

# Dye wastewater treated by Fenton process with ferrous ions electrolytically generated from iron-containing sludge

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## Abstract

Fenton process was employed to treat synthetic dye wastewater with supply of Fe(II) electrolytically generated from iron-containing sludge which was recycled and reused throughout the study. Treated water quality and properties of iron sludge after being repeatedly used were reported and discussed. Experimental results showed that COD was mainly removed by oxidation other than coagulation. Although, the process was quite effective for COD and color removal, conductivity of treated water was enormously high. Meanwhile, repeated use of iron-containing sludge results in accumulation of organic materials embedded in the sludge as indicated by increasing volatile suspended solid (VSS)/TSS ratio and decreasing zeta potential.

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**Keywords:** Electrolysis; Dye; COD removal; Iron sludge; Conductivity

## 1. Introduction

Fenton process has been intensively investigated for oxidation of various contaminants in the past, but its practical application is limited by the huge quantity of iron-containing sludge generated by it [1,2]. Electrochemical regeneration of Fe(II) via reduction of Fe(III), denoted as Fered-Fenton process by Huang et al. [3], as EF-FeRe process by Qiang et al. [2], and as Fenton sludge recycling (FSR) process by Gnann et al. [4], was proposed to alleviate the sludge problem associated with Fenton process.

Concentration of electrolytically-generated Fe(II) depends on initial ferric concentration, pH, temperature, cathodic potential, electrolysis time, cathode area, and cathode-to-anode area ratio [2–6]. Amount of Fe(II) generated and electrolytic current efficiency increase with increasing initial ferric concentration, but are drastically decreased at pH higher than 2.5 because of Fe(OH)<sub>3</sub> precipitation [2,6]. Electrolytic pH as low as 1.0 has been recommended for operating the FSR process to effectively re-dissolve precipitated iron sludge before it can be reduced to

Fe(II) [4]. Increasing concentration of Fe(II) was also observed with increasing cathodic surface area [2], and cathode-to-anode area ratio higher than 8 has been employed [3,6]. Cathodic potential ranging from −0.1 to −0.9 V has little impact on amount of Fe(II) generated, although electrolytic current efficiency decreases with decreasing cathodic potential due to electricity wasted through H<sub>2</sub> evolution [2].

The majority of the above-mentioned studies demonstrated electro-regeneration efficiency of Fe(II) using dissolved ferric salts (e.g., ferric sulfate or ferric nitrate) as the iron sources in batch reactors [2,3,6,7]. Although, electro-regeneration of Fe(II) using precipitated iron oxides as the iron source has been investigated by Gnann et al. [4] and Qiang et al. [2], treated water quality and properties of iron sludge after long-term repeated use had not been elaborated. Since organic materials embedded in the iron oxide precipitates might have adverse effects on the treatment efficiency after iron oxide precipitates are reused [8], and addition of acid and base for lowering pH during the electrolytic Fe(II) regeneration and for raising pH during precipitation of iron oxides will contribute to the overall treated water conductivity, it is worthwhile to investigate and address these issues in great details.

Based on the above discussion, the objectives of this study are (1) to demonstrate the treatment efficiency of dye wastewater

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using Fenton process with Fe(II) electrolytically generated using iron-containing sludge as the iron source, (2) to explore fate of Fe species in the treatment process, (3) to evaluate treated water quality, and (4) to investigate properties of iron sludge with emphasis on their dewaterability and volatile suspended solid (VSS) content.

## 2. Experimental

### 2.1. Materials

All chemicals used were of reagent grade and were diluted to predetermined concentration with deionized water (DI). A synthetic dye wastewater containing a reactive dye, R94H (I-Hwa Industrial Co. Ltd., Taiwan), with dye concentration, COD, and color of  $1000 \text{ mg dm}^{-3}$ ,  $3680 \text{ mg dm}^{-3}$ , and 52460 ADMI units, respectively, was prepared to simulate high strength waste stream (denoted as wastewater A). A low strength synthetic dye wastewater (denoted as wastewater B) was prepared by 10-time dilution of wastewater A to simulate low concentration rinsing water generated from dyeing process.

