. This also means that the model does not explain only about 2.53 % of variation. From the above investigation, it showed that the model was adequate to predict the chemical oxygen demand removal efficiency.

TABLE 4
ANALYSIS OF VARIANCE (ANOVA)

| Source | Sum of Squares | df | Mean Square | F-Value | *p*-Value | Remark |
|---|---|---|---|---|---|---|
| Model | 503.91 | 9 | 55.99 | 60.96 | 0.0001 | Signif. |
| A-pH | 318.78 | 1 | 318.78 | 347.07 | < 0.0001 | |
| B-$H_2O_2$ dosage | 24.85 | 1 | 24.85 | 27.06 | 0.0035 | |
| C-$FeSO_4{\cdot}7H_2O$ dosage | 9.68 | 1 | 9.68 | 10.54 | 0.0228 | |
| AB | 0.9 | 1 | 0.9 | 0.98 | 0.3671 | |
| AC | 2.25 | 1 | 2.25 | 2.45 | 0.1783 | |
| BC | 7.84 | 1 | 7.84 | 8.54 | 0.0330 | |
| $A^2$ | 75.19 | 1 | 75.19 | 81.86 | 0.0003 | |
| $B^2$ | 30.25 | 1 | 30.25 | 32.94 | 0.0023 | |
| $C^2$ | 54.37 | 1 | 54.37 | 59.20 | 0.0006 | |
| Residual | 4.59 | 5 | 0.92 | | | |
| Cor. Total | 508.50 | 14 | | | | |

$R^2 = 0.9910$, adjusted $R^2 = 0.9747$

**Response surface model analysis:** The 3D response surface plot and 2D contour map are generally the graphical representation of the regression equation. This representation showed the relative effects of any two variables when the remaining variable is kept constant. Using Design Expert 8.0 software analysis, response surface plot and contour map on any two variables describes in Figs. 2 to 4. Fig. 2a showed the

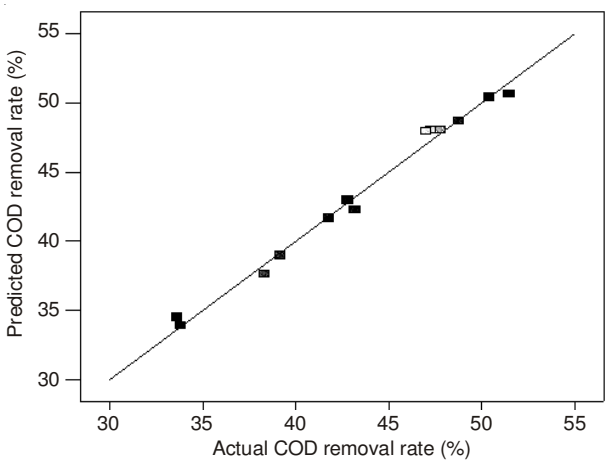


Fig. 1. Relationship between predicted value and observed value

response surface slope is relatively flat, indicated that $H_2O_2$ dosage and $FeSO_4{\cdot}7H_2O$ dosage produce the less effects on chemical oxygen demand removal efficiency. Fig. 2b shows there was a significant interaction between $H_2O_2$ dosage and $FeSO_4{\cdot}7H_2O$ dosage. Therefore, the response was provided with "maximize" the chemical oxygen demand removal efficiency in the selected range of variables. Figs. 3 and 4 showed that the response surface slope is relatively abrupt, indicated that pH value produce the largest effects on chemical oxygen demand removal efficiency. Decreasing pH value, the number of active sites increases and therefore the chemical oxygen demand removal efficiency increases.

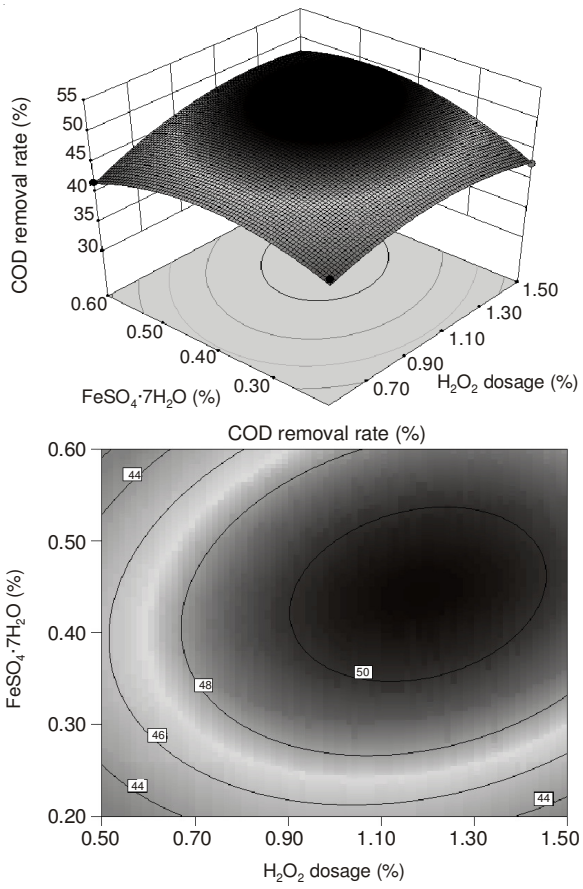


Fig. 2. Response surface plot (a) and contour map (b) on $H_2O_2$ dosage and $FeSO_4{\cdot}7H_2O$ dosage

