RESEARCH NOTES

# Treatment of Landfill Leachate by Fenton Oxidation Process*

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**Abstract** Central composite design (CCD), the most popular design of response surface methodology (RSM), was employed to investigate the effect of total organic carbon(TOC) ratio of high molecular weight organic matter (HMW) to low molecular weight organic matter (LMW), the LMW strength and molar ratio of hydrogen peroxide to ferrous ion on landfill leachate treatment by Fenton process. Based on the experimental data, a response surface quadratic model in terms of actual factors was obtained through analysis of variance (ANOVA). The model showed that TOC removal increased with the increase of HMW to LMW ratio and the decrease of LMW strength. There existed an optimal hydrogen peroxide to ferrous ion molar ratio for TOC removal.

**Keywords** Fenton reagent, landfill leachate, oxidation

## 1 INTRODUCTION

It is known that the composition of leachate varies greatly with the age of landfill. Generally, young leachate contains a very high percentage of organic substances with low molecular weight (LMW), which are recalcitrant but readily biodegradable. This can be proved by the fact that the ratio of $BOD_5/COD$ of young leachate usually exceeds 0.5[1]. On the contrary, old leachate contains a relative high percentage of organic compounds with a high molecular weight (HMW) such as humic acid (HA), which are non-biodegradable but readily destroyed by chemical oxidation such as Fenton process. Thus the oxidation kinetics of old leachate is quite different from that of young leachate due to different chemical composition. Results in our work[2] clearly show that higher total organic carbon(TOC) removal can be achieved with old leachate than young leachate. However there is no report on the relationship between the extent of TOC removal and HMW to LMW ratio. In this study, we would investigate the effect of HMW to LMW ratio and other factors, such as LMW strength and hydrogen peroxide to ferrous ion molar ratio, on TOC removal using response surface methodology (RSM)[3].

## 2 EXPERIMENTAL

### 2.1 Characteristics of the leachate

Leachate samples were collected from Cell 3 on the South Solid Waste Management Center (SSWMC-CELL 3) in Jones Crossroads Landfill, Sussex County, DE. The samples were centrifuged at $10000\,r\cdot min^{-1}$ using sorvall superspeed refrigerated centrifuge (Dupont Co., Wilmington, DE, Model RC-5) for 10 minutes to remove particles and debris. This would minimize particulate effect on oxidation reaction. The centrifuged samples were stored in a 4℃ refrigerator to keep the leachate characteristics unchanged. The characteristics of the leachate was analyzed according to the "Standard Methods for the Examination for Water and Wastewater"[4], "Modified Examination of Water for Pollution Control"[5], or dialysis method[6]. It is summarized as follows:

| | |
|---|---|
| Ammonia-nitrogen, $mg\cdot L^{-1}$[4] | 647.0 |
| $BOD_5$, $mg\cdot L^{-1}$[4] | 4123 |
| Chloride, $mg\cdot L^{-1}$[4] | 1029 |
| COD, $mg\cdot L^{-1}$[4] | 10830 |
| Fluoride, $mg\cdot L^{-1}$[4] | 1.410 |
| IC (inorganic carbon), $mg\cdot L^{-1}$[4] | 431.9 |
| Nitrate-nitrogen, $mg\cdot L^{-1}$[5] | 2.478 |
| TOC, $mg\cdot L^{-1}$[4] | 3810 |
| pH[4] | 6.88 |
| Total alkalinity(based on $CaCO_3$), $mg\cdot L^{-1}$[4] | 2418 |
| TOC of high molecular weight (above 500) organic matter $c_H$, $mg\cdot L^{-1}$[6] | 57.06 |
| TOC of low molecular weight (below 500) organic matter $c_L$, $mg\cdot L^{-1}$[6] | 3753 |

### 2.2 Experimental design

A software of Design-Expert 5 (STAT-EASE Inc.,

Minneapolis, MN) was used for experimental design. The levels of three factors, *i.e.*, the strength of LMW, hydrogen peroxide to ferrous ion molar ratio, and HMW to LMW ratio, were selected according to the leachate characteristics and the previous result[2,6] (see Table 1). Other factors were fixed based on the previous result[2,6] (see Table 2).

A 20 run design was created by central composite design (CCD), one method of RSM, which was shown in the first four columns of Table 3. The run number in the first column was created randomly by the software and was used as the rder of the experiments.