The feed  $\text{H}_2\text{O}_2$  solution with concentration of  $1500 \text{ mg dm}^{-3}$  was diluted from 30% (w/w) stock solution (Merck). Initial iron-containing sludge was obtained from neutralizing R94H containing wastewater treated with Fenton oxidation. A 10-L solution containing 1% (w/w) of R94H was treated with Fenton reaction with  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  molar ratio of 1:3 and Fe(II) concentration of 0.27 M for one day. After pH was adjusted to around 7 to 8, solution was allowed to settle for 2 days. Then, supernatant was decanted, and precipitated iron oxide sludge was collected and repeatedly used throughout the study. Therefore, the precipitated iron-containing sludge has organic materials embedded initially.  $\text{H}_2\text{SO}_4$  with concentration of 9.0 N and NaOH of 5.0 N were used for pH adjustment.

### 2.2. Experimental setup and methods

Fig. 1 shows the schematic experimental setup of this study, including electrolysis tank, Fenton reaction tank, neutralization tank, sedimentation tank, and acidification tank. Electrogeneration of Fe(II) was performed in the electrolysis tank which has volume of  $500 \text{ cm}^3$  and hydraulic retention times (HRT) varying from 100 to 1111 min. The pH of the electrolysis tank was maintained at  $1.0 \pm 0.05$  by a pH control system that consisted of a glass electrode (InLab 439, METTLER TOLEDO, Switzerland) and a pH controller (PC3200, Suntex instruments Co. Ltd., Taiwan), controlling  $\text{H}_2\text{SO}_4$  (9 N) dosing. Both cathode and anode are made of stainless steel with area of 64 and  $6.4 \text{ cm}^2$ , respectively, corresponding to cathode-to-anode area ratio of 10. The current density was fixed at 30 A per  $\text{m}^2$  of cathode area using a power supply (GPS-3030D, Good Will Instrument Co. Ltd., Taiwan).

Dosage of  $\text{H}_2\text{O}_2$  was varied by adjusting flow rates of the corresponding feeding pumps. However, the feeding concentration of Fe(II) depends both on the electrogenerated concentration of Fe(II) in the electrolysis tank and flow rate of Fe(II) feeding pump. In the tests, flow rate of Fe(II) feeding pump was also adjusted to control the electrolysis time in the electrolysis tank. Table 1 shows the experimental conditions and their denoted test numbers. For example, in test number 1, the Fe(II) and  $\text{H}_2\text{O}_2$  feeding pumps have the flow rates of 10 and  $5 \text{ cm}^3 \text{ min}^{-1}$ , respectively, while the dye-containing wastewater (wastewater A) flow rate was set at  $5 \text{ cm}^3 \text{ min}^{-1}$ . Under this condition the electrolysis time is 50 min, which is determined by the flow rate of Fe(II) feeding pump, and the feeding concentration of  $\text{H}_2\text{O}_2$  is  $375 \text{ mg dm}^{-3}$ . As indicated previously, the electrogenerated concentration of Fe(II) depends on initial ferric concentration, pH, temperature, cathodic potential, electrolysis time, and the cathode-to-anode area ratio [5,6]. In this study, electrolytic

