

Degradation of 4-nitrophenol in aqueous medium by electro-Fenton method

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Abstract

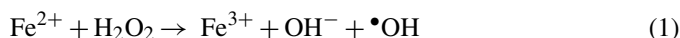
The degradation of 4-nitrophenol by electro-Fenton (E-Fenton) method was carried out in batch recirculation mode. The effect of operating conditions such as electrical current, Fenton's reagent dosage, Fe(II) to H₂O₂ molar ratio, and H₂O₂ feeding time on the efficiency of E-Fenton process was investigated. It was found that E-Fenton method showed the synergetic effect on COD removal. The increase of Fenton's reagent dosage, Fe(II) to H₂O₂ molar ratio, and the electrical current would lead to the increase of COD removal efficiency. Continuous addition of hydrogen peroxide was more effective than the addition of hydrogen peroxide in a single step and there existed an optimal H₂O₂ feeding time for COD removal. The reaction system was modeled as a plug flow reactor (PFR) in series with a continuous stirred tank reactor (CSTR), and the pseudo-first order rate constant of COD removal was determined from the model based on the experimental data.
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Keywords: 4-Nitrophenol; Fenton's reagent; Electro-Fenton; Advanced oxidation process; Wastewater treatment

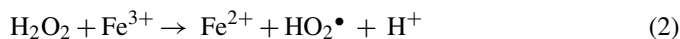
1. Introduction

Nitrophenols are anthropogenic, toxic, inhibitory and bio-refractory organic compounds used extensively in chemical industries for the manufacture of pesticides, pharmaceuticals and synthetic dyes [1]. Therefore, nitrophenols are common pollutants in many natural water and wastewater systems. The destruction and mineralization of wastewaters contaminated with nitrophenols by traditional methods is extremely arduous, since nitrophenols are resistant due to their high stability and solubility in water [1]. 4-Nitrophenol (4-NP) is an important member of the nitrophenol group and is considered to be hazardous wastes and priority toxic pollutants by U.S. Environmental Protection Agency (EPA) [2]. It is a toxic compound that can damage the central nervous system, liver, kidney and blood of humans and animals. The treatment of wastewater containing 4-NP is very difficult since it is resistant to the traditional treatment techniques. A long period of incubation is required for the microbial degradation of 4-NP [3].

Advanced oxidation processes, AOPs, which involve hydroxyl radicals ($\bullet\text{OH}$) as the oxidation agent [4], have been demonstrated to be a reliable alternative to the degradation of 4-NP. Hydroxyl radical is the second strongest oxidant ($E^0 = 2.87\text{ V}$) that is only inferior to fluoride ($E^0 = 3.06\text{ V}$). During the past decades there have been numerous reports on the degradation of 4-NP by AOPs [5–13]. As one of AOPs, Fenton's reagent is known to be a very effective process in the treatment of 4-NP [1,14–17]. During Fenton reaction, hydrogen peroxide is catalyzed by ferrous ions to produce hydroxyl radicals [18],



This reaction is propagated from ferrous ion regeneration mainly by the reduction of the produced ferric species with hydrogen peroxide [19],



The produced hydroxyl radicals would degrade 4-NP. However, in the Fenton chain reactions, the rate constant of reaction (1) is between 53 and 76 $\text{M}^{-1}\text{s}^{-1}$ [18,20–22], while that of reaction (2) is only 0.01 $\text{M}^{-1}\text{s}^{-1}$ [19]. This means ferrous ions are consumed more rapidly than they are produced. In addition, ferrous ions can also be rapidly destroyed by hydroxyl radicals

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with the rate constant in the range of $3.2 - 4.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [22,23],



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 [24].

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 four categories [25], and 4-NP was degraded by one kind of E-Fenton methods in which ferrous ion was externally applied and hydrogen peroxide was generated at carbon felt cathode [26]. Hydroquinone, benzoquinone, 4-nitrocatechol, 1,2,4-trihydroxybenzene and 3,4,5-trihydroxynitrobenzene were observed as major intermediate products. The degradation of 4-NP in terms of TOC was also investigated and mineralization mechanism was proposed. However, the effect of various operation conditions on the degradation of 4-NP was not systematically investigated. Therefore, in this study, we employed a novel electro-Fenton method [25], in which Fenton's reagent was utilized to produce hydroxyl radical in the electrolytic cell and ferrous ion was regenerated via the reduction of ferric ion on the cathode. The effect of Fenton's reagent dosage, H_2O_2 to Fe(II) molar ratio, electrical current, and H_2O_2 feeding time on the efficiency of COD removal was investigated.

