

# Removal of COD from landfill leachate by electro-Fenton method

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## Abstract

The treatment of landfill leachate by electro-Fenton (E-Fenton) method was carried out in a batch electrolytic reactor. The effect of operating conditions such as reaction time, the distance between the electrodes, electrical current, H<sub>2</sub>O<sub>2</sub> to Fe(II) molar ratio, Fenton's reagent dosage and H<sub>2</sub>O<sub>2</sub> feeding mode on the efficacy of E-Fenton process was investigated. It is demonstrated that E-Fenton method can effectively degrade leachate organics. The process was very fast in the first 30 min and then slowed down till it was complete in 75 min. There exists an optimal distance range between the electrodes so that an over 7% higher chemical oxygen demand (COD) removal was achieved than the electrodes positioned beyond this range. COD removal efficiency increased with the increasing current, but further increase of current would reduce the removal efficiency. Organic removal increased as Fenton's reagent dosage increased at the fixed H<sub>2</sub>O<sub>2</sub> to Fe(II) molar ratio. COD removal was only 65% when hydrogen peroxide alone was applied to the electrolytic reactor, and the presence of ferrous ion greatly improved COD removal. COD removal efficiency increased with the increase of ferrous ion dosage at the fixed hydrogen peroxide dose and reached highest at the 0.038 mol/L of ferrous ion concentration. COD removal would decrease when ferrous ion concentration was higher than 0.038 mol/L. The stepwise or continuous addition of hydrogen peroxide was more effective than the addition of hydrogen peroxide in a single step. E-Fenton method showed the synergetic effect for COD removal as it achieved higher COD removal than the total COD removal by electrochemical method and Fenton's reagent.

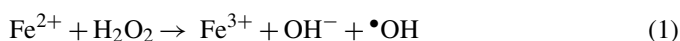
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**Keywords:** Landfill leachate; Fenton's reagent; Electro-Fenton; Chemical oxidation

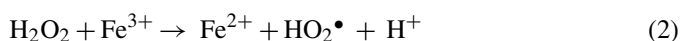
## 1. Introduction

The Fenton process, one of advanced oxidation processes (AOPs), has been widely applied to remove organic matter from landfill leachate as a pre-treatment or post-treatment process [1–15]. However, conventional Fenton process cannot remove chemical oxygen demand (COD) efficiently from landfill leachate.

During the Fenton reaction, hydrogen peroxide is catalyzed by ferrous ions to produce hydroxyl radicals [16],



This reaction is propagated from ferrous ion regeneration mainly by the reduction of the produced ferric species with hydrogen peroxide [17],



The produced hydroxyl radicals would degrade organic matter in the landfill leachate. However, in the Fenton chain reactions, the rate constant of reaction (1) is between 53 and 76 M<sup>-1</sup> s<sup>-1</sup> [16,18–20], while that of reaction (2) is only 0.01 M<sup>-1</sup> s<sup>-1</sup> [17]. This means ferrous ions are consumed more rapidly than they are produced. In addition, ferrous ions can also be rapidly destroyed by hydroxyl radicals with the rate constant in the range of 3.2–4.3 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup> [20,21],



Therefore, more ferrous ion dosage is needed to keep the moderate hydroxyl radicals production. This results in the large amount of ferric hydroxide sludge during neutralization stage of Fenton process, which requires additional separation process and disposal [22].

Recently, the applications of electrochemical method in Fenton process, named electro-Fenton (E-Fenton) method, have been reported. These studies could be generally divided into several categories. In the first one, ferrous ion is externally applied, and both hydrogen peroxide and ferrous ion are concurrently generated at cathode, but primarily focusing on hydrogen

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peroxide generation on mercury pool [23], carbon felt [24], reticulated vitreous carbon [25], graphite [26], activated carbon fiber [27], stainless steel plate [28] or carbon-PTFE [29] cathode. In the second category, hydrogen peroxide is externally applied while a sacrificial iron anode is used as ferrous ion source [30]. In the third category, hydrogen peroxide is externally applied and ferrous ion was electrogenerated via the reduction of ferric ion or ferric hydroxide sludge [22]. In the fourth category, both ferrous ion and hydrogen peroxide are electrogenerated at sacrificial anode and cathode via the two-electro reduction of sparged oxygen, respectively [31]. However, the above E-Fenton processes have seldom been used to treat high strength wastewater [22,25,30–32]. In this study, we proposed a novel E-Fenton method, in which Fenton's reagent was utilized to produce hydroxyl radical in the electrolytic cell and ferrous ion is regenerated via the reduction of ferric ion on the cathode. This method would be used for the treatment of high COD strength landfill leachate. The effect of reaction time, the distance between the electrodes, applied current, Fenton's reagent dosage, Fe(II)/H<sub>2</sub>O<sub>2</sub> molar ratio and the feeding mode of hydrogen peroxide on the efficacy of COD removal from the landfill leachate was investigated.