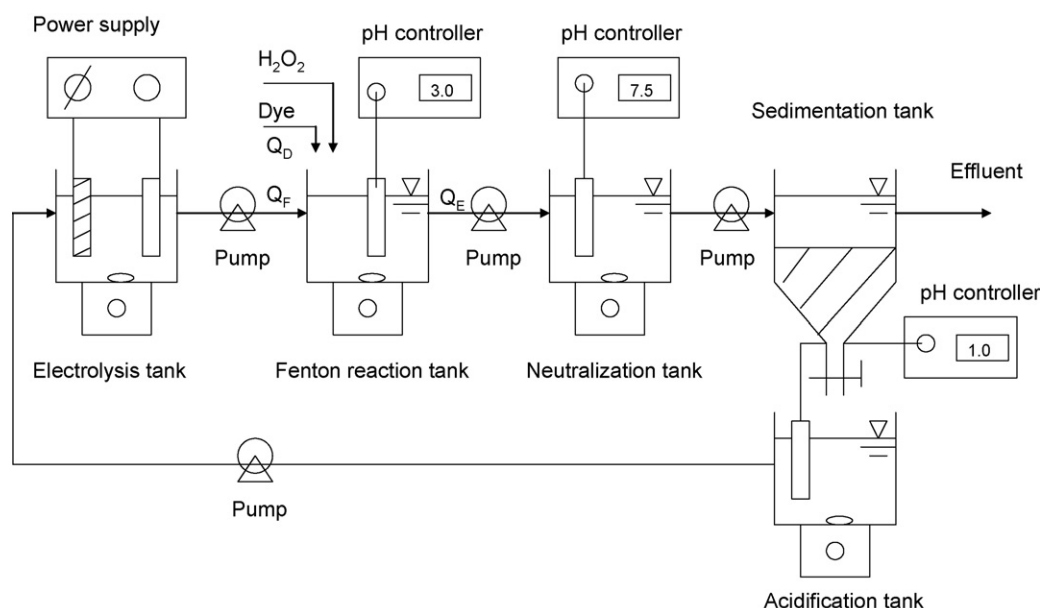


Fig. 1. The schematic experimental setup.

Table 1  
Experimental conditions for various test numbers

Test number	Flow rate (cm <sup>3</sup> min <sup>-1</sup> )			HRT (min)	
	Fe(II) stream	H <sub>2</sub> O <sub>2</sub> stream	Dye waste stream	Electrolysis	Fenton reaction
1	10	5	5 <sup>a</sup>	50	10
2	5	2.5	2.5 <sup>a</sup>	100	10
3	5	2.5	5 <sup>a</sup>	100	10
4	5	2.5	10 <sup>a</sup>	100	10
5	2.5	2.5	5 <sup>a</sup>	200	10
6	1.25	2.5	5 <sup>a</sup>	400	10
7	1.25	2.5	50 <sup>b</sup>	400	10
8	0.45	2.5	50 <sup>b</sup>	1111	10

<sup>a</sup> Wastewater A: COD = 3680 mg dm<sup>-3</sup>; color = 52460 ADMI units.

<sup>b</sup> Wastewater B: COD = 368 mg dm<sup>-3</sup>; color = 5246 ADMI units.

process was operated at fixed current mode by adjusting applied voltage of power supply, which is quite stable throughout the test. Since cathodic potential has little impact on amount of Fe(II) generated electrolytically [2], and pH, temperature (20 °C) and the cathode-to-anode area ratio are fixed in this study, the parameters affecting the performance of the Fe(II) generation are initial ferric concentration and electrolysis time.

The electrogenerated Fe(II) was pumped into the Fenton reaction tank and mixed with hydrogen peroxide and dye-containing wastewater. The pH of the Fenton reaction tank was maintained at pH 3.0 ± 0.05 by the same pH control system described above as it has been shown that the optimum pH for Fenton reaction is around 3.0 [1,9], and the HRT was fixed at 10 min by adjusting volume of the Fenton reaction tank. The Fenton treated solution was continuously pumped out of the Fenton reaction tank to the neutralization tank (with fixed HRT of 15 min) for iron precipitation by adjusting solution pH to around 7.5 ± 0.5 using a pH-controlled system. The precipitated iron was allowed to settle in the sedimentation tank with HRT of 500 min. The concentrated sludge was manually removed from the bottom of the sedimentation tank and discharged into the acidification tank, where the pH was controlled at pH 1.0 ± 0.05 to dissolve the iron precipitates. The dissolved iron was pumped to the electrolysis tank periodically by a pump controlled by a water-level switch installed in the electrolysis tank.

### 2.3. Analyses

After system has been run and stabilized for at least one hour, five consecutive hourly samples were taken from each tank under each test condition. Water quality parameters and sludge properties of these samples were analyzed, and the average values along with one standard deviation from the mean were reported. Samples taken from electrolysis tank and Fenton reaction tank were analyzed for COD directly, while those from neutralization tank were filtered with 0.45 μm filter paper before COD analysis. Since Fe(II) concentration is very high in samples taken from electrolysis tank and 1 mg Fe(II) would contribute to 0.14 mg COD (data not shown), COD contributed from dissolved Fe(II) ions has to be deducted.

COD, TS, SS, and VS were analyzed followed the standard methods [10]. Conductivity was analyzed using a conductivity

meter (Walklab, Trans Instruments, Singapore). Zeta potential of sludge was analyzed using a microelectrophoresis analyzer (Zeta-Meter 3.0+, Zeta-Meter, Inc., USA). CST (capillary suction time), which measures time for free water to pass between two electrodes using filter paper as the medium, is used to represent the dewaterability of treated sludges for the reason that CST is a quick and reliable method for characterizing sludge filterability [8,11]. CST was analyzed using CST apparatus (Type 165, Triton Electronics, Dunmow Essex, England, UK) with Whatman No. 17 filter paper. Five measurements for each sample were taken to obtain the average CST value.

