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# A novel pretreatment process of mature landfill leachate with ultrasonic activated persulfate: Optimization using integrated Taguchi method and response surface methodology

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ABSTRACT

A novel advanced oxidation process (AOP) using ultrasonic activated persulfate oxidation was used to pretreat mature landfill leachate. The effects of different operating variables (e.g., the initial $S_2O_8^{2-}$ concentration, pH, temperature, ultrasonic power and reaction time) on the oxidation performance were investigated regarding the total organic carbon (TOC) removal efficiency, and the variables were optimized using the integrated Taguchi method and response surface methodology (RSM). Based on the Taguchi method under $L_{16}$ ($4^5$) arrays and a grey relational analysis, the most significant variables included the initial $S_2O_8^{2-}$ concentration, temperature and reaction time. The concentrations of these variables were further optimized using RSM. Using the integrated optimization method, the optimal conditions included an initial $S_2O_8^{2-}$ concentration of 8.5 mM, a reaction temperature of 70 °C and a reaction time of 2.46 h, which resulted in a TOC removal efficiency of 77.32%. The experimental results showed that the enhanced TOC removal from mature landfill leachate by sono-activated persulfate oxidation could be attributed to the combined effects of ultrasonic catalysis and sulfate radical-AOP. Overall, ultrasonic activated persulfate oxidation is a promising method for the pretreatment of landfill leachate.


## 1. Introduction

In China, 90% of municipal solid wastes (MSW) are disposed of insanitary landfills (Zhan et al., 2014). However, heavily polluted water, which is known as landfill leachate, is generated when rain water infiltrates and flows through waste layers in municipal landfills. Landfill leachate contains a large amounts of refractory organics (such as humic acids and fulvic acids), ammonia-nitrogen ($NH_4^+$-N), heavy metals, chlorinated organic, and inorganic salts (Li et al., 2010; Liu et al., 2012). Based on the age of the landfill, leachates are categorized as young (typically <2 yrs) or mature leachates (typically >5 yrs) (Deng and Ezyske, 2011). Young leachates have high organic matter contents and are readily degradable.

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However, mature leachate undergoes minimal biodegradability, with a biological oxygen demand/chemical oxygen demand (BOD/COD) ratio of less than 0.1 (Vilar et al., 2013). Therefore, as a pretreatment for biological processes, some conventional treatments are usually used to improve mature leachate biodegradability (Lin and Chang, 2000).

Due to the terrible stench, low biodegradability, and large organic molecules, conventional treatments (biological or physico-chemical) are not sufficient to fully reduce the negative impact of landfill leachates on the environment. Biological processes are efficient in treatment of young landfill leachates which are rich in volatile fatty acids (VFAs), but less useful for the treatment of mature or more stabilized leachates due to the major presence of recalcitrant organic substances (Liu et al., 2012; Renou et al., 2008). In the last two decades, advanced oxidation processes (AOPs), such as Fenton oxidation (Singh et al., 2013), ultrasound (US) irradiation (Neczaj and Kacprzak, 2007), ultraviolet (UV) irradiation/$H_2O_2$ (Hu et al., 2011) and ozonation (Cortez et al., 2010), have been considered as effective pretreatment methods for improving the biodegradability of recalcitrant contaminants in mature leachate (Deng and Englehardt, 2006). Based on a statistical analysis of previously published literature regarding the Fenton oxidation of landfill leachate, Fenton oxidation not only shows potential for removing organic matter (a removal of 30–95% of the initial COD content, which varied from 93 to 34,920 mg/L) but also improves the biodegradability of leachate (an increase of $BOD_5$/COD from less than 0.01 to between 0.15 and 0.70) (Singh and Tang, 2013). The combination of strong oxidants (such as $O_3$ or $H_2O_2$) with high energy sources (such as UV or US) favors the production of hydroxyl radicals ($OH^{\bullet}$) and can accelerate the degradation of recalcitrant organic contaminants in landfill leachate (Cortez et al., 2011). The recent study found that UV–Fenton, UV–$H_2O_2$ and Fenton all could improve the biodegradability of landfill leachate and eliminate the color, among which UV–Fenton process was the most effective (Hu et al., 2011). However, several drawbacks, including high cost and risks related to the storage and transportation of $H_2O_2$ (e.g., electrochemical oxidation and ozonation), accumulation of iron sludge that needs to be removed at the end of the treatment (e.g., Fenton oxidation), and higher operational costs (Brillas et al., 2009), limit the wide applications of these AOPs.