## 2. Materials and methods

Leachate samples were taken with polyethylene bottles from the Erfeishan Landfill at Wuhan, China. Samples taken were preserved in refrigerator at 4 °C in accordance with the Standard Methods [33]. Its characteristics on average were pH 6.4, COD 5000 mg/L, ammonia-nitrogen 650 mg/L and alkalinity as CaCO<sub>3</sub> 5200 mg/L.

Sodium hydroxide was of chemical pure (CP) grade, and other chemicals used were analytical reagent (AR) grade. All solutions were prepared with distilled water.

The solution pH was measured with an Orion 420Aplus pH-meter. Alkalinity and ammonia-nitrogen were determined using colorimetric method according to the Standard Methods [33]. Chemical oxygen demand was determined by using microwave assisted potassium dichromate method adapted from Jardim and Rohwedder [34].

Batch experiments were performed in a rectangular electrolytic reactor (prexy glass) containing 200 mL solution. Electrolyses were operated at constant current (*I*) of 1, 1.5, 2, 2.5 and 3 A using a DC power supply (Model WYK-305) from Yangzhou Jintong Source Co. Ltd. (China). One pair of 5 cm × 11.9 cm anodic (Ti/RuO<sub>2</sub>-IrO<sub>2</sub>) and cathodic electrodes was positioned 0.7, 1.3, 2.1, or 2.8 cm apart from each other and was dipped in the leachate. A magnetic stirrer (Model 78-1, Hangzhou Instrument Motors Factory, China) provided the mixing of the solution in the reactor. In each run, leachate sample was transferred to the electrolytic reactor. Then, a selected amount of ferrous sulfate heptahydrate was dissolved in the leachate. The initial pH value was adjusted using concentrated sulfuric acid and set at 3 [14]. Hydrogen peroxide was applied all at once, in multiple steps, or in continuous mode using a peristaltic pump (Model D100B, Shanghai Qingpu Huxi Instrument Factory, China). At pre-selected time intervals, samples were

taken into the tubes containing sodium hydroxide solution to quench the reaction by increasing pH around 8.0. Then, they were diluted (typically 1:9 water) and settled for 30 min. The supernatant was withdrawn to measure COD.

## 3. Results and discussion

Reaction time effect on E-Fenton process was tested to determine an experimental condition for further research. In this study, we evaluated the efficacy of E-Fenton process in terms of COD. Fig. 1 shows the decrease of organic materials as a function of reaction time. The results demonstrated that organic materials were rapidly degraded by E-Fenton method. Most organic removal occurred in the first 30 min. After 30 min, the decrease of residual COD slowed down. The reaction was nearly completed at 75 min. Based on the result, the reaction time for the E-Fenton treatment with batch reactor was determined to be 75 min for further experiments.

Defining current efficiency as [35],

$$CE = \frac{V(\text{COD}_0 - \text{COD}_t)F}{8It} \quad (4)$$

where COD<sub>0</sub> is the initial chemical oxygen demand, COD<sub>*t*</sub> the chemical oxygen demand at given time *t*, *V* the volume of the electrolyte, *F* the Faraday constant and *I* is the current intensity.