Total iron content was analyzed after sample was digested. A 50-cm<sup>3</sup> sample was transferred to a 100-cm<sup>3</sup> beaker with concentrated nitric acid (5 cm<sup>3</sup>) and a few boiler chips were added. The solution was boiled and evaporated slowly on a hot plate with concentrated nitric acid added, if necessary, until the digestion was completed, indicated by a light-colored (colorless or canary yellow) clear solution. The digested solution was diluted with DI water to the known fixed volume and concentration of total iron was analyzed by a flame atomic absorption spectrometer (Hitachi, Z6100). Fe(II) concentration was determined by light absorbance measurement at 510 nm after complexing with 1,10-phenanthroline using a UV-vis spectrophotometer (Helios beta, Thermo Electron Corporation) according to the method listed in the 20th edition of the standard methods [10]. Since some of the samples contain large amount of Fe(III) which will interfere with the analysis of Fe(II), ammonium fluoride was chosen as a masking agent for Fe(III) according to Tamura et al. [12].

## 3. Results and discussion

### 3.1. Treatment efficiency and treated water quality

Since the system was running continuously and COD come from both wastewater and Fe(II) feed streams, COD removal efficiency in the Fenton reaction tank was calculated by accounting for COD input from Fe(II) feed stream using Eq. (1) shown below.

$$\text{COD}_r(\%) = 100 - \frac{Q_E \times C_E}{Q_F \times C_F + Q_D \times C_D} \times 100 \quad (1)$$

where  $COD_r$  is the percentage of COD removal efficiency.  $Q_F$ ,  $Q_D$ , and  $Q_E$  are flow rates for Fe(II) feed stream, wastewater stream, and effluent stream of Fenton reaction tank, respectively (see Fig. 1).  $C_F$ ,  $C_D$ , and  $C_E$  are COD concentrations for corresponding streams. On the other hand, COD removal in neutralization tank was calculated using the equation similar to Eq. (1) with  $C_E$  replaced by COD concentration of the effluent of the neutralization tank.

As indicated in Table 2, COD of the samples taken from the Fenton reaction tank for treating the synthetic wastewater A (i.e., Test 1 to 6) are ranging from 52 to 260  $mg\ dm^{-3}$ , corresponding to COD removal efficiencies of 95 to 88%. On the other hand, the COD of samples in the Fenton reaction tank for treating the synthetic wastewater B (i.e., Test 7 to 8) are ranging from 22 to 87  $mg\ dm^{-3}$ , corresponding to COD removal efficiencies of 94 to 75%, respectively. The COD concentrations are decreased further after pH neutralization, and are around 24–178  $mg\ dm^{-3}$ , corresponding to COD removal efficiencies of 98–92% for treating wastewater A, while those values are 21 to 50  $mg\ dm^{-3}$ , corresponding to COD removal efficiencies of 94 to 86%, for treating wastewater B. In general, additional COD removal by neutralization is less than 11%, indicating that COD is mainly removed by oxidation other than by coagulation.

Color was measured in the treated effluent after neutralization only. They are ranging from 224 to 2139 ADMI units for treating wastewater A, corresponding to more than 96% in color removal efficiency, and are ranging from 123 to 558 ADMI units for treating wastewater B, corresponding to more than 90% in color removal efficiency.

COD removal efficiency by Fenton process has shown to be affected by concentrations and ratios of Fenton reagents, initial

concentration, and properties of dyes [13–16]. As indicated earlier, Fe(II) feed concentration depends on the electrogenerated concentration of Fe(II) in the electrolysis tank, therefore it is difficult to compare treatment efficiency from run to run. In the current study, interpretation of COD removal is further complicated by COD contributed from recycled and reused iron, i.e., COD from Fe(II) stream. Since organics released from iron-containing sludge in the electrolysis tank were residual from the earlier oxidation cycles and have been subjected to Fenton oxidation previously, they may be refractory to further Fenton oxidation. Thus, fraction of COD fed to the Fenton reaction tank which was contributed by Fe(II) stream might affect the overall COD removal efficiency. As indicated in Table 3, depending on Fe(II) flowrate and COD in the electrolysis tank, fraction of COD contributed from Fe(II) stream to the total COD fed to the Fenton reaction tank, denoted as  $(COD_{Fe(II)\ stream}/COD_{Fenton})$ , is ranging from 2 to 13.6%. However, there is no clear trend between this fraction and overall COD removal efficiency in the Fenton reaction process, indicating that organics contributed by Fe(II) stream are not refractory to further Fenton oxidation, and other factors might govern COD removal efficiency.

