



Treatment of printed circuit board industrial wastewater by Ferrite process combined with Fenton method

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ABSTRACT

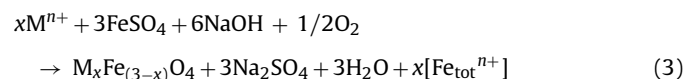
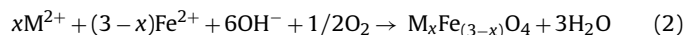
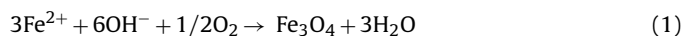
Printed circuit board wastewater typically contains organics and metal ions. The study explored the feasibility of a sequential procedure, FFP (the combination of the Fenton method and the Ferrite process), for treating printed circuit board wastewater, and established the optimum parameters for it. The analytical results showed that the proper pH level was 2 for Fenton oxidation, and the appropriate H₂O₂ dosing type was batch dosing. For the Ferrite process, the suitable Fe/M (Fe is the total dose of Fe²⁺ added to a solution and M is the initial total moles of various metal ions in untreated wastewater) molar ratio was 10 and the sludge met the toxicity characteristic leaching procedure (TCLP) standards. Following FFP treatment, effluent water or sludge easily met Taiwan's standards. Finally, the SEM/EDS test demonstrated that particle sizes of the sludge were approximately 50–80 nm, and the saturation magnetization was 67.5 emu/g.

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1. Introduction

Printed circuit boards, which have generated billions of US dollars in global sales, are important components of electronic products. Taiwan's printed circuit board industry is a major electronic component industry and its production accounts for roughly 13% of global revenue in recent years. Manufacturing of printed circuit boards involves several steps, such as etching, drilling, image transfer and electroplating [1]. Various kinds of organic and inorganic chemicals hazardous to environment and human health such as haloorganic compounds, surfactants, acidic solvents and metal salts are used during each step, which cause difficulties when treating printed circuit board industry wastewater.

Many processes can be applied in such wastewater treatment, and the Ferrite process (FP) is one of them. The FP has long been used to treat wastewater containing metal ions [2–4]. Initially, the FP was applied to generate magnetite (Fe₃O₄) via wet-synthesis. The reaction equation for FP is shown as Eq. (1). However, Eq. (1) is transformed into Eq. (2) when a solution contains other divalent metal ions, and the mechanism is the fundamental principle for the FP to be applied in wastewater treatment. Moreover, the mechanism is further suggested as Eq. (3) for divalent and polyvalent metal ions [5].



Compared with the conventional chemical coagulation method which uses ferrous salt as a coagulator, a characteristic of FP is that it can incorporate the metal ions in a solution into the complete spinel structure, and the metal ions are less mobile in the generated ferrite-bearing sludge than in the ferrous/ferric oxide sludge. In other words, wastewater with metal ions subjected to FP treatment can meet effluent standards, and the resulting sludge can meet the standards of toxicity characteristic leaching procedure (TCLP) under proper treatment conditions. Additionally, the sludge can be recycled as a magnetic material or a catalyst [6,7], and thus, the FP has significant potential for treating wastewater.

The primary factors determining the performance of the FP are pH, reaction temperature and Fe²⁺ dosage [8–10]. The appropriate range of pH in the FP is 9–11, the reaction temperature must be maintained at >70 °C to assist the crystal growth of the ferrosineral, with the Fe²⁺ dosage typically at 5–10 times the total metal content, thus ensuring the sludge stability to fulfill TCLP standards. However, due to the possibility of complex metal ions in wastewater, conventional FP is not sufficient, therefore, a multi-stage FP for the treatment of 10 metal ions (Cd, Cu, Pb, Cr, Zn, Ag, Hg, Ni, Sn, Mn) in a synthesis laboratory waste liquid is proposed [11,12].

