

Optimization of Fenton process for the treatment of landfill leachate

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Abstract

The treatment of landfill leachate by Fenton process was carried out in a batch reactor. The effect of operating conditions such as reaction time, pH, H₂O₂ to Fe(II) molar ratio, Fenton's reagent dosage, initial COD strength, feeding mode, the type of polymer, and temperature on the efficacy of Fenton process was investigated. It is demonstrated that Fenton's reagent can effectively degrade leachate organics. Fenton process was so fast that it was complete in 30 min. 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 1.5, and organic removal increased as dosage increased at the favorable H₂O₂ to Fe(II) molar ratio. The efficacy of Fenton process was improved by adding Fenton's reagent in multiple steps than that in a single step. Furthermore, the stepwise addition of both hydrogen peroxide and ferrous iron was more effective than that of hydrogen peroxide only. Sludge settling characteristics were much improved with the addition of the proper polymer. Temperature gave a positive effect on organic removal. © 2005 Elsevier B.V. All rights reserved.

Keywords: Landfill leachate; Fenton's reagent; Chemical oxidation; Batch mode

1. Introduction

The hydroxyl radical is one of the most reactive free radical and the second strongest oxidant. It has been demonstrated that hydroxyl radicals are the main reactive species governing the degradation reactions of organic pollutants, and many processes to generate effectively hydroxyl radicals have been attempted. Advanced oxidation processes (AOPs) are defined as the oxidation processes that generate hydroxyl radicals in sufficient quantity to effect wastewater treatment [1]. Most of the AOPs use a combination of strong oxidants like ozone, oxygen or hydrogen peroxide with catalysts like transition metals, irons, semiconductor powders, radiation or ultrasound. Typical AOPs includes O₃/UV, H₂O₂/UV, O₃/H₂O₂/UV, H₂O₂/Fe(II), TiO₂/UV, and TiO₂/H₂O₂/UV [2].

The catalyzation of hydrogen peroxide by ferrous sulfate, Fenton's reagent, is one of the most common AOPs. In 1894,

Fenton published a descriptive study describing how ferrous iron in the presence of certain oxidizing agents yielded a solution with powerful and extraordinary oxidizing capabilities, and this mixture is typically referred to as "Fenton's reagent" [3]. Fenton's reagent is defined as the catalytic generation of hydroxyl radicals (•OH) resulting from the chain reaction between ferrous ion and hydrogen peroxide, and the oxidation of organic compounds (RH) by Fenton's reagent can proceed by the following chain reactions [4,5]:



Although Fenton's reagent was discovered over 100 years ago, its application as an oxidizing process for destroying toxic organics was not applied until late 1960s [2,5]. Since 1990s, more and more researches have been focused on the treatment of landfill leachate by Fenton process,

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which was used as a post-treatment or pre-treatment because direct biological treatment is impossible to remove biorefractory organics in leachate [6]. Papadopoulos et al. [7] reported chemical oxidation of leachate (initial COD range of 6500–8900 mg l⁻¹) with Fenton's reagent (100 ml, 30%, w/w H₂O₂ and 40 mg Fe²⁺ per liter leachate) after aerobic biological treatment and observed up to 33% COD reduction. Welander and Henrysson [8] treated landfill leachate containing 400–600 mg l⁻¹ of COD. After nitrified in an activated sludge reactor, leachate was oxidized by Fenton's reagent and 72% COD was removed when hydrogen peroxide was 5 ml l⁻¹ and ferrous ion was 20 mg l⁻¹. Lau et al. [9] employed Fenton coagulation to treat landfill leachate following UASB treatment. Under the optimal condition of 200 mg l⁻¹ of H₂O₂ and 300 mg l⁻¹ of ferrous ion, 70% of residual COD in the UASB effluent was removed. Kim and Huh [10] employed Fenton oxidation to enhance biological treatability of landfill leachate. The ratio of BOD₂₀/COD increased after the oxidation indicating Fenton oxidation could be effective prior to the biological process. Lopez et al. [11] also investigated the effectiveness of Fenton's reagent for the pre-treatment of a municipal landfill leachate with the objective of improving its overall biodegradability. BOD₅/COD ratio of the leachate could be increased from 0.2, the initial value, up to 0.5, the minimum value compatible with a sequent biological post-treatment. Kim et al. [6] used coagulation and Fenton oxidation process to treat leachate produced in stabilized landfills. BOD₅/COD ratio was improved from the range of 0.11–0.17 to 0.45, which suggested that this process was applicable as a biological pre-treatment.