2. Experimental

2.1. Chemicals

4-NP (chemical purity grade, 99%) was obtained from Wujiang Taoyuan Chemicals Reagent Plant (Suzhou, China). Ferrous sulfate heptahydrate (analytical grade, 99%) was obtained from Shanghai Shiyi Chemicals Reagent Co. Ltd. (China). Hydrogen peroxide (analytical grade, 30%) was obtained from Wuhan Zhongnan Chemical Plant (China). Ferrous ammonium sulfate hexahydrate (analytical grade, 99.5%) was obtained from China National Medicine Group Shanghai Chemical Reagent Company. Sodium hydroxide (chemical purity grade, 95%) was obtained from Tianjin Chemical Reagent Factory (China). Sulfuric acid (analytical grade, 95–98%) was obtained from Xinyang Chemicals Reagent Factory (China). Potassium dichromate (analytical grade, 99.8%) was obtained from Beijing Hongxing Chemical Plant (China). *o*-Phenanthroline hydrate (analytical grade) was obtained from Shanghai No. 3 Chemicals Reagent Factory (China). All solution was prepared with distilled water.

2.2. Electrolytic system

The experimental apparatus consisted of an electrochemical reactor, a diaphragm metering pump (Model JWM-80/0.3, Ailipu Pump Co. Ltd., China) to recirculate the solution and a

5-L reservoir. The electrolytic cell contained the cathode, which was a stainless steel cylinder with an inside diameter of 8 cm and a height of 17.5 cm, and the anode, which was a titanium rod coated with $\text{RuO}_2/\text{IrO}_2$ with an outside diameter of 1.5 cm and a height of 16 cm. The anode was located in the center of the cylinder.

2.3. Experiment and analysis procedure

The solution pH was measured with an Orion 420Aplus pH-meter. Chemical oxygen demand (COD) was determined by using microwave assisted potassium dichromate method [27,28].

Batch recirculation mode was employed in this study. The mixing in the electrolytic cell was provided by recycling the solution at 750 mL/min using a diaphragm metering pump. Hydrogen peroxide was applied to the reactor all at once or in continuous mode using a peristaltic pump (Cole-Parmer Instrument Co., Vernon Hills, IL, Masterflex® C/L® Model 77120-70). In each run, a selected amount of ferrous sulfate heptahydrate was dissolved in 2.8 L 4-NP solution, and then transferred to the reservoir. The initial pH value (pH_0) was adjusted using concentrated sulfuric acid and sodium hydroxide. To minimize the dilution effect by the volume of chemicals, a known volume of hydrogen peroxide was diluted to 250 mL and applied to the electrolytic cell, and then DC power supply (Model WYK-305, Yangzhou Jintong Source Co. Ltd., China) was initiated. At pre-selected time intervals, samples were taken into the tubes containing sodium hydroxide solution to quench the reaction by increasing pH around 9.0. Then they were diluted and settled for 30 min. The supernatant was withdrawn to measure COD.

3. Results and discussion

3.1. Degradation of 4-NP in different systems

To investigate the synergistic effect of combined electrochemical method and Fenton's reagent, 200 mg/L 4-NP solution was treated by electrochemical method alone, Fenton's reagent alone and E-Fenton method, respectively. Results showed that electrochemical method could hardly remove COD from 4-NP solution. But in both Fenton process and E-Fenton process, COD was removed rapidly during the first 60 min when hydrogen peroxide was continuously applied into the electrolytic cell. After hydrogen peroxide was stopped feeding, the change of residual COD became insignificant (see Fig. 1). The final COD removal efficiency achieved by E-Fenton method was nearly 10% higher than Fenton's reagent alone. This indicated E-Fenton method had synergistic effect for COD removal. The similar result was observed when landfill leachate was treated by E-Fenton method [25].