Although the FP is proved that it has great potential on the removal of metal ions, another auxiliary process is still needed to

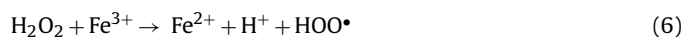
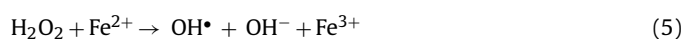
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enhance the efficiency of the FP when the wastewater contains other non-metal pollutants, such as organic matters. Advanced oxidation processes (AOPs) are broadly defined as aqueous-phase oxidation processes based primarily on the high oxidative power of hydroxyl radicals (OH^\bullet) to degrade organic pollutants and the reaction is shown as Eq. (4) [13]. In general, AOPs include photocatalytic oxidation, ozone oxidation (usually combined with H_2O_2 , UV, or both), UV/ H_2O_2 systems and Fenton and Fenton-type methods.



The Fenton method, as compared with other AOPs, is easily operated and maintained. The Fenton reagent is a mixture of Fe^{2+} and H_2O_2 in an acidic solution. In the reaction mechanism (see Eqs. (5)–(8)), strong oxidative OH^\bullet is produced and the ferrous ions are oxidized to ferric ions (Fe^{3+}) [14,15]. These powerful hydroxyl radicals ($E^0 = 2.8 \text{ V}$) can completely mineralize organic compounds to CO_2 and H_2O . The Fenton oxidation process has been applied successfully to treat various industrial wastewaters [16–21].



In general, industrial wastewater such as printed circuit board industrial wastewater usually contains specific chemicals and heavy metal ions; therefore, it is impossible to treat this wastewater with only one method. For example, the previous studies on the FP mostly focus on how the FP deals with industrial or synthetic wastewater contained only metal ions, and it is also well known that Fenton method has great efficiency on the removal of organic matters but the derivative problem is the production of ferrous salt sludge. Therefore, the combination of these two methods based on their advantages leads to a reasonable procedure which can deal with wastewater containing organic compounds and metal ions. Furthermore, the defect of ferrous salt sludge from the Fenton method could also be solved by the following FP and then form Fe_3O_4 which is easily separated due to its firm structure and magnetic property.

The objectives of this investigation were to combine Fenton method (to first decompose the organic matters) with the FP (to remove residual metal ions in wastewater) into a new procedure and apply it to treat printed circuit board wastewater in order to meet the effluent standards of Taiwan, then examine the feasibility of the procedure, and finally qualify properties of the ferrosinels (or called “sludge” because it is generated from the wastewater treatment). Various parameters, including pH, Fe^{2+} and H_2O_2 dosages, reaction time and dosing types, which affect the Fenton method and Fe/M molar ratio which influences the proposed multi-stage FP [11] are fully discussed in this research. Through this study, the Ferrite process combined with Fenton method (FFP) would be developed and tested, proving that FFP can effectively treat wastewater containing organic matters and metal ions.

2. Materials and methods

2.1. Analytical methods and instruments

Chemical oxygen demand (COD) and total organic carbon (TOC) were conducted to determine the organic concentration in untreated and treated wastewater. For COD analysis, samples were pretreated with 2N NaOH, heated to 40°C to remove any residual H_2O_2 that may influence the experimental results [22], and analyzed by the dichromate titrimetric method following the APHA

standard method [23]. The TOC was determined using a TOC analyzer (O.I.C. Model 700 TOC, USA), and all the samples were diluted in the concentration range of 0.5–2 mg/L. A flame atomic absorption spectrophotometer (Thermo Solaar-S2, England) was used to measure the metal ion concentrations (Cu, Fe, Mn, Pb, Cd, Ni, Zn and Cr) in the wastewater.

As to the quality of sludge, the analytical TCLP was introduced and followed with a standard method, as published in Taiwan (NIEA R201.13C). The extraction agent was prepared by adding 5.7 mL glacial acetic acid and 64.3 mL 1 M NaOH to a 1 L volumetric flask, containing 500 mL of deionized water, the mixture was then diluted to 1 L. Theoretically, the pH of the extraction agent should be 4.93 ± 0.05 and was checked before testing. Approximately 2 g of dry sludge was placed into a 100 mL extraction bottle, to which 40 g of extraction agent was added. The extraction bottle was placed on a rotator at 30 ± 2 rpm for 18 ± 2 h. Following this procedure, the concentration of metal ions in the extraction liquid was measured.