Recently, persulfate ($S_2O_8^{2-}$) has received attention as the newest oxidant for treating recalcitrant or hazardous compounds (Anotai et al., 2011; Liang et al., 2008; Yang et al., 2013). Persulfate has a standard oxidation potential ($E_0$) of 2.01 V, which is comparable to $O_3$ (2.07 V) (Kolthoff and Stenger, 1947), and is stable at room temperature (Rodriguez et al., 2012). However, once persulfate is activated by heat, UV light (Eq. (1)), or transition metal ions (Eq. (2)), sulfate radicals ($SO_4^{-\bullet}$, $E_0 = 2.6$ V), which are even stronger oxidants, are generated (House, 1962).

$$S_2O_8^{2-} + \text{heat/UV} \rightarrow 2SO_4^{-\bullet} \quad (1)$$

$$S_2O_8^{2-} + Me^{n+} \rightarrow SO_4^{-\bullet} + SO_4^{2-} + Me^{(n+1)+} \quad (2)$$

A series of studies indicated that heat-activated persulfate oxidation is effective at degrading organic pollutants, such as diuron (Tan et al., 2012), antipyrine (Tan et al., 2013) and Bisphenol A (Olmez Hanci et al., 2013). Furthermore, UV/persulfate and microwave/persulfate systems have been used to eliminate organic contaminants in wastewater (Lin et al., 2011; Yang et al., 2009). Furthermore, other advantages of persulfate, including its low price (lower than $1.0/kg for $Na_2S_2O_8$ in China), high stability at room temperature and safe storage and handling, make persulfate-based AOPs become a great option for wastewater treatment.

In recent years, ultrasound has been used to activate persulfate because the collapse of cavitation bubbles induces localized high temperatures and pressures during ultrasound irradiation (Hou et al., 2012). Combining ultrasonic irradiation and persulfate has become an innovative technique for degrading recalcitrant organic pollutants, including perfluoroether carboxylic acids (Hori et al., 2012), dinitrotoluenes (Chen and Su, 2012) and 1,1,1-trichloroethane (Li et al., 2013). However, to the best of our knowledge, the treatment of mature landfill leachate using sono-activated persulfate oxidation has not been reported.

The main purpose of this research is to assess the feasibility of treating mature landfill leachate by sono-activated persulfate oxidation. Moreover, operating factors, such as the initial $S_2O_8^{2-}$ concentration, pH, temperature, ultrasonic power and reaction time, may be critical for maintaining the performance of the system. Response surface methodology (RSM) involves the integration of mathematical and statistical techniques to analyze the effects of several independent response variables (Zhou et al., 2011). However, it is difficult to consider so many factors simultaneously. The Taguchi method is based on orthogonal arrays (OA) and can use fewer trials to simultaneously optimize many factors by testing pairs of combinations (Maghsoodloo et al., 2004). Therefore, in this paper, the most significant operating factors of sono-activated persulfate oxidation for landfill leachate were tested using the Taguchi method and were based on the selection of significant operating factors (i.e., the initial $S_2O_8^{2-}$ concentration, temperature and reaction time). The removal of total organic carbon (TOC) was optimized regarding significant operating factors by using the RSM with a central composite design (CCD). In addition, the mechanisms of enhanced landfill leachate oxidation by sono-activated persulfate were discussed.

## 2. Materials and methods

### 2.1. Landfill leachate and chemicals

The leachate samples used in this study were taken from the HeiMifeng sanitary landfill located in Changsha, South China. This site covers an area of 146.9 ha and has received approximately 4000 tons of municipal solid waste each day since operations began in 2003. Landfill leachate samples were collected in 15 L glass containers and stored in a refrigerator at 4 °C. Batch experiments were carried out in a 500 mL glass beaker with a certain volume of landfill leachate taken from glass containers. The characteristics of the landfill leachate were as follows: pH 8.57 ± 0.8; ammonia nitrogen 2556 ± 145 mg/L; chemical oxygen demand (COD) 2033 ± 228 mg/L; biological oxygen demand ($BOD_5$) 150.7 ± 24.9 mg/L; and total organic carbon (TOC) 1432 ± 131 mg/L. Comparatively low $BOD_5/COD_0$ ratios (<0.07) imply that this leachate is mature.