## 2.3 Experimental procedure

Semi-batch mode was employed for Fenton oxidation experiments (see Fig. 1). The experiment was performed in a 1 L plexiglass double jacket reactor with four baffles. The inner diameter of the reactor is 11.4 cm (4.5″). Mixing was provided by a variable speed motor (Fisher Scientific Co., Pittsburgh, PA, Dyna-Mixer®) connected to a steel shaft and standard four-blade propeller. It was vertically mounted above one propeller diameter from the reactor bottom. Mixing speed was about 1400 r·min$^{-1}$, which was measured by strobotac electronic stroboscope (General Readi Co., West Concord, MA, Type 1531). During oxidation pH was controlled with a pH controller (Horizon Ecology Co., Chicago, IL, Model 5997-20) connected with an acid pump and a base pump (New Brunswick Scientific Co., Edison, NJ, Model AFP-101). 10% sulfuric acid and 50% sodium hydroxide solution were used to adjust pH. The temperature was maintained at 25℃ using a water jacket and the water was provided by a temperature controller (Brookfield Engineering Laboratory, Inc., Stoughton, MA, Model EX-200). Hydrogen peroxide and ferrous ion were applied to the reactor continuously using a tubing pump (Cole-Parmer Instrument Co., Vernon Hills, IL, Masterflex® C/L® Model 77120-62).

HA (Aldrich Chemical Co., Milwaukee, WI) was used as a source of HMW to adjust HMW to LMW
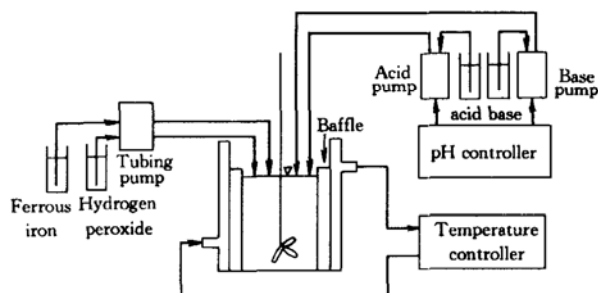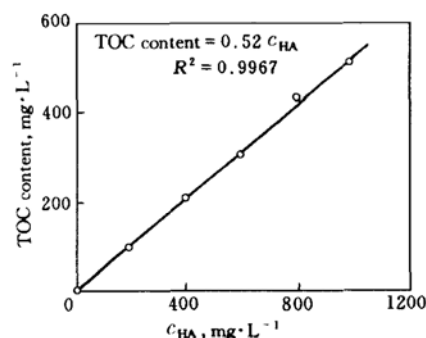


Figure 1    Experimental apparatus



Figure 2    The relationship between concentration of HA and its TOC value

ratio. The relationship between concentration of HA and its TOC content was calibrated first (see Fig. 2).

The procedures for each run were as follows: Apply HA to the leachate sample according to the required HMW to LMW ratio. Then dilute the sample to the desired LMW strength with distilled water. Adjust pH to around 10 and mix the sample for at least one hour to dissolve HA. Measure the TOC value of the sample. Then apply 1 L sample to the reactor. Turn on temperature controller and let 25 ℃ water circulate through the water jacket. Adjust the flow rate of the tubing pump to 1 ml·min$^{-1}$. Prepare aqueous hydrogen peroxide solution by diluting 30% hydrogen peroxide solution (Fisher Scientific Co., Pittsburgh, PA) to the required concentration. Prepare 0.05 mol·L$^{-1}$ ferrous ion solution by dissolving FeSO$_4$·7H$_2$O (Fisher Scientific Co., Pittsburgh, PA) in distilled water.

Table 1    Factor levels for the experiments

| Factor | $c_L$, mg·L$^{-1}$ | $c_{H_2O_2}/c_{Fe(II)}$ | $c_H/c_L$ |
|---|---|---|---|
| star point of low level (−1.68) | 284.7 | 0.98 | 5.82 |
| low level (−1) | 975 | 1.75 | 14 |
| center point (0) | 1987.5 | 2.88 | 26 |
| high level (+1) | 3000 | 4.00 | 28 |
| star point of high level (+1.68) | 3690 | 4.77 | 46.2 |

Table 2    Fixed factors

| $c_{Fe(II)}$ mol·L$^{-1}$ | pH during oxidation | Temperature ℃ | Volume of the tested leachate, L | Feeding time min | Reaction time min | pH during neutralization | Settling time, h |
|---|---|---|---|---|---|---|---|
| 0.05 | 3.0 | 25 | 1 | 60 | 75 | 8.0 | 1 |