To further discuss the properties of sludge, a scanning electron microscope (SEM) and an energy dispersive spectrometer (EDS) (JEOL JSM 6400 Scanning Microscope) were employed to observe the surface of the sludge and verify sludge alloy composition. Meanwhile, an X-ray diffraction (XRD) (SIEMENS D5000) and a superconducting quantum interference device (SQUID) (MPMS-XL7) were also applied to characterize the crystallization and to measure the magnetic field.

2.2. Fenton oxidation

The Fenton system was comprised of a reactor, agitator, peristaltic pump, automatic temperature controller and pH meter. The reactor was a thermostatic, double-walled cylindrical Pyrex cell with a capacity of 2 L. Circulating water was used to maintain a constant temperature of 25°C using an automatic temperature controller. The volume of wastewater was 1 L for each experiment. At the beginning of each reaction, different dosages of FeSO_4 ($[\text{Fe}^{2+}]$ was in the range of 0–1000 mg/L) were added into the reactor. For H_2O_2 , two dosing types, batch and continuous dosing, and dosages (range 2000–7000 mg/L) were used. During batch dosing, various amounts of H_2O_2 were added to the solution when the reaction began. Conversely, during continuous dosing, H_2O_2 was added using a peristaltic pump. The pH value was adjusted from 1 to 7 and controlled in the range of ± 0.2 by adding NaOH or HNO_3 . To mix the reaction solutions thoroughly, an agitator which rotated at 150 rpm consistently was used. Experimental results for reaction times of 60 and 120 min were compared. The degradation efficiency of organic compounds was studied by COD and TOC reductions.

2.3. Ferrite process for removing metal ions

The experimental equipment comprised a reactor, agitator, air pump, automatic temperature controller and pH meter. For the FP, an air pump (supply rate, 3 L/min) provided oxygen to promote the formation of ferrosinels. Aside from the air pump, the other equipment was the same as that in Fenton system. In this experiment, the proposed procedure which is called multi-stage FP was applied [11,12]. Reaction temperature in the first FP stage was 70°C and pH was 9; during the second stage, reaction temperature was 90°C and pH was 9. During the last stage, pH was 10 and reaction temperature was 80°C . The reaction time for each stage was 40 min and air was supplied at a rate of 3 L/min. To identify the optimum dosages of Fe^{2+} , different amounts of Fe^{2+} were investigated. The molar ratio of Fe/M (Fe is total dosages of Fe^{2+} added to the solution and M is the initial total moles of various metal ions in untreated wastewater) was 5–30 in each stage.

Table 1
Summary of wastewater quality and effluent standards.

Parameters	Wastewater	Effluent standards ^a
pH	3.89	6–8
COD (mg/L)	406	120
TOC (mg/L)	134	– ^b
Cu (mg/L)	524	3
Fe (mg/L)	ND ^c	–
Mn (mg/L)	ND	–
Pb (mg/L)	ND	1
Cd (mg/L)	ND	0.03
Ni (mg/L)	ND	1
Zn (mg/L)	ND	5
Cr (mg/L)	ND	2

^a The effluent standards are legislated by Taiwan Environmental Protection Agency.

^b “–” represents “no standards”.

^c “ND” represents “not detectable”.

3. Results and discussion

3.1. Printed circuit board wastewater quality and effluent standards

At the beginning of this research, wastewater was obtained from a printed circuit board factory in Taiwan, and then pretreated with filtration to remove suspended solid (SS). Table 1 presents analytical results for prefiltered wastewater quality with a summary of effluent standards in Taiwan, and it is easily discovered that the concentrations of COD, TOC and Cu are 406, 134 and 524 mg/L. Moreover, it is also noticed that COD and Cu which is the predominant metal contaminant in the wastewater exceed markedly the effluent standards, 120 and 3 mg/L.

In wastewater, the species of organic content were complex (including some particular chemicals used in printed circuit board manufacturing, for which the manufacture was not willing to provide the chemical information), and thus, it was extremely difficult to identify and quantify each compound. Therefore, the presence of organic pollutants was determined instead of COD and TOC and can be regarded as the total amount of the organic matter.