Sodium persulfate ($Na_2S_2O_8$, 98% purity) was purchased from the Sinopharm Chemical Reagent Co., Ltd. (China). Sulfuric acid (98% purity) was bought from the Zhuzhou Chemical

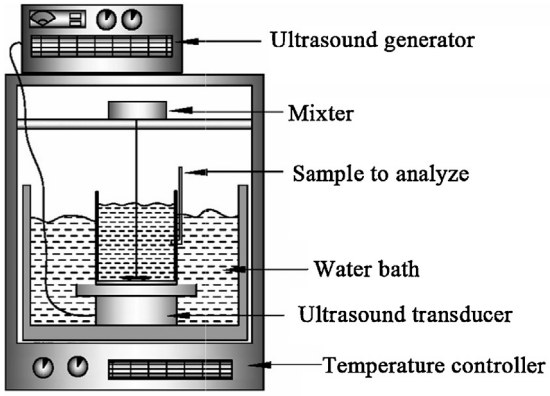


**Fig. 1 – Schematic diagram of experimental apparatus for sono-activated persulfate oxidation.**

Industry Research Institute (China). The purities of all other chemicals were analytical grade or higher.

### 2.2. Experimental procedures

A commercial ultrasonic generator (KQ-300DE model, Kun Shan Ultrasonic Instruments Co., Ltd., China, 40 kHz, maximal output of 800 W, variable power control) was used as the source of ultrasonic irradiation. The maximal power density delivered to the reactor was 10 W/cm$^2$. The solution temperature was maintained by water bath. Fig. 1 shows a schematic diagram of the experimental apparatus.

In a typical run, 100 mL of leachate was placed in 500 mL glass beaker. If necessary, the initial pH of the solution was adjusted with concentrated sulfuric acid. Next, appropriate amounts of sodium persulfate were added as the oxidant. Simultaneously, the ultrasonic generator was switched on, and the ultrasonic power output was kept constant during the experiment. At the designated time intervals, the samples were removed using a syringe filter with 0.45 mm membrane pore size (LC+PVDF membrane, ANPEL Laboratory Technologies Inc., China) and immediately placed in an ice bath (4 °C) to quench the reaction. Next, the TOC concentrations were immediately analyzed.

### 2.3. Analytical methods

The pH of samples was monitored with a standard glass electrode (pHS-3C model, Leici, China). Ammonia nitrogen, COD, and $BOD_5$ were analyzed in accordance with standard methods (Wei, 2002). The TOC contents were measured using a TOC analyzer (TOC-VCPH, Shimadzu, Japan) equipped with a non-dispersive infrared (NDIR) detector. First, the samples were completely acidified by phosphoric acid, and the formed carbon dioxide was stripped by oxygen gas. Next, the organic concentrations in the sample were completely oxidized into carbon dioxide by high temperature catalytic oxidation and quantified using an NDIR detector. The reproducibility of the measurements was determined in duplicate, and the average values were reported.

The removal efficiency of TOC was calculated using the following equation:

$$\text{Removal}\quad (\%) = \left(\frac{1 - C_f}{C_i}\right) \times 100 \tag{3}$$

where $C_i$ and $C_f$ refer to the TOC concentrations in the landfill leachate before and after the reaction, respectively.

### 2.4. Integrated Taguchi method and response surface methodology

#### 2.4.1. Taguchi array design

The Taguchi method emphasizes a mean performance characteristic value near the target value rather than a value within certain specification limits; thus, this method can be used to quickly narrow the scope of a research project (Muhammad et al., 2012). In this study, standard orthogonal $L_{16}$ ($4^5$) arrays were applied to test the variables that potentially affect the removal efficiencies of sono-activated persulfate oxidation in landfill leachate using a five-variable four-level system. The five independent variables included $x_1$ (initial $S_2O_8^{2-}$), $x_2$ (initial pH), $x_3$ (temperature), $x_4$ (radiation power), and $x_5$ (reaction time), which are defined in Table 1. Each selected combination of variables and levels was tested in a sono-activated persulfate oxidation reactor under static conditions.

#### 2.4.2. RSM design

Three significant variables were obtained from the results of the Taguchi array design (initial $S_2O_8^{2-}$ concentration, temperature and reaction time) and were further optimized by RSM. The central composite design (CCD), which is the standard of RSM, was developed with three variables at five levels, as presented in Table 2. The removal efficiency of TOC was used as the response variable. The response was fit using a polynomial quadratic equation to correlate each response with an independent variable. The mathematical form is described as follows in Eq. (4):

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i X_i + \sum_{i=1}^{k}\beta_{ii} X_i^2 + \sum_{i\le j}^{k}\sum_{j}^{k}\beta_{ij} X_i X_j + \cdots + e \tag{4}$$

where Y is the response, $X_i$ and $X_j$ are the variables, $\beta_0$ is the constant coefficient, $k$ is the number optimized in the experiment, and $e$ is the error.