As can be seen, the current efficiency increased for the first 15–30 min to attain high maxima of 174%, and then it dropped gradually (Fig. 1). The similar results have been reported when aniline [31] and chlorophenoxy herbicides [36,37] were destructed, respectively, by the first category of E-Fenton method and apparent current efficiency (ACE) was defined as the ratio of the experimental TOC removal to the theoretically calculated TOC abatement considering that the applied electrical charge is only consumed in the corresponding mineralization reaction. E-Fenton has a very good efficiency during the initial stage of electrolysis when easily oxidizable products were rapidly destroyed by hydroxyl radicals. The decrease of current efficiency was due to the formation of hardly oxidizable products [36,37]. Fig. 1 also shows that the current efficiency could exceed 100%. This can be accounted for the fact that the determination of current efficiency only involves one electrochemical reac-

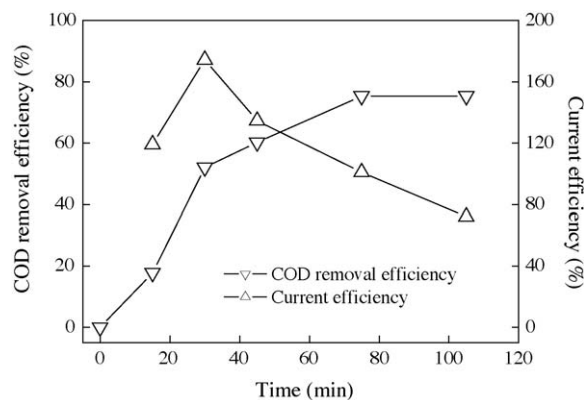


Fig. 1. COD removal efficiency and current efficiency with electrolysis time (H<sub>2</sub>O<sub>2</sub> = 0.34 mol/L, Fe(II) = 0.11 mol/L, pH 3, *I* = 2 A, *d* = 2.1 cm).

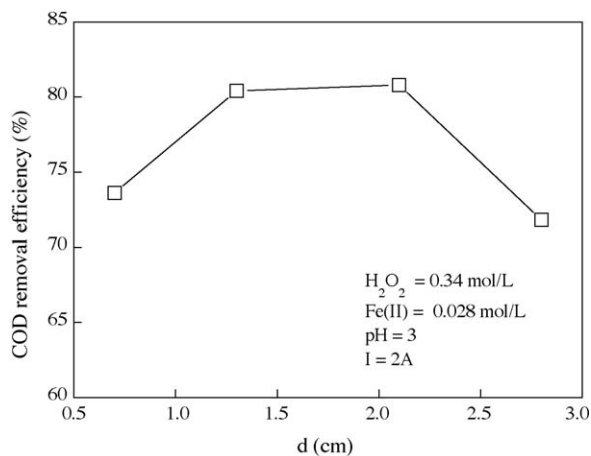


Fig. 2. Effect of the distance between the electrodes on COD removal efficiency.

tion. In E-Fenton process, hydroxyl radicals would be produced at the surface of a high-oxygen overvoltage anode from water oxidation,



Hydroxyl radicals would also be generated by reaction (1) in the medium. The produced ferric ion from reaction (1) would be reduced to ferrous ion at the cathode,



This would induce Fenton chain reaction efficiently. Therefore, in the case of coupled reaction, the maximal efficiency would reach 200% [25,31].

The effect of the distance between the electrodes ( $d$ ) on COD removal efficiency is shown in Fig. 2. As can be seen, COD removal efficiency was nearly the same when the distance was in the range of 1.3–2.1 cm. For example, COD removal efficiency was 80.4% for 1.3 cm of distance and it was 80.8% for 2.1 cm of distance. The shorter or longer distance beyond this range would only achieve the lower COD removal efficiency, i.e., 73.6% of COD removal for 0.7 cm of distance and 71.8% of COD removal for 2.8 cm of distance. In the E-Fenton process, ferrous would be regenerated via the reduction of ferric ion at the cathode by reaction (6). This would induce Fenton chain reactions. However, when the electrodes were placed too short, the electro-regenerated ferrous ion could be easily oxidized to ferric ion at the anode,



This inhibits the efficacy of Fenton chain reactions. On the other hand, longer distance was attributed to the limiting mass transfer of ferric ion to the cathode surface that governs ferrous ion regeneration [38]. Therefore, reaction (1) that produced hydroxyl radicals could not be propagated efficiently from ferrous ion regeneration.