3.2. Optimization of Fenton method on printed circuit board wastewater treatment

The key factors influencing the Fenton method were pH, and Fe^{2+} and H_2O_2 dosages. Fig. 1 presents the effects of pH on COD removal. Experiments were performed at 25 °C at a pH range of 2–8 by maintaining the $[\text{H}_2\text{O}_2]$ and $[\text{Fe}^{2+}]$ at 3000 and 50 mg/L, respectively. Reaction time was 60 min and dosing type for H_2O_2 was continuous. The pH value significantly affected the removal of COD by directly influencing the generation of the OH^\bullet radical (Fig. 1). Increasing the pH from 1 to 2 increased removal efficiency from 28.7% to 43.6%; however, further increasing the pH from 2 to 8 decreased the removal efficiency from 43.6% to 3.9%. The optimum pH range for Fenton oxidation was 2–4 [24]. This ultra low pH may cause competition of the OH^\bullet radicals between H^+ and organic pollutants, indicating the OH^\bullet radical scavenging effects of H^+ ion to reduce the removal efficiency. At a high pH level, formation and precipitation of $\text{Fe}(\text{OH})_3$ might occur, and then further inhibited the reduction of Fe^{3+} to Fe^{2+} with H_2O_2 (see Eq. (6)) or catalyzed H_2O_2 to O_2 and H_2O [25,26]. Moreover, stable Fe (II) complexes could be also formed to impede the reaction of Fe^{2+} with H_2O_2 (see Eq. (5)) [27]. Hence, a pH of 2 was the optimum pH for the Fenton method.

Fig. 2 shows experimental results for the amount of Fe^{2+} that affected COD removal. As the Fe^{2+} dosage was 0 mg/L, which meant the reaction only depending on the oxidizing power of H_2O_2 , the COD removal efficiency was only 28.9%; with the rise of the Fe^{2+}

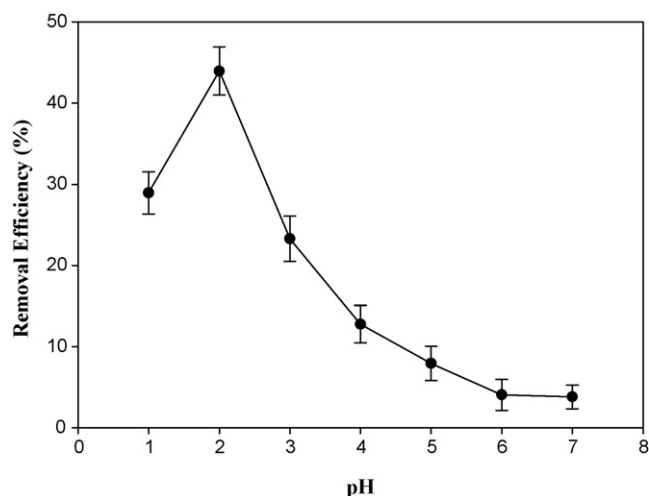


Fig. 1. Effect of pH on COD removal by Fenton method (reaction conditions: $[\text{Fe}^{2+}] = 50$ mg/L, $[\text{H}_2\text{O}_2] = 3000$ mg/L, reaction time = 60 min, temperature = 25 °C, dosing type = continuous dosing).

dosage to 500 mg/L, the removal efficiency increased rapidly to 77.9%. H_2O_2 , which is also frequently applied in wastewater treatment with an oxidation potential of 1.78 V, has less oxidizing power than the OH^\bullet radical (2.80 V). Therefore, the efficiency progressively increased as the Fe^{2+} concentration was increased due to high amounts of the OH^\bullet radical generated from the reaction (see Eq. (5)) [28]. This phenomenon clearly represented the catalysis of Fe^{2+} in Fenton reaction. However, it was also noted that the removal efficiency decreased to 58.8% at the Fe^{2+} dosage of 1000 mg/L, and the reason was proposed that the overdosed Fe^{2+} might react with the OH^\bullet radical as a scavenger and formed Fe^{3+} and OH^- shown as Eq. (8) so that the Fenton oxidation was weakened [29].