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



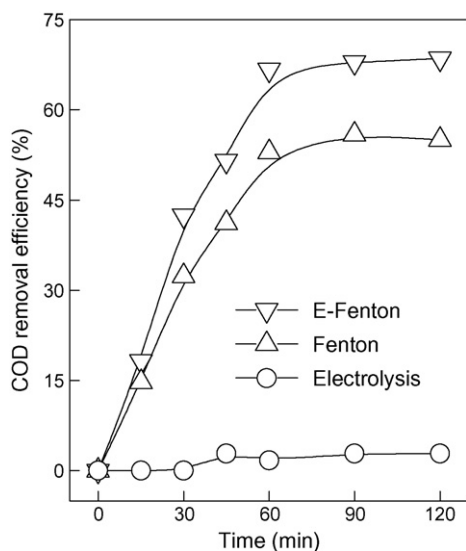


Fig. 1. COD removal efficiency with reaction time in different systems. Electrochemical oxidation: pH_0 5, $I=1.0$ A; Fenton's reagent: $\text{H}_2\text{O}_2=9.12$ mmol/L, H_2O_2 feeding time = 60 min, $\text{Fe(II)/H}_2\text{O}_2=0.050$, pH_0 5; electro-Fenton method: $\text{H}_2\text{O}_2=9.12$ mmol/L, H_2O_2 feeding time = 60 min, $\text{Fe(II)/H}_2\text{O}_2=0.050$, pH_0 5, $I=1.0$ A.

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.

3.2. Effect of electrical current

As can be seen in Fig. 2, COD removal efficiency increased when applied current was raised from 0.5 to 1.0 A, indicating an enhancement of the degradation power. This was due to the

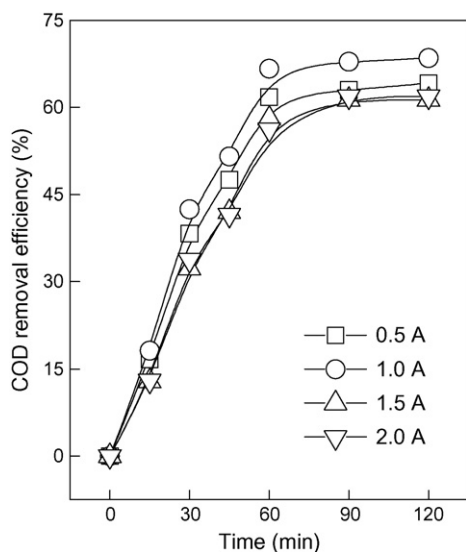


Fig. 2. Effect of electrical current on COD removal efficiency. [4-NP] = 200 mg/L, $\text{H}_2\text{O}_2=9.12$ mmol/L, H_2O_2 feeding time = 60 min, $\text{Fe(II)/H}_2\text{O}_2=0.050$, pH_0 5.

higher electro-regeneration of ferrous ion from ferric ion (reaction (5)) with increasing current, which increased the efficiency of Fenton chain reactions. However, further increase of electrical current would lower COD removal efficiency. At higher current the competitive electrode reactions such as the discharge of oxygen at the anode via reaction (6) and the evolution hydrogen at the cathode via reaction (7) would become pronounced.



These would inhibit main reactions such as reactions (4) and (5).

3.3. Effect of Fenton's reagent dosage

At the fixed Fe(II) to H_2O_2 molar ratio of 0.050, the final COD removal efficiency at 120 min increased from 64.2% to 91.7% when hydrogen peroxide dosage increased from 9.12 to 27.38 mmol/L, i.e., from 0.5 H_2O_2 theoretical dosage to 1.5 H_2O_2 theoretical dosage. However, COD could not be completely eliminated even if hydrogen peroxide dosage reached one theoretical dosage, as can be seen in Fig. 3a. The similar result has been reported when the efficiency of E-Fenton method for the treatment of 4-NP was evaluated in terms of TOC [26]. This is due to the change in the structure of the reaction mixture, from aromatics to aliphatics by ring opening reactions, which are more resistant to mineralization [26]. Defining the efficiency of hydrogen peroxide as [29,30],

$$\eta = \left[\frac{\Delta\text{COD (mg/L)}}{\text{available O}_2 \text{ (mg/L)}} \right] \times 100 \quad (8)$$

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

Fig. 3b shows that efficiency of hydrogen peroxide decreased with the increase of Fenton's reagent dosage, indicating less hydrogen peroxide was used to degrade 4-NP. The efficiency of hydrogen peroxide could also exceed 100%. This is accounted for the fact that in E-Fenton process COD was removed by both oxidation and coagulation. The latter was due to the formation of ferric hydroxide during neutralization step of E-Fenton process.