**Table 3  Design runs by CCD**

| Run No. | Factor A $X_1$ (coded) | Factor B $X_2$ (coded) | Factor C $X_3$ (coded) | Response TOC removal % |
|---------|---------|---------|---------|---------|
| 8 | 1.00 | −1.00 | −1.00 | 31.5 |
| 7 | 0.00 | 1.68 | 0.00 | 39.7 |
| 1 | 0.00 | 0.00 | 0.00 | 57.0 |
| 3 | 1.00 | −1.00 | 1.00 | 51.7 |
| 10 | 0.00 | 0.00 | 0.00 | 49.7 |
| 12 | −1.00 | −1.00 | −1.00 | 63.0 |
| 2 | 0.00 | −1.68 | 0.00 | 86.0 |
| 19 | −1.68 | 0.00 | 0.00 | 35.5 |
| 11 | 0.00 | 0.00 | 0.00 | 46.0 |
| 16 | 0.00 | 0.00 | 0.00 | 39.7 |
| 15 | −1.00 | 1.00 | 1.00 | 39.6 |
| 17 | 0.00 | 0.00 | −1.68 | 37.5 |
| 18 | 0.00 | 0.00 | 0.00 | 45.8 |
| 20 | 1.00 | 1.00 | 1.00 | 29.8 |
| 14 | 1.00 | 1.00 | −1.00 | 26.8 |
| 13 | 0.00 | 0.00 | 0.00 | 39.4 |
| 9 | 0.00 | 0.00 | 1.68 | 54.4 |
| 4 | −1.00 | −1.00 | 1.00 | 63.3 |
| 6 | −1.00 | 1.00 | −1.00 | 47.1 |
| 5 | 1.68 | 0.00 | 0.00 | 38.6 |

Adjust pH of the leachate sample to 3.0 manually with 98% sulfuric acid. When the temperature reaches to 25°C, turn on the tubing pump and pH controller. Let the chemicals feed to the reactor for one hour. Continue mixing for 15 minutes. Then adjust pH to 8.0 manually using 50% sodium hydroxide solution. After settling for one hour, take the supernatant and centrifuge at $10000\,r\cdot min^{-1}$ for 10 minutes. Take the supernatant after centrifugation and measure the TOC value. Calculate the TOC removal efficiency based on the TOC values before and after Fenton process.

## 3  RESULTS AND DISCUSSION

### 3.1  Model equation

The results of 20 runs were summarized in the last column of Table 3. The response surface quadratic model in terms of actual factors through analysis of variance (ANOVA) is,

TOC removal (%)=74.66+4.69$X_1$−0.027$X_2$+0.37$X_3$
　　　　　−3.35$X_1^2$ + 4.76 × $10^{-6}X_2^2$ − 7.605
　　　　　×$10^{-3}X_3^2$+1.427×$10^{-3}X_1X_2$+
　　　　　0.28$X_1X_3$+2.572 × $10^{-4}X_2X_3$

where　$X_1$=$H_2O_2$ to $Fe^{2+}$ molar ratio;
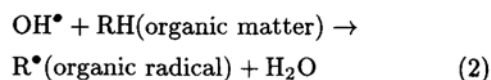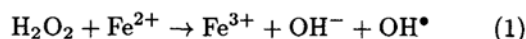　　　$X_2$=LMW content;
　　　$X_3$=HMW to LMW ratio (as TOC)

### 3.2  Model prediction

The relationship between the factors ($X_1$, $X_2$, $X_3$) and the response of TOC removal, which are derived from the model, are shown in Figs. 3—5.

Figures 3 and 4 show that TOC removal increases with the decrease of LMW strength. Low LMW means

low initial TOC strength. When other operating conditions (such as hydrogen peroxide dose) were fixed, the decrease of initial TOC strenght would lead to the fact that the same dose of hydrogen peroxide would treat less organic matter in the leachate. Therefore we can expect the higher TOC removal.

From Figs. 4 and 5 we can see that TOC removal increases with the increase of HMW to LMW ratio. During Fenton oxidation, hydrogen peroxide reacted with ferrous ion and produced hydroxyl radical[7], which would oxidize organic matter in the leachate.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad (1)$$

$$OH^\bullet + RH(\text{organic matter}) \rightarrow$$
$$R^\bullet(\text{organic radical}) + H_2O \qquad (2)$$

The presence of HMW such as HA could alter the rate constant for reaction to produce hydroxyl radical [Reaction(1)] or alter the redox cycling of iron and thereby change the formation rate of hydroxyl radical[8]. On the other hand, the rate constant between HA and hydroxyl radical is high, $3 \times 10^4\,mg^{-1}\cdot L\cdot s^{-1}$ (based on DOC)[9], but the rate constant between LMW and hydroxyl radical is relatively low. Therefore it is concluded that HMW can be oxidized by Fenton reagent more easily and quickly than LMW. We can obtain higher TOC removal for the leachate with higher HMW to LMW ratio.