In Fenton process, iron and hydrogen peroxide are two major chemicals determining operation costs as well as efficacy. To understand better and improve the Fenton process, numerous studies have been conducted to find the optimal reaction conditions and investigate the fundamental natures of the process [12]. Yoo et al. [13] used Fenton's reagent combined with a coagulation process to remove refractory organics in leachate and obtained optimum operation conditions. Kang and Hwang [4] believed Fenton oxidation process was possessed of the advantages of both oxidation and coagulation processes, and the organics were removed at these two processes. By distinguishing COD removal by oxidation with COD removal by coagulation, they got optimal operation conditions of oxidation as well as coagulation process. Yoon et al. [12] also investigated the roles and significances of oxidation and coagulation in the removal of leachate organics. Rivas et al. [14] employed Fenton's like reagent [Fe(III)–H₂O₂] to treat stabilized leachate and observed the oxidation state of the catalyst did not influence the efficacy of the process in terms of COD depletion profiles. Yoon et al. [15] evaluated Fenton process for the removal of landfill leachate organics of specific size. It was found that high molecular weight (MW) groups were more easily removed by Fenton reaction than low MW groups. Similar results were reported by Gau and Chang

[16]. The fraction of high MW groups such as humic substance in leachate varied with landfill age [17]. Zhang and Huang [18] investigated the effect of high MW organic matter/low MW organic matter ratio on the removal efficiency of TOC in landfill leachate by Fenton oxidation process.

As mentioned above, the application of Fenton's reagent to the treatment of landfill leachate was active, but nearly all the researches were bench scale. 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 [13]. The degradation of organics in leachate using Fenton's reagent will depend on the chemical composition of leachate, which was influenced by refuse characteristics, hydrogeology, height of refuse, age of landfill, and climatic conditions surrounding the landfill [19]. Therefore, leachate characteristics are time dependent and site-specific. To design and operate a continuously operated pilot plant with a capacity of 1.136 m³ h⁻¹ at the Northern Solid Waste Management Center of Delaware Solid Waste Authority at Cherry Island in Wilmington, Delaware [20], the effects of major parameters on the Fenton process were evaluated in this study with the traditional one-factor-at-a-time method using a bench-scale batch reactor. These parameters include reaction time, pH, H₂O₂ to Fe(II) molar ratio, Fenton's reagent dosage, initial COD strength, feeding modes, type of flocculants, and temperature.

2. Materials and methods

2.1. Materials and analytical methods

Leachate samples were taken with polyethylene bottles from the Central Solid Waste Management Center (CSWMC) at Sandtown, Delaware. Samples taken were preserved in refrigerator at 4 °C in accordance with the Standard Methods [21]. Prior to the experiments, large particles and debris were removed by centrifuge to minimize particulate effects in oxidation reactions. The leachate samples were centrifuged for 10 min at 10,000 rpm using sorvall super-speed refrigerated centrifuge (Dupont Co., Wilmington, DE, Model RC-5). Its characteristics were pH 6.65–6.69, COD 8298–8894 mg l⁻¹, TOC 2040–2207 mg l⁻¹, and alkalinity as CaCO₃ 3500–4600 mg l⁻¹.

All chemicals used were American Chemical Society (ACS) certified grade and obtained from Fisher Scientific Company, Springfield, NJ, or Aldrich Chemical Company, Milwaukee, WI.

COD were determined by both Hach vials and a closed reflux, colorimetric method at 600 nm with Hach spectrophotometer (Hach DR/2000, Loveland, CO) according to the Standard Methods [21]. The concentration of hydrogen peroxide was analyzed using a titanium sulfate spectrophotometric method [22]. Ferrous iron [Fe(II)] was determined using a 1,10-phenanthroline colorimetric method [21]. Total

iron was measured with the flame atomic absorption (AA) spectrophotometric method, using AA spectrophotometer (Perkin-Elmer Co., Model 5000), according to the Standard Methods [21]. The combustion-infrared method using TOC analyzer (Rosemount Dohrmann, Model-190) was used for TOC measurement. TOC was determined by the difference between TC and IC [21].

2.2. Experimental procedure

Batch experiments were performed in a 1-l double jacket spherical plastic reactor with four baffles to minimize vortexing and rotational flow (see Fig. 1). Mixing was provided by a variable speed motor connected to an epoxy-coated steel shaft and Teflon standard three-blade propeller. It was vertically mounted above one propeller diameter from the reactor bottom. Mixing speed was about 1750 rpm, which was measured by stroboscopic electronic stroboscope (General Readi Co., West Concord, MA, Type 1531). The acidic condition on the reactor was controlled with an automatic pH controller (New Brunswick Scientific Co., Model pH 2) using 1 M sulfuric acid and 10 M sodium hydroxide. The reactor temperature was maintained by a water circulator.