The effect of electrical current on COD removal efficiency is shown in Fig. 3. More COD was removed when current increased, indicating an enhancement of the degradation power. This is due to the higher electro-regeneration of ferrous ion from

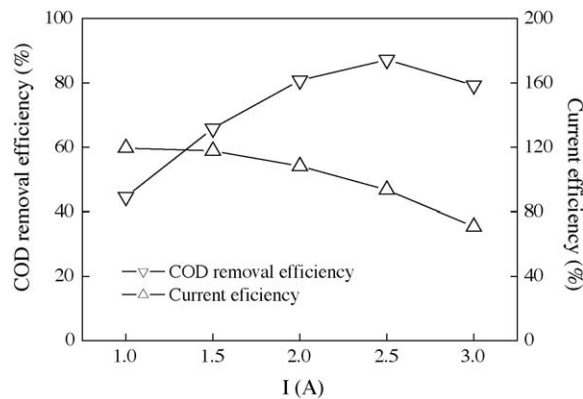


Fig. 3. COD removal efficiency and current efficiency at various electrical currents ( $\text{H}_2\text{O}_2 = 0.34 \text{ mol/L}$ ,  $\text{Fe(II)} = 0.028 \text{ mol/L}$ ,  $\text{pH} = 3$ ,  $d = 2.1 \text{ cm}$ ).

ferric ion (reaction (5)) with increasing current, which increased the efficacy of Fenton chain reactions. However, COD removal efficiency decreased when the current exceeds 2.5 A. The COD removal efficiency was only 79.3% at 3.0 A compared with 87.2% at 2.5 A. At higher current the competitive electrode reactions such as the discharge of oxygen at the anode via reaction (8) and the evolution hydrogen at the cathode via reaction (9) would become pronounced.



These would inhibit main reactions such as reactions (5) and (6).

The decay of current efficiency with current is also observed in Fig. 3. This indicated that parasite reactions of hydroxyl radical became more predominant when it was more rapidly generated [37]. In addition, the further increase of current would lead to the competitive electrode reactions of discharge of oxygen and hydrogen (reactions (8) and (9)).

The effect of Fenton's reagent dosage on COD removal efficiency was evaluated at the fixed  $\text{H}_2\text{O}_2/\text{Fe(II)}$  molar ratio of 12. COD removal efficiency increased almost linearly with the increase of  $\text{H}_2\text{O}_2$  concentration by 0.34 mol/L (Fig. 4). But further improvement in COD removal efficiency beyond 0.34 mol/L

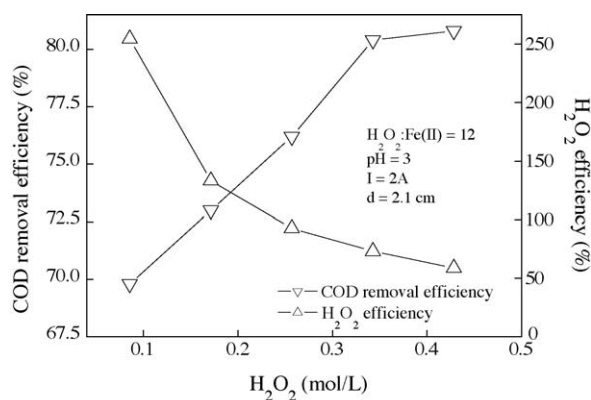


Fig. 4. COD removal efficiency and efficiency of hydrogen peroxide at various Fenton's reagent dosages ( $\text{H}_2\text{O}_2/\text{Fe(II)} = 12$ ,  $\text{pH} = 3$ ,  $I = 2 \text{ A}$ ,  $d = 2.1 \text{ cm}$ ).

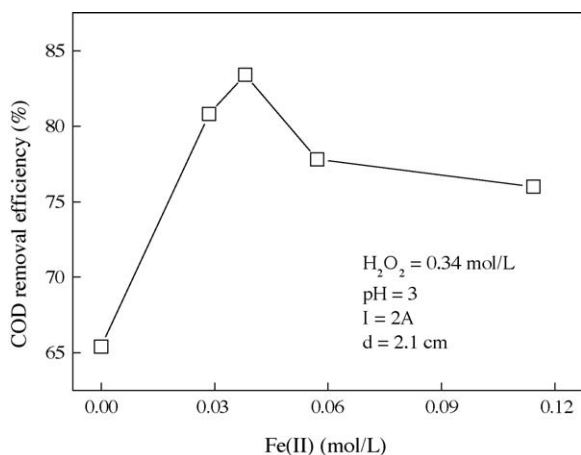


Fig. 5. Effect of ferrous ion dosage on COD removal efficiency.