The analyses were conducted using three-dimensional (3D) response surface plots constructed for each polynomial equation using the Design Expert software (version 8.0.6). The model was evaluated using analysis of variance (ANOVA) tests. The quality of the polynomial model was expressed by the correlation coefficient ($R^2$), and its statistical significance was examined using an $F$-test. The model terms were estimated at a 95% confidence level based on the $P$-value (probability) (Bashir et al., 2010).

## 3. Results and discussion

### 3.1. Significant variable optimization by Taguchi array design

Table 3 depicts the orthogonal array of $L_{16}$ ($4^5$) for mixed designs and the layout used for statistical analyses.

To determine the most significant variable for the removal of sono-activated persulfate oxidation for landfill leachate, a linear normalization of the removal efficiencies of TOC was performed between zero and one. The normalized processing

**Table 1 – Taguchi array design of five independent variables with four levels.**

| Independent variables | Symbol | Levels | | | |
|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 |
| Initial $S_2O_8^{2-}$ (mM) | $x_1$ | 8.75 | 10.00 | 11.25 | 12.50 |
| Initial pH | $x_2$ | 4 | 5 | 6 | 7 |
| Temperature (°C) | $x_3$ | 40 | 50 | 60 | 70 |
| Radiation power (W) | $x_4$ | 210 | 240 | 270 | 300 |
| Reaction time (h) | $x_5$ | 1.5 | 2 | 2.5 | 3 |

**Table 2 – Levels of the variable tested in the CCD.**

| Independent variables | Symbol | Range and levels | | | | |
|---|---|---|---|---|---|---|
| | | −2 | −1 | 0 | 1 | 2 |
| Temperature (°C) | $x_3$ | 43 | 50 | 60 | 70 | 77 |
| Initial $S_2O_8^{2-}$ (mM) | $x_1$ | 6.65 | 7.50 | 8.75 | 10.00 | 10.85 |
| Reaction time (h) | $x_5$ | 1.7 | 2 | 2.5 | 3 | 3.3 |

**Table 3 – Orthogonal array experimental design on an $L_{16}$ ($4^5$) array with the observed response.**

| Run order | Independent variables level | | | | | TOC removal (%) |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $x_4$ | $x_5$ | |
| 1 | 1 | 1 | 1 | 1 | 1 | 46.89 |
| 2 | 1 | 2 | 2 | 2 | 2 | 52.27 |
| 3 | 1 | 3 | 3 | 3 | 3 | 50.07 |
| 4 | 1 | 4 | 4 | 4 | 4 | 59.48 |
| 5 | 2 | 1 | 2 | 3 | 4 | 54.14 |
| 6 | 2 | 2 | 1 | 4 | 3 | 50.75 |
| 7 | 2 | 3 | 4 | 1 | 2 | 62.43 |
| 8 | 2 | 4 | 3 | 2 | 1 | 47.54 |
| 9 | 3 | 1 | 3 | 4 | 2 | 59.13 |
| 10 | 3 | 2 | 4 | 3 | 1 | 70.71 |
| 11 | 3 | 3 | 1 | 2 | 4 | 48.20 |
| 12 | 3 | 4 | 2 | 1 | 3 | 41.74 |
| 13 | 4 | 1 | 4 | 2 | 3 | 83.31 |
| 14 | 4 | 2 | 3 | 1 | 4 | 64.40 |
| 15 | 4 | 3 | 2 | 4 | 1 | 45.93 |
| 16 | 4 | 4 | 1 | 3 | 2 | 44.03 |

that corresponded to the larger-the-better characteristic can be described as follows (Liu et al., 2008):

$$X_i(k) = \frac{\eta_i(k) - \min_{\forall k}\eta_i(k)}{\max_{\forall k}\eta_i(k) - \min_{\forall k}\eta_i(k)} \quad (5)$$

where $X_i(k)$ ($i \neq 0$) is the value after generating a grey relational, $\eta_i(k)$ is the original experimental value for the $k$th response in the $i$th experiment, and $\min_{\forall k}\eta_i(k)$ and $\max_{\forall k}\eta_i(k)$ are the smallest and largest values for the $k$th response, respectively.

Then, the grey relational coefficient ($\xi_i(k)$) from the normalized experimental values was expressed as follows (Zhai et al., 2012):

$$\xi_i(k) = \frac{\Delta\min + \xi\Delta\max}{\Delta_{oi}(k) + \xi\Delta\max} \quad (6)$$

where $\Delta_{oi}(k) = \|x_o(k) - x_{i(k)}\|$ is the difference of the absolute value between $x_0(k)$ and $x_i(k)$, and $\xi$ is the distinguished coefficient between zero and one that is used to adjust the difference of the relational coefficient. In this study, $\xi$ is equal to 0.5. $\Delta$max and $\Delta$min refer to the largest and smallest $\Delta_{oi}$ values, respectively.