Leachate samples were diluted to the desired COD strengths with distilled water, and transferred to the reactor. Temperature and pH were adjusted to a desired value. For most runs except for multiple dosages, a selected amount of ferrous sulfate was dissolved, and hydrogen peroxide was added in a single step. Samples were taken at pre-selected time intervals with syringe. Residual hydrogen peroxide, ferrous iron, and total iron were measured after filtering with a 0.45 μm filter. Separate aliquots without filtration were taken at the same intervals, and neutralized to about pH 7.5–8.0 with 10 M sodium hydroxide and 1 M sulfuric acid. They were mixed for 10 min with magnetic stirred bar. After leaving alone for 20 min, the supernatant was centrifuged for 10 min at 15,000 rpm. Both COD and TOC in the supernatant were then measured.

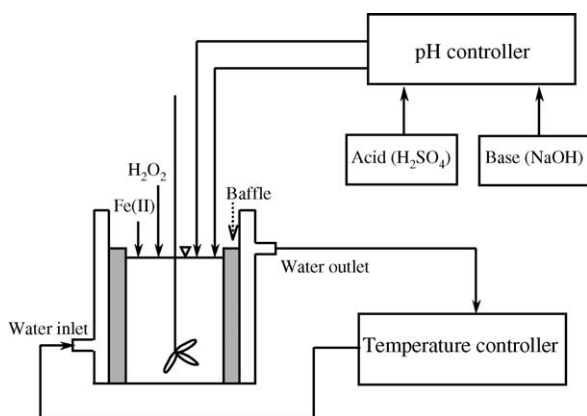


Fig. 1. Schematic of batch experimental apparatus for the Fenton process.

3. Results and discussions

3.1. Effect of reaction time

Reaction time effect on Fenton process was tested to determine an experimental condition for further research. In this study, we evaluated the efficacy of Fenton process in terms of COD and TOC. COD test is based on the assumption that all the organic materials can be oxidized by the strong oxidizing agent under acidic conditions. However, COD test also has some restrictions. Organic nitrogen will be converted to ammonia. In addition, some reduced substances such as sulfides, sulfites, ferrous iron, and hydrogen peroxide will be oxidized. All of them reported as COD [21]. TOC is a more convenient and direct expression of total organic content than COD. TOC is independent of the oxidation state of the organic matter and does not measure other organically bound elements such as nitrogen, hydrogen and inorganics that can contribute to the oxygen demand measured by COD. Using COD and TOC as well as their relationship, the efficacy of chemical oxidation and the state of oxidation can be interpreted. When organic materials are oxidized by Fenton's reagent, three types of degradation of organic materials, even though they are refractory, toxic or inhibitory, are described by Lyman et al. [23] as: primary degradation, a structural change in the parent compound where biodegradability may be improved; acceptable degradation, degradation to the extent that toxicity is reduced; ultimate degradation, complete to carbon dioxide, water and other inorganics. COD (the degree of oxidation) will change during the various degradation stages. On the other hand, TOC (the amount of ultimate conversion) may decrease or remain constant depending on what kinds of oxidation occur. If ultimate degradation to carbon dioxide and water occur, TOC may decrease, but if primary and acceptable degradation occur, it may remain constant. Stumm and Morgan [24] expressed the average oxidation state of organic carbon in the wastewater mixture with COD and TOC as:

$$\text{oxidation state} = \frac{4(\text{TOC} - \text{COD})}{\text{TOC}} \quad (5)$$

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

The amount of carbon converted to carbon dioxide can be determined from TOC, while the ratio of COD to TOC is defined as oxygen demand and can be converted to mean oxidation state for each reaction time using equation (5), which is related to the degree of change in the structure of the organic compounds after oxidation.

Fig. 2 showed the decrease of organic materials as a function of reaction time. The results demonstrated that organic materials were rapidly degraded by Fenton's reagent. Most organic removal occurred in the first 20 min. After 20 min, the change of residual COD became insignificant. More foam was observed on the top layer of leachate as the oxidation proceeded. This was evidence of carbon dioxide formation. During 30 min time of reaction, TOC decreased from 248 mg l^{-1}

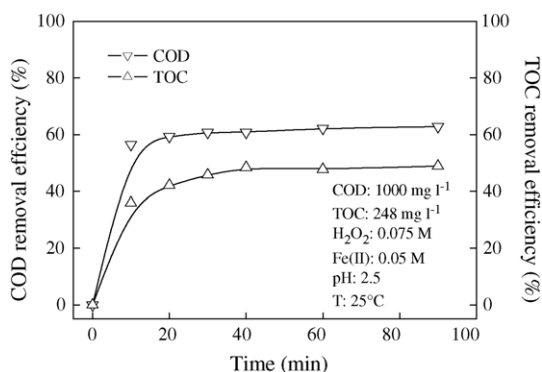


Fig. 2. Effect of reaction time on COD and TOC removal efficiencies.