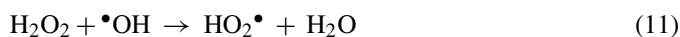
gave milder increased removal efficiency. This indicated that the end by-products of oxidation reactions are mainly made of short chain organic acids that are difficult to be further oxidized [14]. Defining the efficiency of hydrogen peroxide as [7,39],

$$\eta = \left[ \frac{\Delta \text{COD (mg/L)}}{\text{available O}_2 \text{ (mg/L)}} \right] \times 100 \quad (10)$$

where the available oxygen was the theoretical amount of reactive oxygen in the added hydrogen peroxide.

Results showed that efficiency of hydrogen peroxide decreased with the increase of Fenton's reagent dosage (Fig. 4), indicating less hydrogen peroxide was used to oxidize organic materials in the leachate. Similar to the current efficiency, the efficiency of hydrogen peroxide could also exceed 100% (Fig. 4). This is accounted for the fact that in Fenton process COD was removed by both oxidation and coagulation [7]. The latter is due to the formation ferric hydroxide during neutralization step of E-Fenton process.

The effect of Fe(II) concentration on COD removal efficiency is shown in Fig. 5. It can be seen that COD removal efficiency was only 65.4% in the absence of ferrous ion. The addition of ferrous ion greatly improved COD removal. COD removal efficiency increased rapidly when Fe(II) concentration increased. It achieved 83.4% of the highest removal efficiency at the 0.038 mol/L of ferrous ion. Further increase in ferrous ion dosage would lead to the decrease of COD removal efficiency. This indicated that there is an optimum Fe(II)/H<sub>2</sub>O<sub>2</sub> molar ratio for COD removal. Higher Fe(II)/H<sub>2</sub>O<sub>2</sub> molar ratio would lead to the faster disappearance rate of ferrous ion as well as hydroxyl radical via reaction (3). On the other hand, lower Fe(II)/H<sub>2</sub>O<sub>2</sub> molar ratio was attributed to the side reaction between hydrogen peroxide and hydroxyl radical via reaction (11),



This reaction results in the consumption of hydrogen peroxide as well hydroxyl radical, and the production of hydroperoxy radical, a species with much weaker oxidizing power compared with hydroxyl radical. Therefore, there existed an optimum Fe(II)/H<sub>2</sub>O<sub>2</sub> molar ratio so that the consumption of hydroxyl

Table 1

COD removal efficiency versus number of feedings (H<sub>2</sub>O<sub>2</sub> = 0.17 mol/L, Fe(II) = 0.014 mol/L, pH 3, I = 2 A, d = 1.3 cm)

Number of feedings	COD removal efficiency (%)
1	73.0
2	73.4
3	74.3
4	74.9
Continuous	79.4

radical by ferrous ion or hydrogen peroxide would be in minimum via reaction (3) or (11).

Our previous work showed that the efficacy of Fenton process for the treatment of landfill leachate was improved by adding Fenton's reagent in multiple steps than that in a single step [15]. Therefore, the stepwise or continuous addition of hydrogen peroxide was employed in this study, i.e., hydrogen peroxide (0.17 mol/L) was added in a single step (at 0 min), in two steps (at 0 and 30 min), in three steps (at 0, 15 and 30 min), in four steps (at 0, 10, 20 and 30 min) or in continuous mode for 30 min. Total reaction time was kept at 75 min. The results showed that COD removal efficiency increased with the times of dosage and the highest removal efficiency was achieved when continuous addition mode was employed (see Table 1). The addition of hydrogen peroxide all at once in the beginning of the experiments results in a rapid and efficient production of hydroxyl radicals. Therefore, parasite reactions of hydroxyl radicals with hydrogen peroxide (reaction (11)) as well as ferrous ion (reaction (3)) become predominant. Stepwise addition keeps the hydrogen peroxide concentration at relatively low levels, reducing the detrimental effect of hydroxyl radical scavenging (reaction (11)). Furthermore, the continuous addition of hydrogen peroxide would keep the hydrogen peroxide concentration at the lowest level and reduce the side reaction (reaction (11)) to the utmost extent. Therefore, the highest COD removal was achieved when continuous addition mode of hydrogen peroxide was employed.