Treatment efficiency of Fenton process generally increases with increasing  $(H_2O_2/Fe_{(II)})$  molar ratio (e.g., [9,13,15,16]), but reaches a plateau or decreases when  $(H_2O_2/Fe_{(II)})$  molar ratio passes its optimum value which varies among studies. It is believed that reaction between OH radical and  $H_2O_2$  is dominated and responsible for the decreases in treatment efficiency at  $(H_2O_2/Fe_{(II)})$  molar ratio higher than its optimum value [9]. Table 3 shows the feed concentrations of Fe(II),  $H_2O_2$ , and COD into the Fenton reaction tank along with  $(H_2O_2/Fe_{(II)})$  molar ratios and  $(COD/Fe_{(II)})$  weight ratios. Although, it is meaning-

Table 2  
Water quality parameters of samples taken from the process for various experimental conditions

Test number	Electrolysis tank			Fenton reaction tank			Neutralization tank			
	$Fe_{tot}$	Fe(II)	COD	Fe(II)	COD	$COD_r(\%)$	COD	$COD_r(\%)$	Color	Cond. (ms)
1	1920 (1342) <sup>a</sup>	318 (102)	183 (23)	1.1 (1.1)	91 (48)	91	50 (71)	95	224 (26)	67.8 (2.0)
2	5919 (2638)	1308 (342)	289 (29)	7.3 (13)	52 (6)	95	24 (6.1)	98	258 (45)	45.1 (8.1)
3	7259 (1250)	595 (70)	277 (22)	2.8 (0.6)	94 (3)	94	54 (19)	97	449 (54)	43.9 (3.9)
4	11699 (827)	708 (416)	284 (31)	7.5 (0.9)	260 (32)	88	178 (47)	92	2139 (1166)	30.7 (1.4)
5	2913 (923)	1193 (466)	442 (14)	3.9 (1.5)	136 (7)	93	72 (2.9)	96	672 (175)	30.9 (1.0)
6	7102 (1653)	1623 (800)	573 (51)	4.1 (1.9)	183 (43)	92	159 (22)	93	489 (70)	18.4 (1.4)
7	6445 (1167)	2232 (488)	606 (57)	12.9 (6.9)	22 (5)	94	21 (3)	94	123 (20)	5.4 (0.2)
8	5997 (1336)	3625 (1306)	830 (69)	2.1 (1.9)	87 (12)	75	50 (13)	86	558 (268)	1.0 (0.1)

$Fe_{tot}$ : Total iron content, Units:  $mg\ dm^{-3}$  unless specified.

<sup>a</sup> Numbers in parentheses are one standard deviation from the mean. Number of samples = 5 except Test 1 which has only three data points.

Table 3  
Concentrations of Fenton reagents and COD into Fenton reaction tank

Test number	Feed concentrations to Fenton reaction tank ( $\text{mg dm}^{-3}$ )			$\text{H}_2\text{O}_2/\text{Fe(II)}$ (mol/mol)	COD/Fe(II) (mg/mg)	$(\text{COD}_{\text{Fe(II) stream}} / \text{COD}_{\text{Fenton}}) (\%)$
	Fe(II)	$\text{H}_2\text{O}_2$	COD			
1	159	375	1012	4.1	6.4	9.0
2	654	375	1065	1.0	1.6	13.6
3	238	300	1583	2.2	6.7	7.0
4	202	214	2184	1.8	10.8	3.7
5	298	375	1951	2.2	6.5	5.7
6	232	429	2185	3.2	9.4	3.7
7	52	70	356	2.3	6.9	4.0
8	31	70	355	4.0	11.5	2.0

less to compare its effect among various studies due to different concentration and type of dye investigated, ( $\text{H}_2\text{O}_2/\text{Fe(II)}$ ) molar ratios ranging from 1.0 to 4.1 investigated in this study is much less than the optimum value of 7.5 reported by Xu et al. [9] and 4.9 reported by Lucas and Peres [15]. Examining ( $\text{H}_2\text{O}_2/\text{Fe(II)}$ ) molar ratio and COD removal efficiency shows no meaningful correlation, indicating that this ratio is not responsible for the discrepancies of COD removal observed among test runs. However, COD removal increases with decreasing COD/Fe(II) weight ratio and reaches a plateau at the ratio of less than 10 as indicated in Fig. 2, showing that the Fe(II) feed dosage is important for controlling COD removal efficiency of Fenton process.

