

Treatment of landfill leachate by Fenton's reagent in a continuous stirred tank reactor

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Received 9 August 2005; received in revised form 21 December 2005; accepted 21 December 2005

Available online 8 February 2006

Abstract

The treatment of landfill leachate by Fenton process was carried out in a continuous stirred tank reactor (CSTR). The effect of operating conditions such as reaction time, hydraulic retention time, pH, H₂O₂ to Fe(II) molar ratio, Fenton's reagent dosage, initial COD strength, and temperature on the efficacy of Fenton process was investigated. It is demonstrated that Fenton's reagent can effectively degrade leachate organics. Fenton process reached the steady state after three times of hydraulic retention. The oxidation of organic materials in the leachate was pH dependent and the optimal pH was 2.5. The favorable H₂O₂ to Fe(II) molar ratio was 3, and organic removal increased as dosage increased at the favorable H₂O₂ to Fe(II) molar ratio. Temperature gave a positive effect on organic removal.

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Keywords: Chemical oxidation; CSTR; Fenton's reagent; Landfill leachate

1. Introduction

It is well known that the composition of landfill leachate is complex, due in part to the conditions within a landfill such as chemical and biological activities, moisture content and the degree of stabilization. In spite of many attempts to treat landfill leachate, it appears that no general recommendations of universal validity for leachate treatment can be made at the present time. Treatment methods must be matched to the actual characteristics of the leachate under examination. In particular, conventional biological methods, which are frequently used to treat landfill leachate, have not achieved the same level of success as they have in municipal wastewater treatment due to a great extent to the presence of non-biodegradable and toxic organic compounds contained in landfill leachate [1,2].

Chemical oxidation has been employed to decompose refractory organic substances and subsequently enhance the biological treatability of wastewater [3–5]. Advanced oxidation processes [6], AOPs, which involve hydroxyl radicals ($\bullet\text{OH}$) as the oxidation agent, have been demonstrated to be a reliable alternative

to landfill leachate treatment. Hydroxyl radical is the second strongest oxidant ($E^0 = 2.87\text{ V}$) that is only inferior to fluoride ($E^0 = 3.06\text{ V}$).

Recently there have been numeral reports about landfill leachate treatment by AOPs such as ozone (O₃), ozone with hydrogen peroxide (O₃/H₂O₂), ozone with ultraviolet light (O₃/UV), hydrogen peroxide with ultraviolet light (H₂O₂/UV), Fenton process (H₂O₂/Fe²⁺), and photo-Fenton process (H₂O₂/Fe²⁺/UV) [7]. Fenton process was more readily employed to treat landfill leachate, as it is much cheaper and easier to operate compared with other AOPs such as O₃/H₂O₂. Although photo-Fenton process is superior to conventional Fenton process, it is technically less practicable in that the penetration distance of UV light would be limited in the leachate, and that the effectiveness of photolysis depends on the wavelength [8] and accordingly the optimized quantum yield is obtained in a narrow range of wavelength. Therefore, the photo-Fenton process would not be successful in field application.

Compared with active bench scale research on Fenton process, the reported practical application of Fenton's reagent is scarce except for a pilot plant with a capacity of 1 m³ day⁻¹ operated in Korea [9]. The degradation of organics in leachate using Fenton's reagent will depend on the chemical composition of leachate, which was influenced by refuse characteristics,

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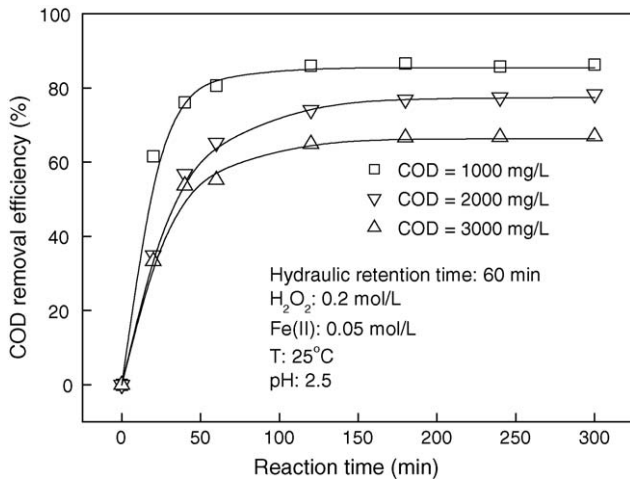


Fig. 2. COD removal efficiencies at different initial COD strengths vs. reaction time.