To investigate the synergistic effect of combined electrochemical method and Fenton's reagent, landfill leachate was treated by electrochemical method alone, Fenton's reagent alone and E-Fenton method, respectively. As shown in Fig. 6, electrochemical method alone could only remove 10% of COD from the leachate. This is accounted for the fact that the main oxidizing agent in this process is hydroxyl radical, produced in small concentration by the anodic decomposition of water via reaction (5) [40,41]. The similar results were reported when Ti/Pt anode was employed to degrade aniline [31] and Pt anode was used to mineralize chlorophenoxy herbicides [40,41]. COD removal efficiency reached 34% with Fenton's reagent, indicating higher generation of hydroxyl radicals by homogenous reaction (1) than reaction (5). COD removal increased to 81% when Fenton's reagent was applied to the electrolytic, which was higher than electrochemical method, Fenton's reagent, and even the total removal by electrochemical method and Fenton's reagent. This indicated E-Fenton method had synergistic effect for COD removal.

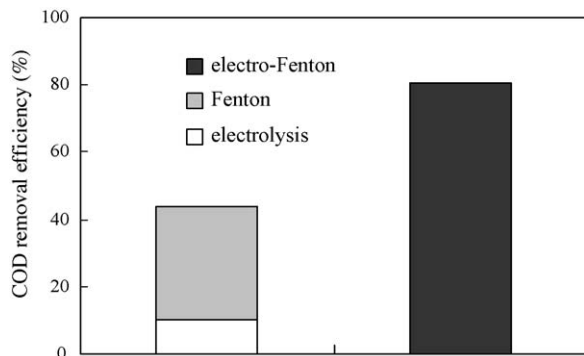


Fig. 6. Comparison of COD removal by electrochemical oxidation, Fenton's reagent and electro-Fenton method. Electrochemical oxidation: pH 3,  $I=2$  A,  $d=2.1$  cm; Fenton's reagent:  $H_2O_2=0.34$  mol/L,  $Fe(II)=0.028$  mol/L, pH 3; electro-Fenton method:  $H_2O_2=0.34$  mol/L,  $Fe(II)=0.028$  mol/L, pH 3,  $I=2$  A,  $d=2.1$  cm.

As E-Fenton method could achieve much higher COD removal than conventional Fenton method, the treatment costs were analyzed for both E-Fenton and conventional Fenton methods. To simplify the analysis, only Fenton's reagent and electricity were considered. The prices of hydrogen peroxide (27.5%) and ferrous sulfate heptahydrate (98%) were RMB 1250 and 420 per 1000 kg, respectively, which were provided by China industry portal ([www.hc360.com](http://www.hc360.com)). The electricity rate was RMB  $0.689$  kWh<sup>-1</sup>, provided by Wuhan municipal government ([www.wh.gov.cn](http://www.wh.gov.cn)). Then, the operation costs were calculated to be RMB 33 for conventional Fenton method and RMB 18 for E-Fenton method, respectively, when 1 kg COD needs to be removed. This indicates that E-Fenton method is superior to conventional Fenton method not only from the conversion point of view but also from the economic point of view.

#### 4. Conclusion

Electro-Fenton method could effectively remove COD from landfill leachate. The process was very fast in the first 30 min and then slowed down till it was complete in 75 min. There exists an optimal distance range between the electrodes so that an over 7% higher COD removal was achieved than the electrodes positioned beyond this range. COD removal efficiency increased with the increasing current, but further increase of current would reduce the removal efficiency. Organic removal increased as Fenton's reagent dosage increased at the fixed  $H_2O_2$  to  $Fe(II)$  molar ratio. COD removal efficiency increased with the increase of ferrous ion dosage at the fixed hydrogen peroxide dose, but further increase of ferrous ion dosage would reduce the removal efficiency. The stepwise or continuous addition of hydrogen peroxide was more effective than the addition of hydrogen peroxide in a single step. E-Fenton method is superior to conventional Fenton method not only from the conversion point of view but also from the economic point of view.