3.4. Effect of Fe(II) to H_2O_2 molar ratio

At the fixed H_2O_2 dosage, COD removal efficiency at 120 min increased from 66.0% to 93.1% when Fe(II) to H_2O_2 molar ratio increased from 0.017 to 0.1 (Fig. 4). This indicated that Fe(II) to H_2O_2 molar ratio is a very important operational parameter of the E-Fenton process. Hydrogen peroxide would be catalyzed by ferrous ion to produce hydroxyl radicals through reaction (1), and greater hydroxyl radicals could be generated with increasing ferrous ion concentration. Accordingly, more ferric hydroxide would be formed to remove COD during neutralization step. Therefore, COD removal efficiency increased with the increasing Fe(II) to H_2O_2 molar ratio.

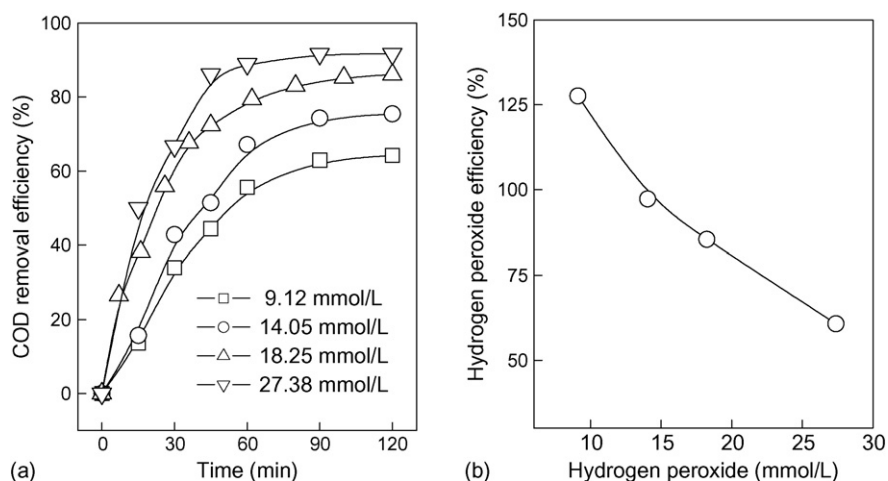


Fig. 3. Effect of Fenton's reagent dosage on (a) COD removal efficiency. (b) Hydrogen peroxide efficiency. [4-NP] = 200 mg/L, H_2O_2 feeding time = 60 min, $\text{Fe(II)/H}_2\text{O}_2 = 0.050$, $\text{pH}_0 = 6$, $I = 0.5$ A.

3.5. Effect of hydrogen peroxide feeding time

Our previous work showed that feeding Fenton's reagent in multiple steps or continuous mode would improve the efficiency of E-Fenton process [25]. Therefore, the continuous addition of hydrogen peroxide was employed in this study, and the effect of hydrogen peroxide feeding time was investigated. Hydrogen peroxide was added in a single step and in continuous mode with feeding time of 30, 60 and 120 min, respectively. Total reaction time was kept at 150 min and the hydrogen peroxide dosage was fixed at 18.25 mmol/L. As can be seen in Fig. 5, the initial COD removal rate increased with the decreasing feeding time and it reached highest when hydrogen peroxide was applied all at once. With the decrease of feeding time, the concentration of hydrogen peroxide during the initial period would increase. Then more hydroxyl radicals would be generated resulting from the chain reaction between hydrogen peroxide and ferrous ion. This would lead to an increase of initial COD removal rate.

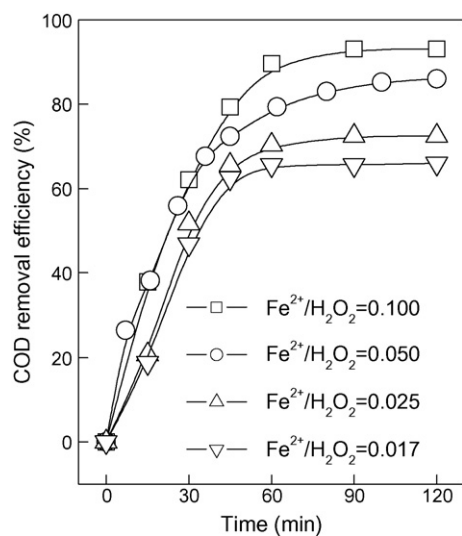


Fig. 4. Effect of Fe(II) to H_2O_2 molar ratio on COD removal efficiency. [4-NP] = 200 mg/L, $\text{H}_2\text{O}_2 = 18.25$ mmol/L, H_2O_2 feeding time = 60 min, $\text{pH}_0 = 6$, $I = 0.5$ A.