Other than COD and color removal, conductivity of treated water is worth to discuss. Although, no unified water reused standard, which might vary from plant to plant and from industry to industry, has been proposed, conductivity parameter is usually listed [17–19]. The conductivities of the treated water ranging from 1.0 to 67.8 mS are shown in Table 2, posing problem to recycle and reuse the treated water. As indicated in Fig. 3, conductivities of the effluent depend on the ratio of Fe(II) flow to the total flow into the Fenton reaction tank. The results are not surprising, considering the very low pH required and adjusted in the acidification tank. Therefore, by increasing concentration of Fe(II) generated in the electrolysis tank (to be discussed next) to decrease flowrate of the Fe(II) feed stream without sacrificing COD removal efficiency of the process, conductivity of the treated effluent can be lowered.

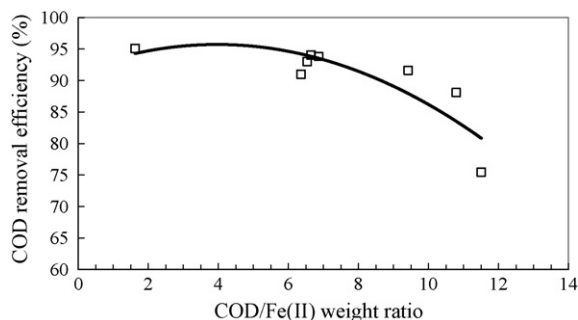


Fig. 2. COD removal efficiency in the Fenton reaction tank as a function of COD/Fe(II) weight ratio.

### 3.2. Fe(II) generation and dissolution of COD from the sludges in the electrolysis tank

As indicated above, increasing Fe(II) generation in the electrolysis tank to decrease flowrate of the Fe(II) feed stream would lower conductivity of the treated water. In current study, electrolytically-generated Fe(II) concentration could be increased by increasing total iron concentration and electrolysis time of the electrolysis tank [5,6] since other parameters such as pH, temperature, cathodic potential, cathode area, and cathode-to-anode area ratio are fixed.

Table 2 shows iron concentration (both Fe(II) and total Fe content) of samples taken from electrolysis tank. The total Fe content concentrations, denoted as  $\text{Fe}_{\text{tot}}$ , on average are ranging from 1920 to 11699  $\text{mg dm}^{-3}$ , depending on the efficiency of sludges settled on the sedimentation tank. On the other hand, the concentrations of Fe(II) generated on average are ranging from 318 to 3625  $\text{mg dm}^{-3}$ . The effect of  $\text{Fe}_{\text{tot}}$  on the generation of Fe(II) was obscured by wide ranges of electrolysis times tested as indicated in Fig. 4(a). However, the concentration of Fe(II) increases linearly ( $r^2$  of 0.94) with increasing electrolysis time as shown in Fig. 4(b). These results indicate that the amount of  $\text{Fe}_{\text{tot}}$  provided is enough and not the limited factor for the electrogeneration of Fe(II).

As mentioned above, COD in the electrolysis tank was released from reused sludge. Although, it contributes for only 2 to 13.6% of the total COD fed to the Fenton reaction tank, the possibility of COD accumulation in sludge is worth close exam-

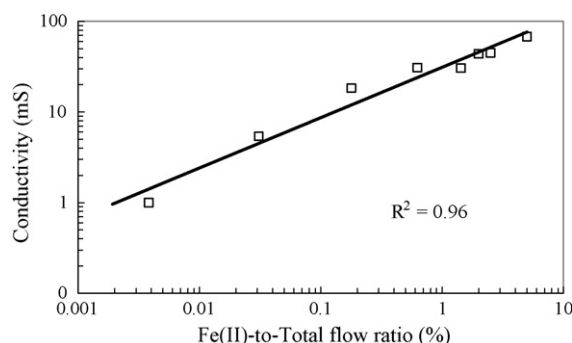


Fig. 3. Conductivity as a function of the Fe(II)-to-Total flow ratio.