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#### References

- [1] M. Loizidou, A. Papadopoulos, E.G. Kapetanios, Application of chemical oxidation for the treatment of refractory substances in leachates, *J. Environ. Sci. Heal.* A28 (1993) 385–394.
- [2] S.-H. Gau, F.-S. Chang, Improved Fenton method to remove recalcitrant organics in landfill leachate, *Water Sci. Technol.* 34 (1996) 445–462.
- [3] Y.-K. Kim, I.R. Huh, Enhancing biological treatability of landfill leachate by chemical oxidation, *Environ. Eng. Sci.* 14 (1997) 73–79.
- [4] A. Papadopoulos, D. Fatta, M. Loizidou, Treatment of stabilized landfill leachate by physico-chemical and bio-oxidation processes, *J. Environ. Sci. Heal.* A33 (1998) 651–670.
- [5] U. Welander, T. Henrysson, Physical and chemical treatment of a nitrified leachate from a municipal landfill, *Environ. Technol.* 19 (1998) 591–599.
- [6] J. Yoon, S. Cho, Y. Cho, S. Kim, The characteristics of coagulation of Fenton reaction in the removal of landfill leachate organics, *Water Sci. Technol.* 38 (1998) 209–214.
- [7] Y.W. Kang, K.-Y. Hwang, Effects of reaction conditions on the oxidation efficiency in the Fenton process, *Water Res.* 34 (2000) 2786–2790.
- [8] P. Wang, I.W.C. Lau, H.H.P. Fang, D. Zhou, Landfill leachate treatment with combined UASB and Fenton coagulation, *J. Environ. Sci. Heal.* A35 (2000) 1981–1988.
- [9] J.-S. Kim, H.-Y. Kim, C.-H. Won, J.-G. Kim, Treatment of leachate produced in stabilized landfills by coagulation and Fenton oxidation process, *J. Chin. Inst. Chem. Eng.* 32 (2001) 425–429.
- [10] I.W.C. Lau, P. Wang, H.H.P. Fang, Organic removal of anaerobically treated leachate by Fenton coagulation, *J. Environ. Eng. ASCE* 127 (2001) 666–669.
- [11] H.-C. Yoo, S.-H. Cho, S.-O. Ko, Modification of coagulation and Fenton oxidation processes for cost-effective leachate treatment, *J. Environ. Sci. Heal.* A36 (2001) 39–48.
- [12] J. Yoon, Y. Kim, J. Huh, Y. Lee, D. Lee, Roles of oxidation and coagulation in Fenton process for the removal of organics in landfill leachate, *J. Ind. Eng. Chem.* 8 (2002) 410–418.
- [13] H. Zhang, C.-P. Huang, Treatment of landfill leachate by Fenton oxidation process, *Chin. J. Chem. Eng.* 19 (2002) 128–131.
- [14] A. Lopez, M. Pagano, A. Volpe, A.C. Di Pinto, Fenton's pre-treatment of mature landfill leachate, *Chemosphere* 54 (2004) 1005–1010.
- [15] H. Zhang, H.J. Choi, C.-P. Huang, Optimization of Fenton process for the treatment of landfill leachate, *J. Hazard. Mater.* 125 (2005) 166–174.
- [16] C. Walling, Fenton's reagent revisited, *Acc. Chem. Res.* 8 (1975) 125–131.
- [17] C. Walling, A. Goosen, Mechanism of the ferric ion catalysed decomposition of hydrogen peroxide: effects of organic substrate, *J. Am. Chem. Soc.* 95 (1973) 2987–2991.
- [18] T. Rigg, W. Taylor, J. Weiss, The rate constant of the reaction between hydrogen peroxide and ferrous ions, *J. Chem. Phys.* 22 (1954) 575–577.
- [19] D.I. Metelitsa, Mechanisms of the hydroxylation of aromatic compounds, *Russ. Chem. Rev.* 40 (1971) 563–580.
- [20] Y. Sun, J.J. Pignatello, Photochemical reactions involved in the total mineralization of 2,4-D by  $Fe^{3+}/H_2O_2/UV$ , *Environ. Sci. Technol.* 27 (1993) 304–310.
- [21] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reaction of hydrated electrons, hydrogen atoms and hydroxyl radicals ( $\cdot OH/\cdot O^-$ ) in aqueous solution, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886.
- [22] S.S. Chou, Y.H. Huang, S.N. Lee, G.H. Huang, C.P. Huang, Treatment of high strength hexamine-containing wastewater by electro-Fenton method, *Water Res.* 33 (1999) 751–759.
- [23] E. Kusvuran, O. Gulnaz, S. Irmak, O.M. Atanur, H.I. Yavuz, O. Erbatır, Comparison of several advanced oxidation processes for the decolorization of Reactive Red 120 azo dye in aqueous solution, *J. Hazard. Mater.* B109 (2004) 85–93.