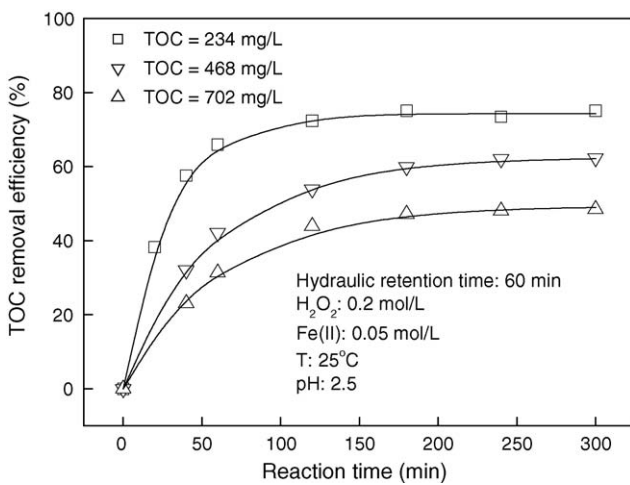


Fig. 3. TOC removal efficiencies at different initial TOC strengths vs. reaction time.

in which C_0 the influent concentration, C is the effluent concentration as well as the concentration in the reactor, Q is the leachate flowrate, and V is the reactor volume.

Solving the differential Eq. (2) with the initial condition:

$$t = 0, \quad C = C_0 \quad (3)$$

We get the following equation,

$$\frac{C_0 - C}{C_0} = \frac{\tau k_{\text{exp}}}{1 + \tau k_{\text{exp}}} \left\{ 1 - \exp \left[- \left(k_{\text{exp}} + \frac{1}{\tau} \right) t \right] \right\} \quad (4)$$

in which τ is hydraulic retention time, $\tau = V/Q$.

Table 1
First order rate constants at different initial COD or TOC strengths

Initial COD (mg/L)	k_{exp} (min^{-1})	R^2	Initial TOC (mg/L)	k_{exp} (min^{-1})	R^2
1000	0.0733	0.9157	234	0.0379	0.8467
2000	0.0385	0.7732	468	0.0202	0.7842
3000	0.0292	0.8953	702	0.0131	0.8020

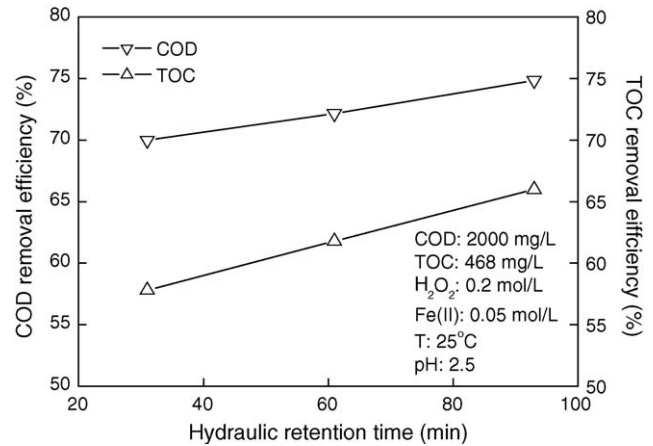


Fig. 4. COD and TOC removal efficiencies at different hydraulic retention time.

From Eq. (4) we know that even if k_{exp} were not considered in the exponential term, the removal efficiency would reach 95% steady value of $\tau k_{\text{exp}} / (1 + \tau k_{\text{exp}})$ when t/τ is 3, i.e., reaction time is three times of hydraulic retention time. Therefore, the steady state would be achieved after three times of hydraulic retention time. The first order rate constants were determined based on the data of removal efficiency versus time using Matlab as shown in Table 1.

Table 1 indicated that rate constants would decrease with the increase of initial COD or TOC strength. In addition, rate constants of TOC removal are lower than those of COD removal under the same operating conditions. This can be explained by the change of average oxidation state. The average oxidation state is defined as [15],

$$\text{Average oxidation state} = 4 \left[1 - \left(\frac{\text{COD}}{\text{TOC}} \right) \right] \quad (5)$$

where COD is expressed in moles of O_2 per liter and TOC in moles C per liter.

The average oxidation state usually increases during oxidation process such as Fenton oxidation [16]. This means that COD to TOC ratio should decrease, i.e., the rate of TOC decrease is lower than that of COD.