(0.0207 M of carbon) to 125.5 mg l^{-1} (0.0104 M of carbon). Net decreased organic carbon was 0.0207 to 0.0104 M. It turned to inorganic carbon as carbon dioxide. Also, inorganic carbon concentration of untreated leachate was 246 mg l^{-1} as CO_2 ($10^{-2.25}$ M of carbon), and turned from bicarbonate ions to carbonic acid as the pH was adjusted to acidic. The carbonic acid would dissolve in liquid or escape to air as carbon dioxide.

The change of mean oxidation state of organic carbon was shown in Fig. 3. Mean oxidation state of organic carbon in the leachate was -2.04 . It increased rapidly by 10 min of reaction time, but kept almost the same level after 20 min. The original organic materials were drastically changed by Fenton's reagent to other more highly oxidized by-products. However, ultimate conversion of organic carbon to inorganic carbon was not completed. It indicates that early oxidation reactions were both partial oxidations (primary degradation and/or acceptable degradation) and ultimate conversion to inorganic carbon with an abundant amount of hydroxyl radicals but further reactions with residual hydroxyl radicals prevailed partial oxidations rather than ultimate conversion.

Residual ferrous iron and hydrogen peroxide was measured during Fenton reaction. In first 10 min, most of the Fenton's reagent was consumed. Residual ferrous iron and hydrogen peroxide decreased from 5×10^{-2} to about 10^{-4} M, and from 7.5×10^{-2} to about 10^{-3} M,

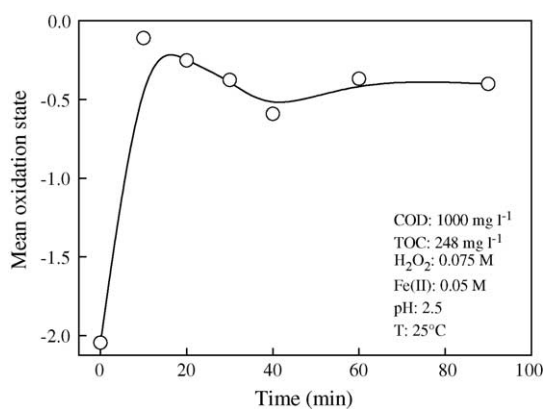


Fig. 3. Evolution of mean oxidation state with time.

respectively. This means that the reaction between ferrous iron and hydrogen peroxide with the production of hydroxyl radical was almost complete in 10 min.

Based on the results, the reaction time for the Fenton's treatment with batch reactor was determined to be 30 min for further experiments.

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 [25] 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 [26]. Inorganic carbons can be easily removed by controlling the pH to the acidic condition. Fig. 4 showed the effect of pH on the COD removal efficiencies. Low pH between 2 and 3 has been found effective for Fenton's reagent, and best removal efficiency was obtained at pH 2.5. These results agree with other studies on the oxidation of organic compounds in wastewaters, such as fermentation brines [27], landfill leachate [4,9], phenolic wastewater [28,29], textile wastewater [30], and dye wastewater [31]. 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 except for the reaction time effect were not shown in this paper.

Residual ferrous iron concentration and ferric iron concentrations are shown in Fig. 5. Most ferrous irons were consumed by the reaction with hydrogen peroxide in all tested pH values. Ferric irons generated by the oxidation of ferrous irons rapidly increased by pH 2.5. Further increase of pH showed drastic decrease of the soluble species. Considering the added total iron concentration, most irons precipitated as

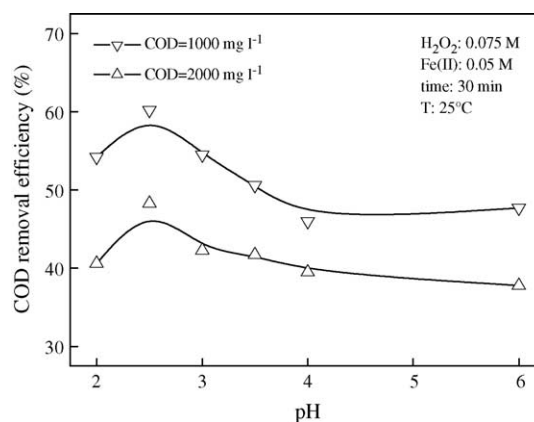


Fig. 4. COD removal efficiencies at different reaction pH values.