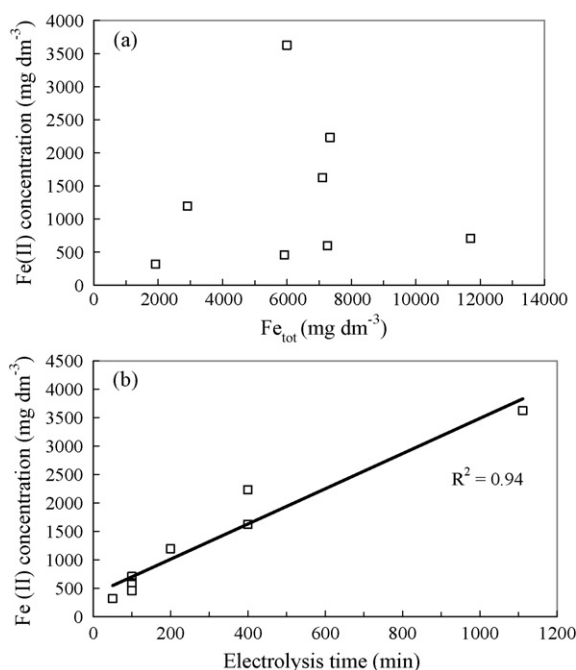


Fig. 4. The concentration of Fe(II) for samples taken from the electrolysis tank as a function of (a) Fe<sub>tot</sub> and (b) electrolysis time.

ination. As indicated in Table 2, COD in the electrolysis tank is on average ranging from 183 to 1499 mg dm<sup>-3</sup>, and increases with increasing test number (Fig. 5), signifying accumulation of COD with repeated use of the sludge.

### 3.3. Sludge property

In this study, HRT of 500 min in the sedimentation tank seems long enough, and sludge settled quite effectively as indicated by clarity of effluent from the sedimentation tank through visual observation. Therefore, samples were taken from the neutralization tank instead to show and imply how well these samples can be concentrated and settled before reused in the electrolysis tank. Table 4 shows results for CST, zeta potential, VSS/TSS ratio, and TSS analyses. Since these tests were conducted under various flowrate of wastewater and Fe(II) streams and most of solids were originated from Fe(II) feed stream, TSS of samples are linearly related to the Fe(II)-to-Total flow ratio as indicated in Fig. 6(a). Although, CST is frequently used to represent the

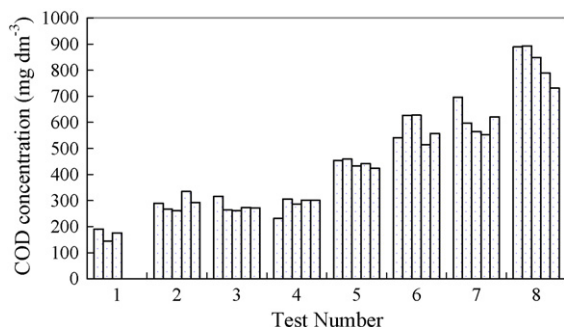


Fig. 5. COD vs. test number in the electrolysis tank.

Table 4  
Sludge properties for samples taken from neutralization tank

Test number	CST (sec)	Zeta potential	VSS/TSS (%)	TSS (mg dm <sup>-3</sup> )
1	52.4 (8.7)	-7.3 (2.1)	11.8 (0.7)	11930
2	43.6 (4.1)	-11.2 (1.1)	11.9 (2.5)	10302
3	43.0 (6.2)	-11.5 (2.4)	15.6 (3.3)	10408
4	31.0 (2.0)	-45.0 (1.9)	31.8 (20.3)	5932
5	32.2 (1.9)	-32.7 (1.0)	30.0 (3.7)	6800
6	28.7 (1.8)	-40.9 (2.7)	43.4 (7.3)	3660
7	17.3 (1.8)	-33.5 (4.7)	85.6 (5.4)	760
8	15.2 (0.4)	-22.3 (3.3)	67.5 (15.8)	165