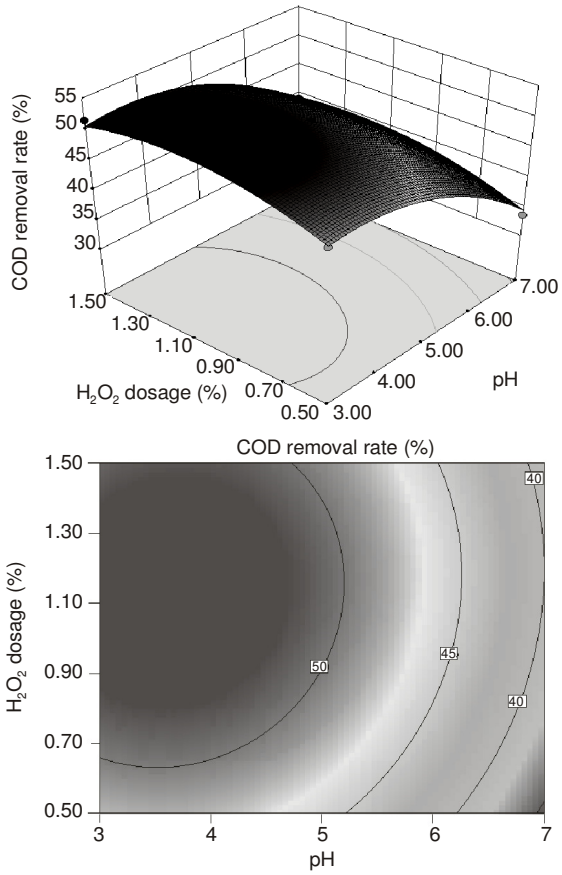


Fig. 3. Response surface plot (a) and contour map (b) on pH and $H_2O_2$ dosage

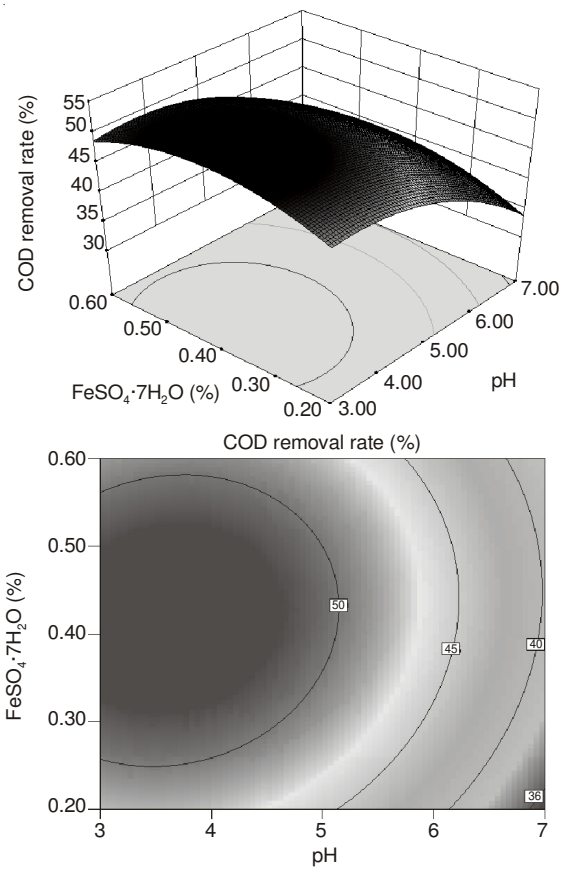


Fig. 4. Response surface plot (a) and contour map (b) on pH and $FeSO_4{\cdot}7H_2O$ dosage

**Optimization of Fenton process:** In order to determine the optimum point, the model (eqn. 3) predicted the landfill leachate chemical oxygen demand removal efficiency of 59.2 % could be achieved at leachate pH of 3.2, $H_2O_2$ dosage of 1.1 % and $FeSO_4 \cdot 7H_2O$ dosage of 0.4 % using the Design Expert 8 software response analysis. Three groups of parallel verification experiment was carried out, the average landfill leachate chemical oxygen demand removal efficiency chemical oxygen demand is 59.1 %. Here, the obtained results indicated that the experimental values of chemical oxygen demand removal efficiency are very close to the predicted one in the model and the error is only ± 0.1 %.

## Conclusion

In this study, the response surface model of landfill leachate treatment is significant effect was followed by pH value, $H_2O_2$ dosage and $FeSO_4 \cdot 7H_2O$ dosage. The model (eqn. 2) predicted the landfill leachate chemical oxygen demand removal efficiency of 59.2 % could be achieved at leachate pH of 3.2, $H_2O_2$ dosage of 1.1 % and $FeSO_4 \cdot 7H_2O$ dosage of 0.4 % using the Design Expert 8 software response analysis. The average chemical oxygen demand removal efficiency chemical oxygen demand of parallel verification experiment is 59.1 %. Here, this experimental value was in a good agreement with predicted one, which proved the validity of the model.

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