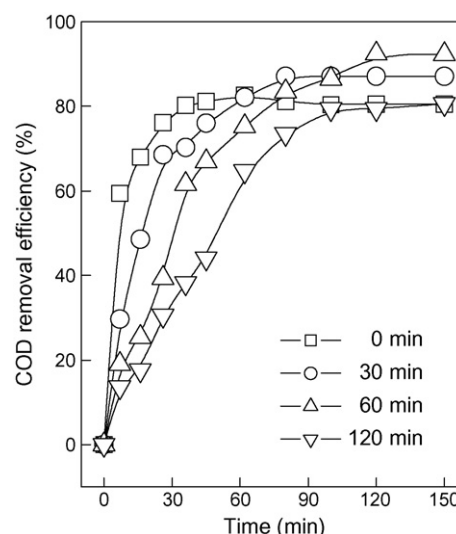


Fig. 5. Effect of hydrogen peroxide feeding time on COD removal efficiency. [4-NP] = 200 mg/L, $\text{H}_2\text{O}_2 = 18.25$ mmol/L, $\text{Fe(II)/H}_2\text{O}_2 = 0.050$, $\text{pH}_0 = 6$, $I = 1.0$ A.

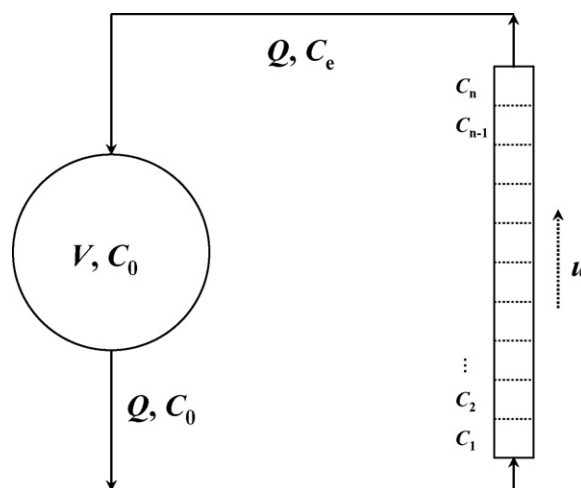
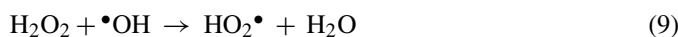


Fig. 6. Schematic diagram of the electrochemical reactor in batch recirculation mode.

Table 1
The apparent pseudo-first-order rate constants under various operating conditions

Run	[4-NP] (mg/L)	Fe(II)/H ₂ O ₂	H ₂ O ₂ (mmol/L)	H ₂ O ₂ feeding time (min)	pH ₀	I (A)	k ₁ (min ⁻¹)	R ²
I-1	200	0.050	9.12	60	5	0.5	0.055	0.9921
I-2	200	0.050	9.12	60	5	1.0	0.062	0.9898
I-3	200	0.050	9.12	60	5	1.5	0.048	0.9849
I-4	200	0.050	9.12	60	5	2.0	0.047	0.9858
H-1	200	0.050	9.12	60	6	0.5	0.045	0.9926
H-2	200	0.050	14.05	60	6	0.5	0.061	0.9820
H-3	200	0.050	18.25	60	6	0.5	0.12	0.9885
H-4	200	0.050	27.38	60	6	0.5	0.15	0.9911
R-1	200	0.100	18.25	60	6	0.5	0.13	0.9981
R-2	200	0.050	18.25	60	6	0.5	0.12	0.9885
R-3	200	0.025	18.25	60	6	0.5	0.080	0.9801
R-4	200	0.017	18.25	60	6	0.5	0.072	0.9782
T-1	200	0.050	18.25	30	6	0.5	0.17	0.9834
T-2	200	0.050	18.25	60	6	0.5	0.12	0.9885
T-3	200	0.050	18.25	120	6	0.5	0.05	0.9850