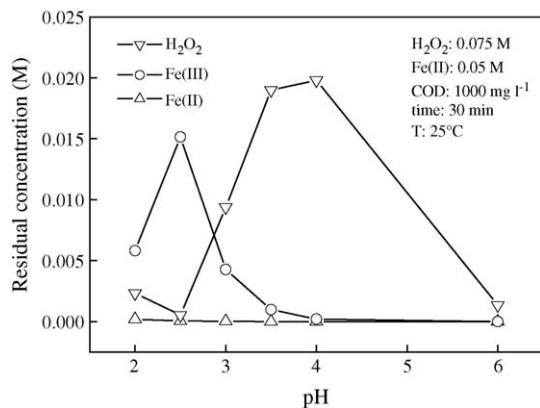
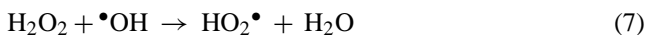
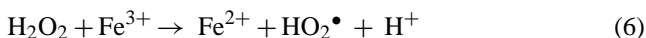


Fig. 5. Dependence of residual ferrous iron, ferric iron, and hydrogen peroxide on pH.

Haag and Yao [32] found, and oxidation became less efficient. The hydrolysis of ferric iron is a function of pH and total ferric iron concentration [24]. It is known that the solution with 0.05 M of soluble iron concentration becomes oversaturated with respect to $\text{Fe}(\text{OH})_3(\text{s})$ around pH 2.5, and additional polynuclear hydrolysis species occur. These complexes have a pronounced tendency to polymerize within pH 3.5 and 7. As a result coagulation would occur. Remaining organic materials could be coagulated and precipitated. It could make up for the disadvantage of the oxidation and minimize the amount of sludge after treatment [31].

Fig. 5 also showed the change of residual hydrogen peroxide concentration. It is known that the production of organic acids and other oxidation products, and the possibilities for the variation may be responsible for the variation in the behavior of the hydrogen peroxide decomposition rate [33]. Initial ferrous ions added reacted rapidly with hydrogen peroxide to produce hydroxyl radicals. The residual hydrogen peroxide was then slowly decomposed by ferric ions. The decomposition of more than the stoichiometric reduction in hydrogen peroxide was attributed to the reactions of hydrogen peroxide with ferric ions generated as well as hydroxyl radicals produced:



Maximum decomposition of hydrogen peroxide occurred at pH 2.5. As pH increased above that pH value, residual hydrogen peroxide concentrations increased by pH 4, then rapidly decreased at pH 6. More soluble irons were available in acidic condition so that they could accelerate the decomposition of hydrogen peroxide whether the decomposed hydrogen peroxide produced hydroxyl radicals or was only consumed by other competitive reactions. Therefore, low residual hydrogen peroxide concentrations were observed at $\text{pH} \leq 2.5$. Meanwhile, as pH increased above pH 2.5, the amount of soluble irons reacting with hydrogen peroxide was decreased by precipitation resulting higher residual

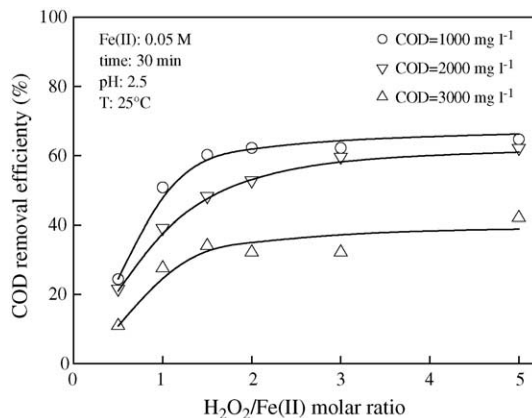
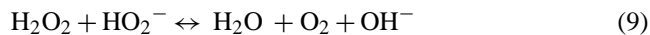
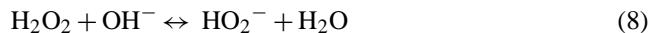


Fig. 6. COD removal efficiencies at different $\text{H}_2\text{O}_2/\text{Fe}(\text{II})$ molar ratios.

hydrogen peroxide concentration. However, above pH 4, more hydrogen peroxide was decomposed without improving oxidation even though soluble iron concentration was so low. It indicated a change in decomposition mechanism. Hydrogen peroxide was decomposed to oxygen without producing hydroxyl radicals by alkaline conditions [14]:



It is interesting that both maximum decomposition of hydrogen peroxide and maximum oxidation occurred at pH 2.5. It means that the rate of hydrogen peroxide decomposition and the efficiency of hydroxyl radical production were best at this pH condition. It is known that more soluble ferric irons are available at pH below 3 [24]. The predominant soluble ferric iron species is hydrated ferric iron ($[\text{Fe}(\text{H}_2\text{O})_4]^{3+}$) at $\text{pH} < 3$, and hydrated ferric iron complex ($[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$) in the pH range of 3–4, respectively.