After averaging the grey relational coefficients, the grey relational grades were calculated as follows:

$$\gamma_i = \frac{1}{n}\sum_{k=1}^{n}\xi_i(k) \quad (7)$$

where $n$ is the number of the experimental responses.

The grey relational grades ($\gamma_i$) of each response are summarized in Table 4. The grey relational grades for TOC removal were ranked as follows: temperature ($x_3$) > initial $S_2O_8^{2-}$ concentration ($x_1$) > reaction time ($x_5$) > radiation power ($x_4$) > initial pH ($x_2$). Meanwhile, according to the value of the grey relational grade, the influences of variables on the response can be categorized into four grades: marked influence ($\gamma_i > 0.9$), relatively marked influence ($0.8 < \gamma_i < 0.9$),

**Table 4 – Grey relational grade of reponses of each variable.**

| Independent variables | Symbol | Grey relational grade ($\gamma_i$) |
|---|---|---|
| Temperature (°C) | $x_3$ | 0.8416 |
| Initial $S_2O_8^{2-}$ (mM) | $x_1$ | 0.7895 |
| Reaction time (h) | $x_5$ | 0.7370 |
| Radiation power (W) | $x_4$ | 0.6348 |
| Initial pH | $x_2$ | 0.5088 |

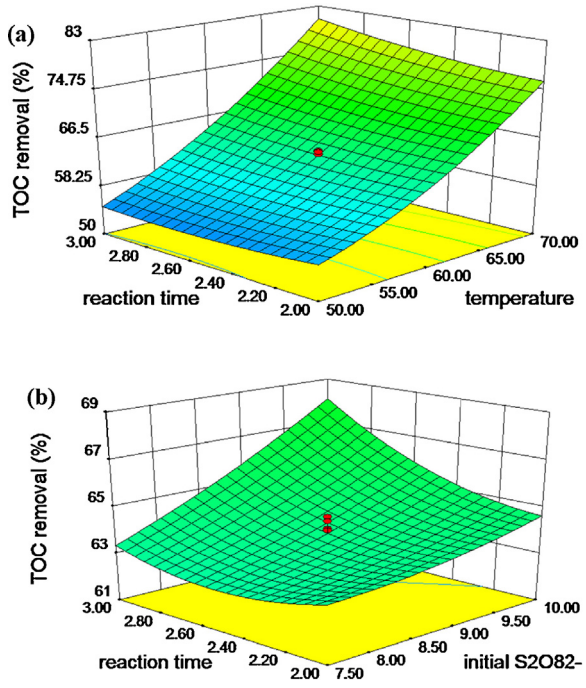


**Fig. 2 – 3D surface plots for TOC removal efficiency: (a) the effect of temperature and reaction time on TOC removal (initial $S_2O_8^{2-}$: 8.75 mM; pH: 4.0; radiation power: 300 W) and (b) the effect of initial $S_2O_8^{2-}$ and reaction time on TOC removal (temperature: 60 °C; pH: 4.0; radiation power: 300 W).**

noticeable influence ($0.7 < \gamma_i < 0.8$) and negligible influence ($\gamma_i < 0.6$) (Liu et al., 2008). Therefore, according to the results in Table 4, the initial $S_2O_8^{2-}$ concentration ($x_1$), temperature ($x_3$) and reaction time ($x_5$) were selected as significant variables for further optimization by RSM. Because additional sulfate radicals can be formed during acid catalysis (Liang et al., 2007), the two negligible variables of initial pH and radiation power were maintained at 4 W and 300 W, respectively, during subsequent optimum experiments.

### 3.2. *Response factors based on the RSM*

The most significant variables of the sono-activated persulfate oxidation for landfill leachate were designed using the Taguchi array design. The RSM is a statistical technique that can be applied to the model to analyze problems in which the response of interest is influenced by several factors (Xin Hui et al., 2011). In this section, a standard RSM design known as CCD was applied to optimize the variable levels. Three variables, the initial $S_2O_8^{2-}$, temperature and reaction time, were chosen as independent variables, and their respective coded values are listed in Table 2. Twenty runs were performed for each complete experimental set, including replications at the center point. In addition, Table 5 shows the complete design matrixes with the response values obtained from the experiment.