Also, COD or TOC removal efficiencies after three hydraulic retention times at different hydraulic retention times were tested (see Fig. 4). It is shown that COD or TOC removal efficiency will increase with the increase of hydraulic retention time.

Based on the results, further experiments were performed at three times of hydraulic retention time.

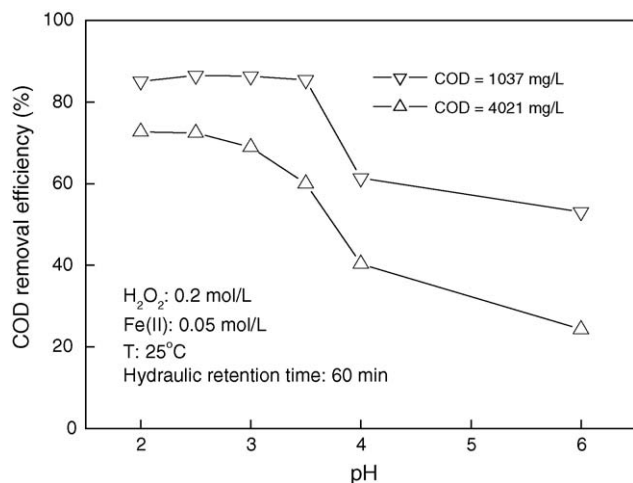


Fig. 5. COD removal efficiencies at different pH values.

3.2. Effect of pH

Fenton process has a typically sharp, preferred pH region in which it is optimally operated. pH affects the activity of both the oxidant and the substrate, the speciation of iron, and hydrogen peroxide decomposition. Sedlak and Andren [17] explained higher hydroxyl radical product yields in the pH range of 2–4 by a reaction involving the organometallic complex where either hydrogen peroxide is regenerated or reaction rates are increased. Also, it is better to remove inorganic carbons from wastewater because they can scavenge hydroxyl radicals [18]. Inorganic carbons can be easily removed by controlling the pH to the acidic condition. Fig. 5 showed the effect of pH on the COD removal efficiencies. Higher removal efficiency was achieved when pH is not higher than 3.5 for lower strength (COD = 1037 mg/L), while the optimal pH range is only 2–2.5 for higher strength (COD = 4021 mg/L). Based on the results, further experiments were performed at pH 2.5.

The effect of pH on TOC removal efficiency was also obtained and it was observed to be similar to that on COD removal efficiency. And TOC removal efficiency was a little lower than COD removal efficiency under the same operating conditions. Therefore, all the data related to TOC were not shown in this paper except for the reaction time and hydraulic retention time effects.

3.3. Effect of $H_2O_2/Fe(II)$ molar ratio

The ratios of hydrogen peroxide to ferrous iron [$H_2O_2/Fe(II)$] and of organic materials to ferrous iron [$RH/Fe(II)$] are very important operational parameters of the Fenton process. In order to investigate the optimum $H_2O_2/Fe(II)$ molar ratio, six different $H_2O_2/Fe(II)$ molar ratios were tested with three different COD strengths (1000, 2000, and 4000 mg/L). The ferrous iron dosage was held constant (0.05 M) while hydrogen peroxide dosage changed from 0.025 to 0.25 M. This would yield a $H_2O_2/Fe(II)$ molar ratio ranging from 0.5 to 5. pH and temperature were kept at 2.5 ± 0.1 , and 25 ± 1 °C, respectively. Hydraulic retention time was 60 min. After 180 min of reaction time, an aliquot of the sample was taken from the overflow in order to measure resid-

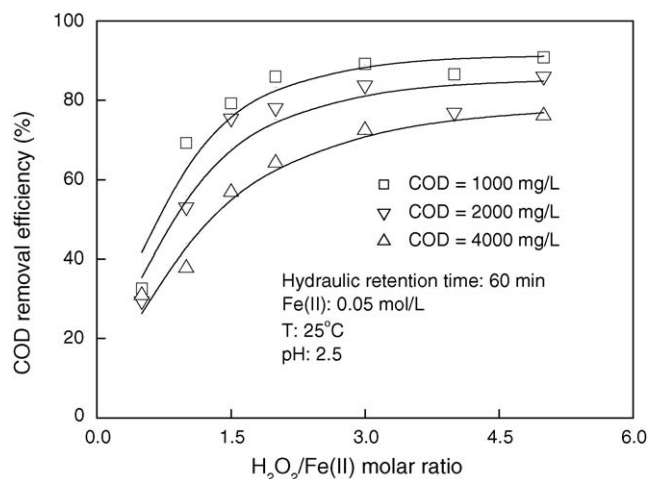


Fig. 6. COD removal efficiencies at different $H_2O_2/Fe(II)$ molar ratios.