The selection of a pH condition for further experiments was pH 2.5 based on organic removal efficiencies.

3.3. Effect of H_2O_2 to $\text{Fe}(\text{II})$ molar ratio

In Fenton process, iron and hydrogen peroxide are two major chemicals determining operation costs as well as efficacy. Determination of the favorable amount of the Fenton's reagent is highly important. In order to investigate the optimum $\text{H}_2\text{O}_2/\text{Fe}(\text{II})$ molar ratio, six different $\text{H}_2\text{O}_2/\text{Fe}(\text{II})$ molar ratios were tested with three different COD strengths. It is shown that COD removal efficiencies increased almost linearly with the increase of $\text{H}_2\text{O}_2/\text{Fe}(\text{II})$ molar ratio by 1.5 of molar ratio (Fig. 6). Further increase in $\text{H}_2\text{O}_2/\text{Fe}(\text{II})$ molar ratio over 2 produced less efficient improvement in removals. This may be due to the fact that Fenton's reaction mechanisms proposed by Haber and Weiss [34], Barb et al. [35], and Metelitsa [36]. When $\text{H}_2\text{O}_2/\text{Fe}(\text{II})$ molar ratio is low, the reaction rate follows second order and the stoichiometry of $2\text{Fe}(\text{II}) \cong \text{H}_2\text{O}_2$. But, when the $\text{H}_2\text{O}_2/\text{Fe}(\text{II})$ molar ratio

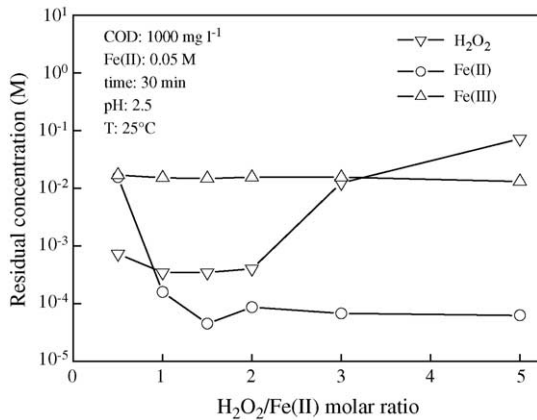
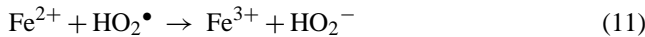
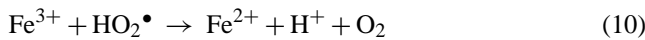


Fig. 7. Dependence of residual ferrous iron, ferric iron, and hydrogen peroxide on H₂O₂/Fe(II) molar ratio.

increases, the reaction kinetics approaches as zero order. That is, at low H₂O₂/Fe(II) molar ratios, both reactions (1) and (2) would occur.

However, at high H₂O₂/Fe(II) molar ratios, one or more side reactions would occur [reactions (6), (7), (10), and (11)]. The mechanism changed [37] and the reaction became independent of hydrogen peroxide



Sludge settling characteristics were excellent at the H₂O₂/Fe(II) molar ratio of 1.5, but became poor above the H₂O₂/Fe(II) molar ratio of 2.0. It seems that excessive hydrogen peroxide, when decomposed, would produce oxygen bubbles that made sludge settling difficult. Therefore, molar ratio of 1.5 was chosen for further experiments.

Residual ferrous iron was observed significantly only at the H₂O₂/Fe(II) molar ratio of 0.5, but it decreased drastically above that value (Fig. 7). Ferric iron concentrations were about 0.015 M over all tested H₂O₂/Fe(II) molar ratios. This means more than 70% of irons turned to insoluble for most of H₂O₂/Fe(II) molar ratios. Residual hydrogen peroxide concentration was not significant by the H₂O₂/Fe(II) molar ratio of 2 but increased significantly above that value (Fig. 7).

3.4. Effects of dosage and initial COD strength

The amount of Fenton's reagent necessary for an effective treatment depending on initial COD strength must be determined. This can differ depending on whether the Fenton process has a role of pretreatment or ultimate pretreatment. Bowers et al. [29] noted that a primary or acceptable degradation may occur in a relatively low consumption and be much more efficient than ultimate degradation.