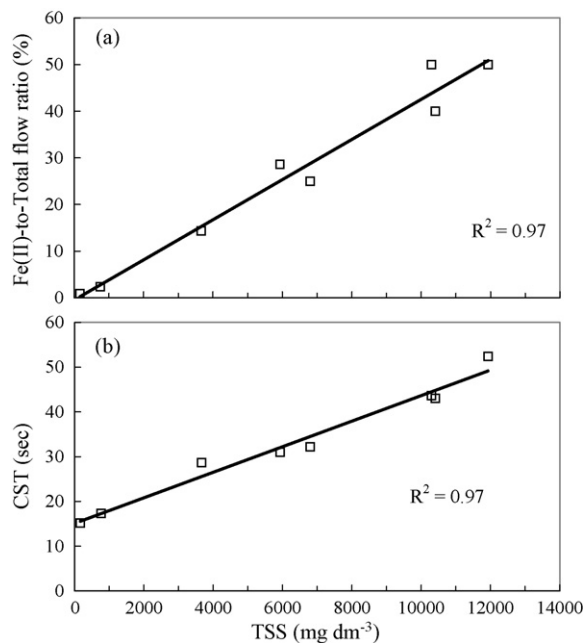


Fig. 6. (a) Fe(II)-to-Total flow rate ratio (%) and (b) CST for samples taken from the neutralization tank as function of TSS.

dewaterability of treated sludges [8,11], it is not suitable for this study for the reason that it is closely related to TSS as shown in Fig. 6(b).

According to several studies [8,20], negatively zeta potential of sludge particles would have negative impact on the performance of sludge dewatering and settling. Organics from dye molecules and their oxidized products embedded in the iron oxide precipitates during precipitation process might lower zeta

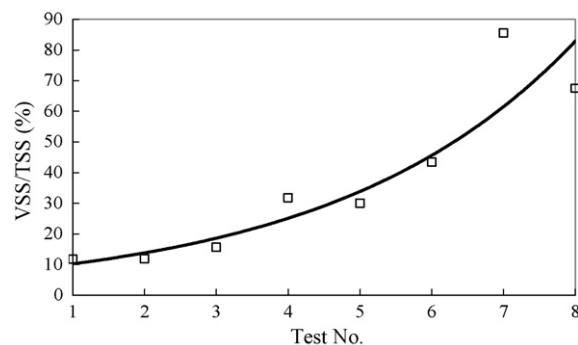


Fig. 7. VSS/TSS ratio as a function of test number.

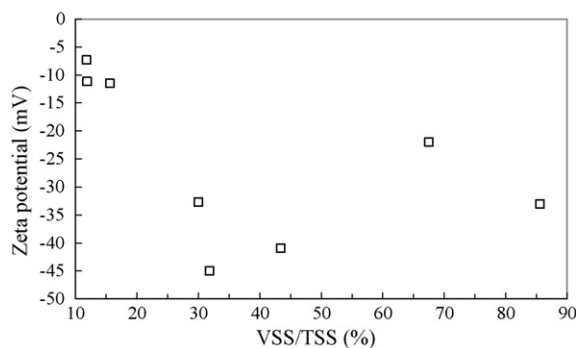


Fig. 8. Zeta potential vs. VSS/TSS ratio for the effluent samples.

potential of sludges. Fig. 7 shows VSS/TSS increases with increasing test number, indicating organic materials accumulated from run to run. As a result, zeta potential of sludge decreases generally with increasing VSS/TSS ratio (see Fig. 8), implying that reuse of iron-containing sludge might eventually run into problems of dewatering and concentrating sludge.

#### 4. Conclusions

This study demonstrated treatment efficiency of dye wastewater using the Fenton process with Fe(II) electrolytically generated using iron-containing sludge as the iron source. Although, the process was quite effective for COD and color removal for synthetic dyeing wastewater, conductivity of treated water was enormously high. It is the result of extremely low pH needed for re-dissolving sludge in the acidification tank. Meanwhile, repeated use of sludge results in increasing the amount of organic material accumulated as indicated by increasing VSS/TSS ratio and decreasing zeta potential. Negative zeta potential of sludge particles would have negative impact on the performance of sludge dewatering.

Future research should focus on how to decrease the amount of organics accumulated and the amount of acid needed during Fe(II) regeneration process. Possibility of Fe recovery using cationic exchange membrane such as the process employed for coagulant recovery from water treatment plant residuals by Prakash and SenGupta [21] might be the right direction to solve the problem. As indicated by these authors, high quality of recovered coagulant that is essentially free of particulate matter, NOM, and other trace metals can be obtained.

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