Fig. 3 reveals how various H_2O_2 concentrations influenced COD removal efficiency at a Fe^{2+} dosage of 500 mg/L. The increase in H_2O_2 from 2000 to 3000 mg/L increased COD removal from 71.2% to 77.9% (residual COD concentration was 89.7 mg/L, lower than the effluent standard of 120 mg/L) due to the increased OH^\bullet radical concentration. However, at a high dosage of H_2O_2 (3000–7000 mg/L), the decrease in COD removal resulted from the OH^\bullet radical scavenging effect. At a high dosage of H_2O_2 , the OH^\bullet radical reacted with the H_2O_2 and produced H_2O and the HOO^\bullet radical. The HOO^\bullet rad-

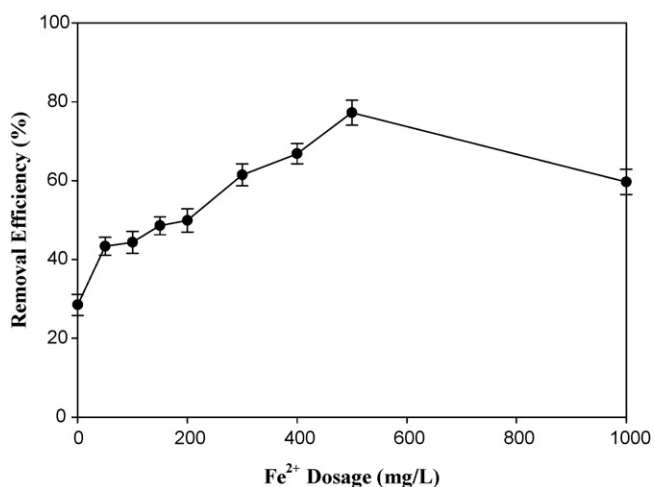


Fig. 2. Effect of $[\text{Fe}^{2+}]$ on COD removal by Fenton method (reaction conditions: pH 2, $[\text{H}_2\text{O}_2] = 3000$ mg/L, reaction time = 60 min, temperature = 25 °C, dosing type = continuous dosing).

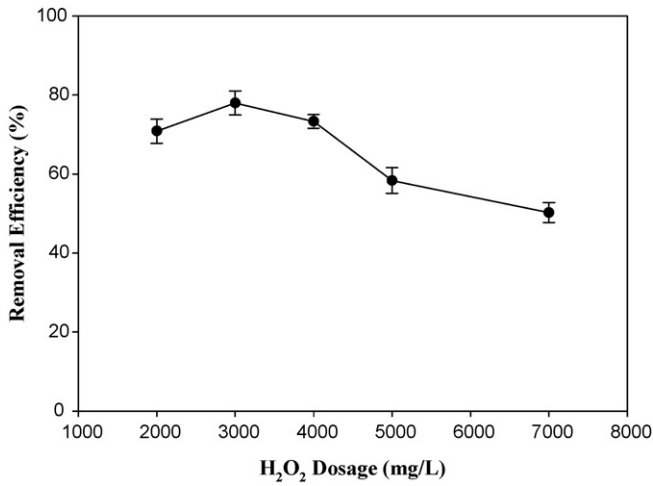


Fig. 3. Effect of [H₂O₂] on COD removal by Fenton method (reaction conditions: pH 2, [Fe²⁺]=500 mg/L, reaction time=60 min, temperature = 25 °C, dosing type = continuous dosing).

ical with an oxidation potential of 1.70 V, which is lower than that of the OH• radical, accounts for the reduction in removal efficiency [30].

Reaction times and dosing types of H₂O₂ were additional variables that affect the removal efficiency for COD and TOC; Fig. 4 presents the experimental results. The COD removal efficiency was 77.9% (continuous dosing) and 79.1% (batch dosing) at 60 min reaction time; and 81.1% (continuous dosing) and 86.6% (batch dosing) at 120 min reaction time. In TOC removal efficiency, experimental results showed the same trend; the TOC removal efficiency was 52.6% (continuous dosing) and 56.5% (batch dosing) at 60 min reaction time; and 61.6% (continuous dosing) and 63.1% (batch dosing) at 120 min reaction time. Through the results in this part, COD/TOC ratio could be also calculated. The COD/TOC of raw wastewater was 3.03, and after treatment they were decreased to 1.45 (batch dosing) and 1.33 (continuous dosing) at 60 min, and 1.11 (batch dosing) and 1.47 (continuous dosing) at 120 min.