However, the final COD removal efficiency increased with the decreasing feeding time and reached highest when feeding time was 60 min. Further decrease of feeding time would decrease final COD removal efficiency. This is due to the side reactions hindered the efficiency of E-Fenton process to remove COD. The concentration of hydrogen peroxide during the initial period would be higher when hydrogen peroxide was added in a single step or fed more quickly in continuous mode, the produced hydroxyl radicals would be scavenged by hydrogen peroxide as follows:



This reaction leads to the production of hydroperoxyl radical, a species with much weaker oxidizing power compared with hydroxyl radical.

On the other hand, when hydrogen peroxide was added too slowly, the concentration of hydrogen peroxide would be very low during the whole feeding time. This would result in very high molar ratio of ferrous ion to hydrogen peroxide, and the produced hydroxyl radicals would also be scavenged by excess ferrous ion via reaction (3).

3.6. COD removal kinetics

To model COD removal in the electrochemical reactor in batch recirculation mode, we assumed that the electrolytic cell could be modeled as a plug flow reactor (PFR) and the reservoir as a continuous stirred tank reactor (CSTR), respectively (Fig. 6). COD was removed only in PFR and the removal followed pseudo-first order kinetics. No COD was destructed beyond PFR. Then mass balance equations in CSTR and PFR can be written as,

$$V \frac{dC_0}{dt} = Q(C_e - C_0) \quad (10)$$

$$u \frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} + k_1 C = 0 \quad (11)$$

where C_0 and C_e are the COD values entering and leaving the electrolytic cell, respectively, V the reservoir value, Q the recirculation flow rate, u the liquid velocity in PFR, z the liquid flow direction along PFR. C is COD at position z , t the reaction time, and k_1 is pseudo-first order rate constant.

To solve ordinary differential Eq. (10) and partial differential Eq. (11), the electrolytic cell was first divided into 10 small sections along z direction so that partial differential Eq. (11) could be converted into a series of ordinary differential equations, i.e., Eqs. (12.1)–(12.10) as below. Ten sections were chosen as the results revealed there was little difference between the division of 10 sections and the division of 20 sections. Hence mass balance equation in PFR can be rewritten as,

$$\frac{dC_1}{dt} = - \left(k_1 + \frac{u}{\Delta z} \right) C_1 + \frac{u}{\Delta z} C_0 \quad (12.1)$$

$$\frac{dC_2}{dt} = - \left(k_1 + \frac{u}{\Delta z} \right) C_2 + \frac{u}{\Delta z} C_1 \quad (12.2)$$

⋮

$$\frac{dC_n}{dt} = - \left(k_1 + \frac{u}{\Delta z} \right) C_n + \frac{u}{\Delta z} C_{n-1} \quad (12.10)$$

in this case $n=10$, and the initial conditions were $C_i = \text{COD}_0$ at $t=0$ ($i=0, 1, 2, \dots, 10$).

This system of equations was solved numerically by using the mathematical computer software Matlab 6.5. Only data obtained during H₂O₂ feeding time was employed to determine the pseudo-first order rate constant k_1 by non-linear least squares method [31], considering the kinetics may change when hydrogen peroxide was stopped feeding. As can be seen in Table 1, the pseudo-first order rate constant k_1 decreased with H₂O₂ feeding time. It increased with Fe(II) to H₂O₂ molar ratio, Fenton's reagent dosage, and electrical current, but further increase of electrical current would decrease k_1 .

4. Conclusion

The effect of major parameters on E-Fenton process was evaluated using a flow reactor in batch recirculation mode. It was proved that COD could be successfully removed by E-Fenton method. E-Fenton method showed the synergetic effect on COD removal. COD removal efficiency increased with Fe(II) to H₂O₂ molar ratio and electrical current, but further increase of current would reduce the efficiency. At the fixed Fe(II) to H₂O₂ molar ratio, COD removal efficiency increased as Fenton's reagent dosage increased. Continuous addition of hydrogen peroxide was more effective than the addition of hydrogen peroxide in a single step and there existed an optimal feeding time for COD removal. The pseudo-first order rate constant k_1 was obtained based on CSTR-PFR model.

Acknowledgements

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