COD removal efficiency increased rapidly with the increase of dosage (Fig. 8). But further improvement in COD removal efficiency beyond a certain amount of dosage

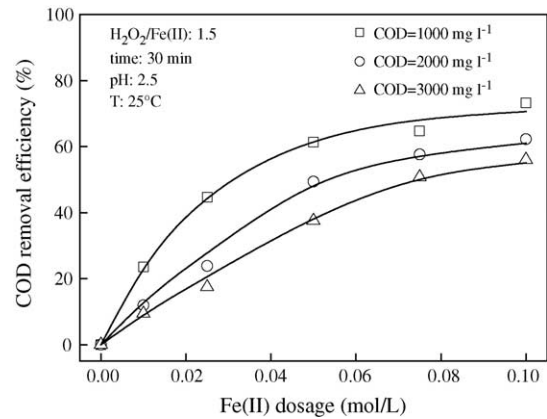


Fig. 8. COD removal efficiencies at different dosages.

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 [11]. 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 (H₂O₂/Fe(II)=0.075 M/0.05 M) was 61.3%, 49.4%, and 37.5% when initial COD was 1000, 2000, and 3000 mg l⁻¹, respectively, whereas COD removal was 613, 988, and 1124 mg l⁻¹, respectively. Inferring these results, dosage on COD strength to get a target removal efficiently can be chosen.

3.5. Effect of feeding modes

The mechanisms of Fenton's reaction would vary with the ratio of RH to Fe(II). When a significant amount of Fe(II) comparing with RH is available, Fe(II) and RH compete to react with hydroxyl radicals. Thus, Fe(II) consumes hydroxyl radical. With the change of feeding mode, the RH to Fe(II) ratio as well as COD removal efficiency may vary. In order to investigate feeding mode effect, Fenton's reagent was fed with two different methods as follows:

- (i) Ferrous iron (0.05 M) was added in a single step (at 0 min), but hydrogen peroxide (0.075 M) was added in a single step (at 0 min) or in two steps (at 0 and 30 min). Total reaction time was 60 min.
- (ii) Both ferrous iron (0.05 M) and hydrogen peroxide (0.075 M) were added simultaneously in one feeding (at 0 min), two feedings (at 0 and 30 min), three feedings (at 0, 15, and 30 min), and five feedings (at 0, 7.5, 15, 22.5, and 30 min), respectively. All feedings were finished in 30 min, and total reaction time was 60 min.

In case (i), when hydrogen peroxide was added at two times, better COD removal was obtained than a single-dose of hydrogen peroxide. The same result was found by Bowers et al. [29]. COD removal efficiencies were increased

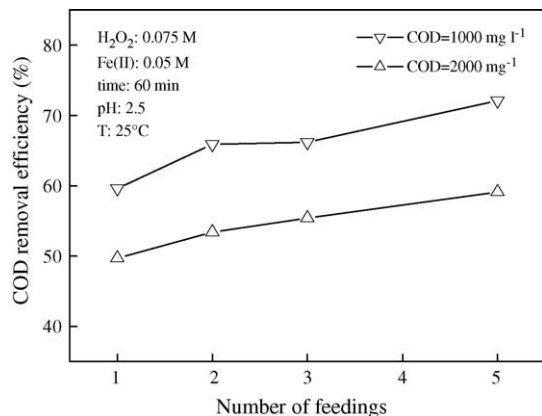


Fig. 9. COD removal efficiency vs. number of feedings.

from 57.4% to 63.6% with COD 1000 mg l⁻¹, and from 42% to 49.7% with COD 2000 mg l⁻¹, respectively. It also means that a better environment was obtained with separated feedings, and that more hydrogen peroxide was used to oxidize organic materials. This could be due to scavenging of hydroxyl radicals by hydrogen peroxide, according to reaction (7), when applying a large initial dose of H₂O₂. Reaction (7) competes with reaction (3) better at higher concentrations of H₂O₂, reducing the oxidation rate of organic materials. Stepwise addition keeps the H₂O₂ concentration at relatively low levels, reducing the detrimental effect of hydroxyl radical scavenging [38].