ual COD, TOC, ferrous iron, and hydrogen peroxide. Residual hydrogen peroxide, both before neutralization and after neutralization to pH 7.5–8.0, was measured to investigate whether the dosages of hydrogen peroxide were deficient or excessive for the ferrous iron dosage, and to correct the COD interference from residual hydrogen peroxide, respectively.

The changes of COD removal efficiencies are shown in Fig. 6. These increased almost linearly with the increase of $H_2O_2/Fe(II)$ molar ratio by 1.5. Further increase in $H_2O_2/Fe(II)$ molar ratio over 3 did not show significant improvement in removals. Compared with the result of a batch reactor with a single dosage of Fenton's reagent [16], much higher removals were obtained with a continuous stirred tank reactor. At the molar ratio of 1.5, COD removal was only 60% in the batch reactor but increased to 79% in the continuous stirred tank reactor at 1000 mg/L of COD strength, while the improvement of COD removal was from 62% to 89% at the molar ratio of 3. It might be caused by the change of the reaction condition between organic materials and Fenton's reagent. Contrasted with the batch reactor, both organic materials and Fenton's reagent are continuously fed into the continuous stirred tank reactor so that their compositions in the reactor are quite different from those in the batch reactor. In the batch reactor, their concentrations are relatively high at the initial stage when they are added simultaneously but continuously decrease as the oxidation reactions proceed. Most of the reactions, whether oxidations or oxidant formations, occurs intensively at the initial stage, and may promote side reactions that cannot contribute oxidation. However, both organic materials and Fenton's reagent are continuously fed and mixed in bulk solution in the continuous stirred tank reactor so that their concentrations are relatively low throughout the reaction time. This environment may minimize side reactions.

Residual ferrous iron was observed significantly only at the $H_2O_2/Fe(II)$ molar ratio of 0.5 meaning the deficiency of hydrogen peroxide. For example, residual ferrous iron was 0.014, 0.016, and 0.014 M when COD was 1000, 2000, and 4000 mg/L, respectively. It was negligible above the $H_2O_2/Fe(II)$ molar ratio of 1, i.e., below 0.00036 M.

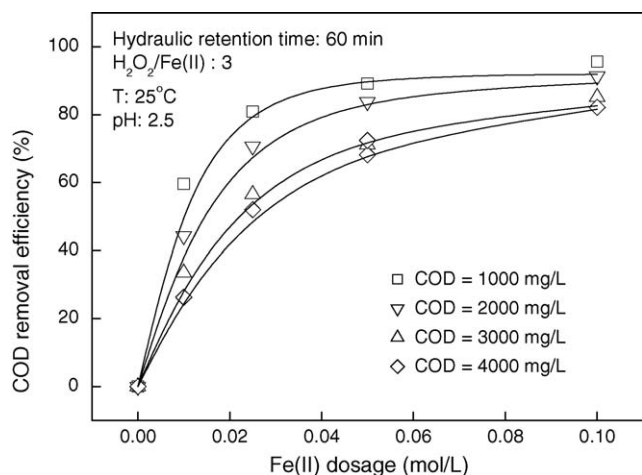


Fig. 7. COD removal efficiencies at different dosages.

Residual hydrogen peroxide concentration was in the range of 0.0002–0.001 M over the $\text{H}_2\text{O}_2/\text{Fe(II)}$ molar ratios tested. Residual COD contributed by residual hydrogen peroxide was negligible over the $\text{H}_2\text{O}_2/\text{Fe(II)}$ molar ratios tested. In contrast to the results of the batch experiment, most of the hydrogen peroxide fed was decomposed over all molar ratios tested [16]. Whether the hydrogen peroxide fed was deficient or excessive, it was consumed without leaving any considerable level behind. Sludge settling characteristics were excellent over all molar ratios tested.

The $\text{H}_2\text{O}_2/\text{Fe(II)}$ molar ratio of 3 was chosen for further experiments based on the removal efficiencies.