To assess the interactive relationships between independent variables and the response (TOC removal), 3D surface response plots were created using the Design Expert 8.0.6 software and are shown in Fig. 2. In addition, Fig. 2(a) shows that TOC removal increased from 54.52% to 79.42% as the temperature increased from 50 to 70 °C. This result indicated that a higher reaction temperature is beneficial for the sono-activated persulfate oxidation of landfill leachate. Under higher temperature conditions, $S_2O_8^{2-}$ can be heat-activated to produce stronger oxidant $SO_4^{-\bullet}$, enhancing the oxidation capacity of the system. However, based on Fig. 2(b), when the initial $S_2O_8^{2-}$ concentration reached a certain value (above 8.75 mM), further increase did not improve the TOC removal efficiency. Furthermore, Yang et al. reported that increases in the initial $S_2O_8^{2-}$ concentration result in saturation of $SO_4^{\bullet-}$ concentration and that the saturated concentrations were different between different treatments (Yang et al., 2013). When the $S_2O_8^{2-}$ concentration was excessive, the amount of $SO_4^{-\bullet}$ in the system decreased, potentially due to scavenging reactions by the sulfate radicals themselves and with the excess $S_2O_8^{2-}$ or $H_2O$ (Hori et al., 2005).

The above results indicate that sono-activated persulfate oxidation can be effective for degrading organic pollutants in mature landfill leachate. In this system, the sulfate radicals and hydroxyl radicals ($OH^{\bullet}$) were enhanced by activating persulfate using the comprehensive actions of ultrasound and heat. Previous research demonstrated that $SO_4^{-\bullet}$ and $OH^{\bullet}$ played important roles in degrading tetracycline when using ultrasound enhanced heterogeneous activation of peroxydisulfate (Hou et al., 2012). In addition, the synergistic effect eliminated the nitrotoluene in the wastewater during sono-activated persulfate oxidation. During this process, a combination of ultrasonic irradiation and persulfate anions resulted in a TOC removal percentage of 75%, which was significantly higher than TOC removal by sonolysis (12.8%) or persulfate oxidation (32%) (Chen and Su, 2012).

By applying a factorial regression analysis to the experimental data, final quadratic models were expressed by following a second-order polynomial equation in which the TOC removal efficiency (Y) was assessed as a function of the initial $S_2O_8^{2-}$ concentration ($x_1$), temperature ($x_3$) and reaction time ($x_5$).

$$Y = 63.95 + 11.58x_3 + 1.49x_1 + 0.85x_5 + 0.27x_3x_1 + 1.36x_3x_5 + 0.86x_1x_5 + 2.35x_3^2 + 0.26x_1^2 + 0.71x_5^2 \quad (8)$$

The ANOVA results presented in Table 6 confirm the adequacy of the quadratic model (the model Prob > F is less than 0.05). The adequate precision of the model (30.159) implied that the model was significant for TOC removal efficiency. Higher $R^2$ values (0.9834) indicated that the data were near the predicted values from the model. Meanwhile, the model is considered reproducible if the coefficient of variance (CV) for the model is less than 10% (Douglas, 2001). In addition, a CV of 2.76% suggested that this model is highly credible and accurate.

Diagnostic plots, such as the predicted values versus the actual values, can be used to determine the suitability of the model (Ghafari et al., 2009). Fig. 3(a) shows the normal probability plots of the student residuals for TOC removal. Although some scattering is expected even with normal data, the points nearly followed a straight line in this study, which suggested that the data in Fig. 3(a) were normally distributed in the responses of the model. The predicted versus actual value plots of the responses presented in Fig. 3(b) indicated excellent agreement between the actual and predicated data obtained from the model.

The following optimal independent variables for the sono-activated persulfate oxidation of landfill leachate were

**Table 5 – Central composite design matrix and response results.**

| Run order | $x_3$ Temperature (°C) | $x_1$ Initial $S_2O_8^{2-}$ (mM) | $x_5$ Reaction time (h) | TOC removal (%) |
|---|---|---|---|---|
| 1 | 0 | 0 | 0 | 64.13 |
| 2 | 0 | 0 | 0 | 64.06 |
| 3 | 1 | −1 | −1 | 77.16 |
| 4 | 0 | 0 | 0 | 63.88 |
| 5 | 0 | 0 | 0 | 64.46 |
| 6 | −1 | 1 | 1 | 58.03 |
| 7 | −1 | 1 | −1 | 57.77 |
| 8 | 0 | 0 | −2 | 62.20 |
| 9 | 0 | 0 | 0 | 64.65 |
| 10 | −1 | −1 | 1 | 54.52 |
| 11 | 1 | 1 | 1 | 83.61 |
| 12 | 0 | 0 | 2 | 66.57 |
| 13 | −2 | 0 | 0 | 48.78 |
| 14 | 0 | 0 | 0 | 63.03 |
| 15 | 2 | 0 | 0 | 89.28 |
| 16 | −1 | −1 | −1 | 58.07 |
| 17 | 1 | 1 | −1 | 78.30 |
| 18 | 0 | 2 | 0 | 66.66 |
| 19 | 0 | −2 | 0 | 59.60 |
| 20 | 1 | −1 | 1 | 79.42 |