Better COD removals were also obtained with multiple feedings of Fenton's reagent in case (ii) (Fig. 9). This means that more hydroxyl radicals could be produced and used to oxidize organic materials by making the environment of the high RH/Fe(II) ratio with multiple feedings of both hydrogen peroxide and ferrous iron. The similar result was reported by Yoo et al. [13]. A stepwise addition of Fenton's reagent was more effective than a large initial input. Residual ferrous iron and hydrogen peroxide were in the range of $(1.9\text{--}2.8) \times 10^{-5}$ and $(1.0\text{--}2.7) \times 10^{-3}$ M, respectively, which indicated that they were almost negligible for all tests. Furthermore, simultaneous multiple feeding of Fenton's reagent could achieve a little higher COD removal that multiple feeding of hydrogen peroxide only when two-steps addition was employed, i.e., 65.9% versus 63.6% with COD 1000 mg l⁻¹, and 53.4% versus 49.7% with COD 2000 mg l⁻¹. The favorable H₂O₂ to Fe(II) molar ratio was obtained to be 1.5 in Section 3.3. In either case (i) or case (ii), the total dosage ratio was kept at this value, i.e., H₂O₂/Fe(II) = 0.075 M/0.05 M. However, in case (i), hydrogen peroxide was added at two times while ferrous iron was applied in a single step. This means that ferrous iron was overdosed comparing with hydrogen peroxide in the first addition. The undesired hydroxyl radicals scavenging reaction (2) would compete with reaction (3) significantly at higher concentrations of ferrous iron, reducing the oxidation rate of organic materials. In case (ii) both ferrous iron and hydrogen peroxide were applied simultaneously in multiple steps, which made H₂O₂ to Fe(II) molar ratio keep at the

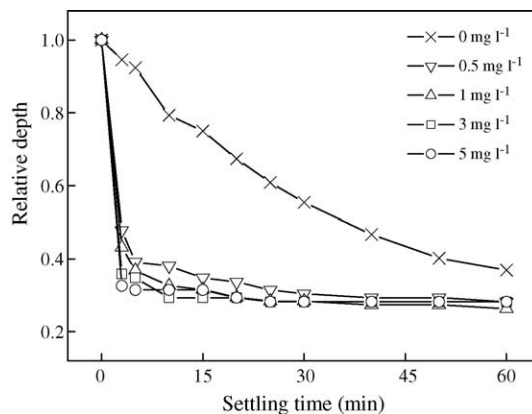


Fig. 10. Relative depth with flocculant 710 vs. settling time.

favorable value of 1.5 at every addition. Therefore, the scavenging effects such as reactions (2) and (7) were minimized, and a little higher COD removal efficiency was achieved.

3.6. Effect of flocculant

Synthetic polymers were added to improve settling characteristics. Two anionic liquid dispersion polymers of Allied Colloids Inc., Percol 710 and Percol 712, were used to test the efficacy of polymers. It was observed that the addition of polymer did not significantly reduce residual COD for all cases (data not shown), and the polymer Percol 712 has little effect on sludge settling (data not shown). With the addition of an effective polymer, Percol 710, as low as 0.5 mg l⁻¹, sludge settling characteristics improved greatly (Fig. 10). Although the polymer dosage had a little effect on sludge settling during the initial period, the volume of sludge decreased by over 50% in 3 min for all the polymer concentrations tested, and the ultimate volume of sludge could be reduced to about 28% after 60 min of settling time. In the absence of the polymer, the volume of sludge dropped by only 5% in 3 min and the ultimate volume was about 37%.

3.7. Effect of temperature

Temperature is one of the important factors influencing catalytic oxidation reaction rates. In order to investigate the effect of temperature, three different temperatures between 13 and 37 °C were tested for three COD strengths. The results showed that COD removal efficiency increased slightly as the temperature increased. With initial COD of 1000 mg l⁻¹, COD removal efficiency increased from 42.3% to 56.2% as temperature increased from 13 to 37 °C. With initial COD of 2000 mg l⁻¹, COD removal efficiency increased from 31.6% to 44.8% as temperature increased from 15 to 35 °C. With initial COD of 3000 mg l⁻¹, COD removal efficiency increased from 24.8% to 32.6% as temperature increased from 15 to 36 °C. 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 process were evaluated using a batch reactor. 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 oxidation of organic materials by Fenton's reagent was so fast that it was complete in 30 min with batch experiments. The oxidation of organic materials in the leachate showed a pH dependence and was most efficient in the pH range of 2–3. A favorable $\text{H}_2\text{O}_2/\text{Fe(II)}$ molar ratio was 1.5, and organic removal increased as dosage increased at the favorable $\text{H}_2\text{O}_2/\text{Fe(II)}$ molar ratio. A stepwise addition of Fenton's reagent was more effective than a large addition simultaneously. Sludge settling characteristics were much improved with the addition of the proper polymer. Temperature gave a positive effect on organic removal.

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