- [24] M.A. Oturan, J. Peiroten, P. Chartrin, A.J. Acher, Complete destruction of *p*-nitrophenol in aqueous medium by electro-Fenton method, *Environ. Sci. Technol.* 34 (2000) 3474–3479.
- [25] E. Fockedey, A. Van Lierde, Coupling of anodic and cathodic reactions for phenol electro-oxidation using three-dimensional electrodes, *Water Res.* 36 (2002) 4169–4175.
- [26] M. Panizza, G. Cerisola, Removal of organic pollutants from industrial wastewater by electrogenerated Fenton's reagent, *Water Res.* 35 (2001) 3987–3992.
- [27] A.M. Wang, J.H. Qu, J. Ru, H.J. Liu, J.T. Ge, Mineralization of an azo dye Acid Red 14 by electro-Fenton's reagent using an activated carbon fiber cathode, *Dyes Pigment.* 65 (2005) 227–233.
- [28] T.S.N.S. Narayanan, G. Magesh, N. Rajendran, Degradation of *o*-chlorophenol from aqueous solution by electro-Fenton process, *Fresenius Environ. Bull.* 12 (2003) 776–780.
- [29] B. Boye, M.M. Dieng, E. Brillas, Degradation of herbicide 4-chlorophenoxyacetic acid by advanced electrochemical oxidation methods, *Environ. Sci. Technol.* 36 (2002) 3030–3035.
- [30] S.H. Lin, C.C. Chang, Treatment of landfill leachate by combined electro-Fenton oxidation and sequencing batch reactor method, *Water Res.* 34 (2000) 4243–4249.
- [31] E. Brillas, J. Casado, Aniline degradation by Electro-Fenton® and peroxi-coagulation processes using a flow reactor for wastewater treatment, *Chemosphere* 47 (2002) 241–248.
- [32] P.H. Chang, Y.H. Huang, C.L. Hsueh, M.C. Lu, G.H. Huang, Treatment of non-biodegradable wastewater by electro-Fenton method, *Water Sci. Technol.* 49 (2004) 213–218.
- [33] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 18th ed., American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, DC, USA, 1992.
- [34] W.F. Jardim, J.J.R. Rohwedder, Chemical oxygen demand (COD) using microwave digestion, *Water Res.* 23 (1989) 1069–1071.
- [35] C.H. Comninellis, C. Pulgarin, Anodic oxidation of phenol for waste water treatment, *J. Appl. Electrochem.* 21 (1991) 703–708.
- [36] B. Boye, M.M. Dieng, E. Brillas, Anodic oxidation, electro-Fenton and photoelectro-Fenton treatments of 2,4,5-trichlorophenoxyacetic acid, *J. Electroanal. Chem.* 557 (2003) 135–146.
- [37] E. Brillas, B. Boye, I. Sirés, J.A. Garrido, R.M. Rodríguez, C. Arias, P.L. Cabot, C. Comninellis, Electrochemical destruction of chlorophenoxy herbicides by anodic oxidation and electro-Fenton using a boron-doped diamond electrode, *Electrochim. Acta* 49 (2004) 4487–4496.
- [38] Z.M. Qiang, J.H. Chang, C.P. Huang, Electrochemical regeneration of Fe<sup>2+</sup> in Fenton oxidation processes, *Water Res.* 37 (2003) 1308–1319.
- [39] D.F. Bishop, G. Stern, M. Fleischman, L.S. Marshall, Hydrogen peroxide catalytic oxidation of refractory organics in municipal wastewaters, *Ind. Eng. Chem. Proc. Des. Dev.* 7 (1968) 110–117.
- [40] E. Brillas, J.C. Calpe, J. Casado, Mineralization of 2,4-D by advanced electrochemical oxidation processes, *Water Res.* 34 (2000) 2253–2262.
- [41] E. Brillas, M.Á. Baños, J.A. Garrido, Mineralization of herbicide 3,6-dichloro-2-methoxybenzoic acid in aqueous medium by anodic oxidation, electro-Fenton and photoelectro-Fenton, *Electrochim. Acta* 48 (2003) 1697–1705.