**Table 6 – ANOVA for analysis of variance and adequacy of the quadratic model.**

| Source | Sum of squares | Degree of freedom | Mean square | F-Value | P > F |
|---|---|---|---|---|---|
| Model | 1977.13 | 9 | 219.68 | 65.80 | <0.0001 |
| Residual | 33.39 | 10 | 3.34 | | |
| Lack of fit | 31.78 | 5 | 6.36 | 19.83 | 0.0026 |
| Pure error | 1.60 | 5 | 0.32 | | |

S.D. = 1.83, C.V. = 2.76, PRESS = 242.66, $R^2$ = 0.9834, $R^2_{adj}$ = 0.9684, Adeq. precision = 30.159.

suggested by the Design Expert 8.0.6 software: an initial $S_2O_8^{2-}$ concentration of 8.5 mM, an initial temperature of 70 °C and an initial reaction time of 2.46 h. The experimental value for TOC removal efficiency (75.88%) agreed with the value predicted by the models (77.32%).

### 3.3. *Synergetic TOC removal by sono-activated persulfate oxidation*

To elucidate the synergetic effects of sono-activated persulfate oxidation on the treatment of landfill leachate, sonolysis, persulfate oxidation and sono-activated persulfate oxidation experiments were conducted at 70 °C, respectively. As shown in Table 7, $S_2O_8^{2-}$ was activated by heat energy to form $SO_4^{-\bullet}$, resulting in a TOC removal efficiency of 67.58%. This TOC removal efficiency was greater than that resulting from sonolysis (59.01%). Nevertheless, an enhanced effect was observed upon sono-activated persulfate oxidation, as shown by the significantly higher maximum TOC removal relative to the sonolysis and persulfate oxidation treatments. These results are consistent with those of previous studies (Chen and Su, 2012; Lorimer et al., 1991).

**Table 7 – Synergetic TOC removal from landfill leachate by the sono-activated persulfate oxidation.**

| Experimental conditions | TOC removal (%) |
|---|---|
| Sonolysis (P[a]: 300 W, t[b]: 3.0 h, T[c]: 70 °C, pH: 4) | 59.01 |
| Persulfate oxidation (initial $S_2O_8^{2-}$: 8.75 mM, t[b]: 3.0 h, T[c]: 70 °C) | 67.58 |
| Sono-activated persulfate oxidation: (initial $S_2O_8^{2-}$: 8.5 mM, t[b]: 2.46 h, T[c]: 70 °C, P[a]: 300 W, pH: 4) | 77.32 |

[a] Power.
[b] Reaction time.
[c] Temperature.

The enhanced mechanism potentially occurred because ultrasound accelerated the activation of persulfate to produce $SO_4^{-\bullet}$, which further captured hydrogen atoms from the water to form $OH^\bullet$ (Price et al., 1996). Both $SO_4^{-\bullet}$ and $OH^\bullet$ were powerful oxidants that could enhance the degradation rate of organic pollutants in landfill leachate.

$$S_2O_8^{2-} + US \rightarrow 2SO_4^{-\bullet} \quad (9)$$

$$SO_4^{-\bullet} + H_2O \rightarrow HSO_4^- + OH^\bullet \quad (10)$$

Furthermore, multiple cavitation bubbles were produced in liquid solutions under ultrasonic irradiation. The violent collapse of these cavitation bubbles will cause certain extreme microenvironments with high temperatures (up to 5000 °C) and pressures (approximately 500 atm) (Mason, 1990). Consequently, the organic pollutants near the bubble/water interface could undergo thermal decomposition and react with reactive radicals such as $H^\bullet$, $OH^\bullet$ and $O^\bullet$.