3.4. Effects of dosage and initial COD strength

In order to find the effect of Fenton's reagent dosage, investigation has carried out at different initial COD strengths. The $\text{H}_2\text{O}_2/\text{Fe(II)}$ molar ratio, pH, temperature, and hydraulic retention time were fixed at 3 and 2.5 ± 0.1 , $25 \pm 1^\circ\text{C}$, and 60 min, respectively. After adjusting to the experimental conditions, four different amounts of ferrous iron (1, 2.5, 5, and 10×10^{-2} M) and their equivalent amount of hydrogen peroxides were continuously fed into the reactor. All flow rates were kept the same for all Fenton's dosage, to minimize the dilution effect by the volume of chemicals.

Fig. 7 showed the changes of COD removal efficiencies as a function of ferrous iron dosage. These increased rapidly with the increase of dosage. But further improvement in the COD removal efficiency beyond a certain amount gave milder increased removal efficiency. This indicated that the end by-products of oxidation reactions are mainly made of short chain organic acids that are difficult to be further oxidized [19]. In addition, more COD was removed at higher COD strengths than lower COD with the same amount of dosage though COD removal efficiency decreased with initial COD. For example, COD removal efficiency ($\text{H}_2\text{O}_2/\text{Fe(II)} = 0.15 \text{ M}/0.05 \text{ M}$) was 89.2%, 83.8%, 71.2%, and 68.2% when initial COD was 1000, 2000, 3000, and 4000 mg/L respectively, whereas COD removal was 892, 1675, 2136 and 2726 mg/L respectively. Inferring these

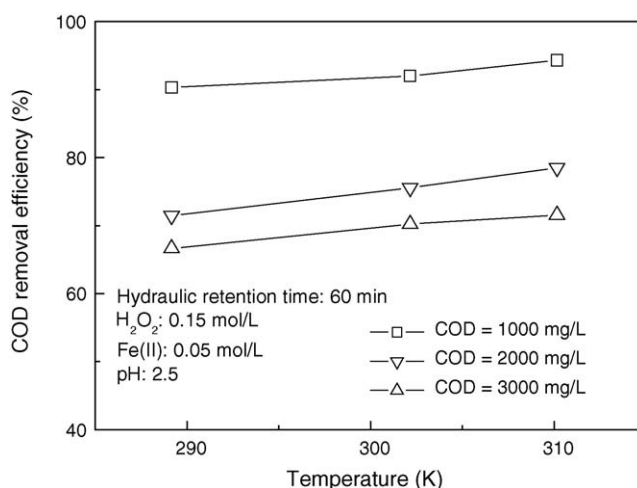


Fig. 8. COD removal efficiency vs. temperature plot.

results, dosage on COD strength to get a target removal efficiency can be chosen.

3.5. Effect of temperature

In order to investigate the effect of temperature, three different temperatures between 16 and 37°C were tested for three COD strengths (1000, 2000, and 3000 mg/L). Other experiment conditions except temperature were kept the same.

The results showed that COD removal efficiencies increased slightly as the temperature increased (Fig. 8). The results showed that COD removal efficiency increased slightly as the temperature increased. As temperature increased from 13 to 37°C , COD removal efficiency increased from 90.3% to 94.3%, from 71.4% to 78.5%, and from 66.6% to 76.6% when initial COD was 1000, 2000, and 3000 mg/L, respectively. Higher temperature was beneficial for organic removal, even though the increase of organic removal is relatively small.

4. Conclusion

The effects of major parameters on the Fenton's process were evaluated in a continuous stirred tank reactor (CSTR). It was proved that organic materials in leachate could be successfully removed by Fenton's reagent. Favorable operation conditions were thoroughly investigated and uncovered with the traditional "one-factor-at-a-time" method.

The steady state was reached after three times of hydraulic retention time. The oxidation of organic materials in the leachate showed pH dependence. The favorable $\text{H}_2\text{O}_2/\text{Fe(II)}$ molar ratio was 3. Organic removal increased with the increase of dosage at the favorable $\text{H}_2\text{O}_2/\text{Fe(II)}$ molar ratio. Temperature gave a positive effect on organic removal.

Acknowledgements

This study was supported by Delaware Solid Waste Authority (DSWA), DE, USA. The first author would like to acknowledge the financial support by SRF for ROCS, SEM, China (Grant

No. [2001]498), and Hubei Provincial Science and Technology Department through “The Gongguan Project”, China (Grant No. 2003AA307B01).

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