Figure 5 shows that the same amount of TOC removal can be obtained at two different molar ratios of hydrogen peroxide to ferrous ion. This indicates that there exists an optimal molar ratio of hydrogen peroxide to ferrous ion so that the highest TOC removal could be achieved when other conditions are fixed.
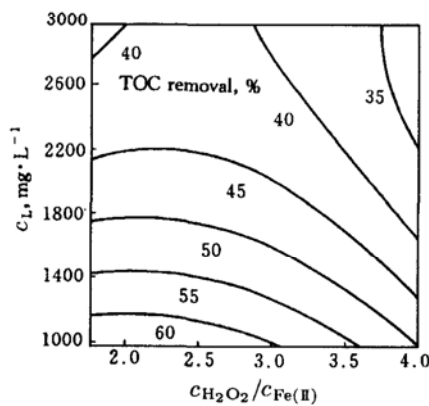


**Figure 3**  TOC removal contour plot as a function of $c_L$ and $c_{H_2O_2}/c_{Fe(II)}$
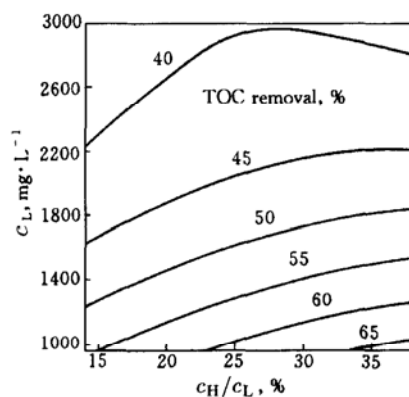($c_H/c_L$ is fixed at 26%)

**Figure 4**  TOC removal contour plot as a function of $c_L$ and $c_H/c_L$
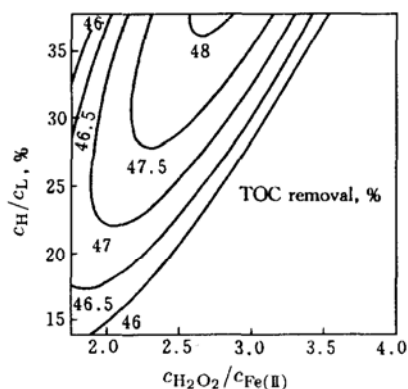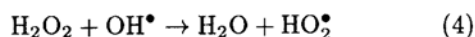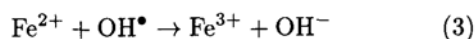
($c_{H_2O_2}/c_{Fe(II)}$ is fixed at 2.88)



**Figure 5**  TOC removal contour plot as a function of $c_{H_2O_2}/c_{Fe(II)}$ and $c_H/c_L$

($c_L$ is fixed at 1987.5 mg·L$^{-1}$)

When hydroxyl radical is produced *via* iron-hydrogen peroxide reaction [Reaction (1)], ferrous ion and hydrogen peroxide would react with hydroxyl radical respectively and consume the radicals produced.

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \qquad (3)$$

$$H_2O_2 + OH^\bullet \rightarrow H_2O + HO_2^\bullet \qquad (4)$$

No matter which chemical is in excess, ferrous ion or hydrogen peroxide, Reaction (3) or (4) would be-come obvious. Therefore the utility of hydroxyl radical would decrease. There existed an optimal hydrogen peroxide to ferrous ion molar ratio such that the production of hydroxyl radical would be at maximum *via* Reaction (1) and the consumption of hydroxyl radical by ferrous ion or hydrogen peroxide would be at minimum *via* Reaction (3) or (4). In this case the highest TOC removal would be achieved.

## NOMENCLATURE

| | |
|---|---|
| $c$ | concentration, mol·L$^{-1}$ |
| $c_H$ | concentration of HMW based on TOC, mg·L$^{-1}$ |
| $c_{HA}$ | concentration of humic acid, mg·L$^{-1}$ |
| $c_L$ | concentration of LMW based on TOC, mg·L$^{-1}$ |
| $X_1$ | $H_2O_2$ to $Fe^{2+}$ molar ratio |
| $X_2$ | LMW content |
| $X_3$ | HMW to LMW ratio (as TOC) |

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