Compared with other AOP (Wang et al., 2012; Xiao et al., 2013; Zhao et al., 2010), the sono-activated persulfate oxidation exhibited similar or better performance to the mature landfill leachate in term of TOC removal (Table 8). The concentration and composition of landfill leachate could explain these performance differences. However, sono-activated persulfate oxidation combines the advantages of ultrasonic

**Table 8 – Performance of different $AOP_S$ to landfill leachate in term of TOC removal.**

| Leachate characteristics | | $AOP_S$ type | Reaction conditions | TOC | | Reference |
|---|---|---|---|---|---|---|
| COD (mg/L) | BOD/COD | | | Initial (mg/L) | Removal (%) | |
| 560 | / | Photoelectrochemical oxidation | Current density, 67.1 mA/cm$^2$; reaction time, 2.5 h | 190 | 41.6 | Zhao et al. (2010) |
| 3896 | 0.0007 | Electro-Fenton treatment | Current density, 30 mA/cm$^2$; $FeSO_4$, 10 mM; initial pH, 3; cathode area, 20 cm$^2$; reaction time, 6 h | 1347 | 82.0 | Wang et al. (2012) |
| 6635 | 0.0215 | Electro-Fenton treatment | Cathode, carbon-PTFE electrode; current, 350 mA; reaction time, 4 h | 1650 | 71.0 | Li et al. (2013) |
| 2033 | 0.0741 | Sono-activated persulfate oxidation | Initial $S_2O_8^{2-}$, 8.5 mM; reaction time, 2.46 h; temperature, 70 °C; radiation power, 300 W; pH, 4 | 1432 | 77.3 | In this study |

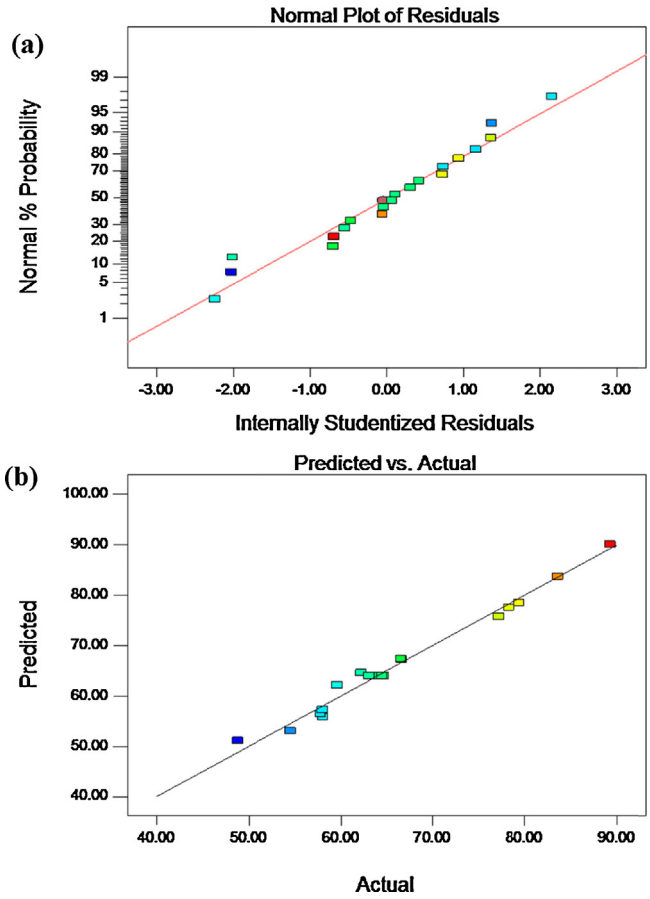


**Fig. 3 – Design-expert plot: (a) normal probability plot of the internally studentized residuals for TOC removal and (b) predicted versus actual values plot for TOC removal.**

catalysis and sulfate radical-AOP, which are effective and novel pretreatment processes for mature landfill leachate.

## 4. Conclusions

In this study, the ultrasonic activated persulfate oxidation was proved to be a novel and effective pretreatment process for mature landfill leachate from a sanitary landfill located in Changsha, south of China. The pretest experiments using the Taguchi method with grey relational analysis showed that the most significant TOC removal variables were temperature, initial $S_2O_8^{2-}$ concentration and reaction time. Further optimal testing regarding the variable level was investigated using a RSM. The prediction results of the model generally agreed with the experimental results. The optimal conditions included an initial $S_2O_8^{2-}$ concentration of 8.5 mM, an initial temperature of 70 °C and a reaction time of 2.46 h, which resulted in 77.32% TOC removal at pH 4 when the ultrasonic power was 300 W. Relative to other techniques, the enhanced TOC removal by ultrasonic activated persulfate oxidation is attributed to the comprehensive action of ultrasonic catalysis and sulfate radical-AOP.

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