These analytical results indicate that the same reaction time (60 or 120 min) of different dosing types had no influence on COD removal efficiency, and the difference in COD removal efficiency, between 60 and 120 min reaction time was negligible. Meanwhile,

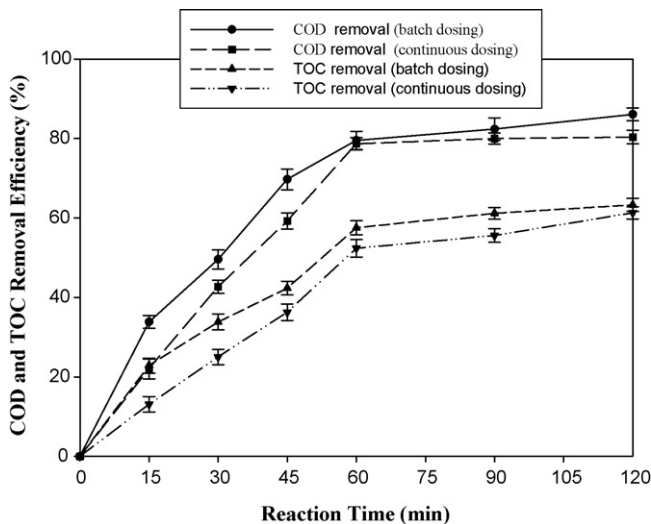


Fig. 4. COD and TOC removal with reaction time by Fenton method (Reaction conditions: pH 2, [Fe²⁺]=500 mg/L, [H₂O₂]=3000 mg/L, temperature = 25 °C).

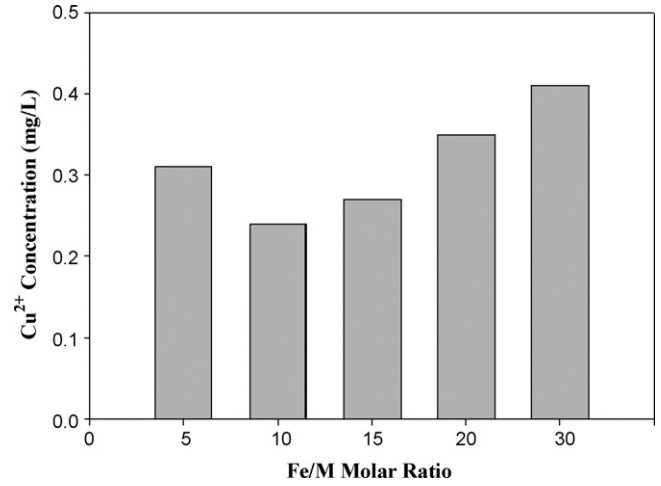


Fig. 5. Effect of Fe/M on residual Cu concentration in effluent water.

for the reaction times of 60 and 120 min, the residual COD concentrations were all lower than the effluent standard of 120 mg/L; therefore, 60 min was regarded as the proper reaction time. Furthermore, as to the choice of dosing types, the procedures of batch dosing were easier and more convenient to perform continuous dosing. Consequently, the optimum conditions for the Fenton method are: pH of 2, Fe²⁺ dosage of 500 mg/L, H₂O₂ dosage of 3000 mg/L, reaction time of 60 min and the H₂O₂ batch dosing type. Moreover, under these conditions, the COD and TOC of the treated wastewater were 84.9 and 58.3 mg/L, respectively.

3.3. Optimization of Ferrite process on printed circuit board wastewater treatment

To further discuss the application of the multi-stage FP on wastewater treatment, the Fe/M ratio was taken as the key parameter. In this section, the wastewater was first treated using the Fenton method as the source for the multi-stage FP. Fig. 5 shows the quality of treated water, and Fig. 6 presents the sludge TCLP test results, under different Fe/M ratio. All tests indicate that the Cu concentration was markedly below the effluent standard of 3 mg/L, and the concentration was 0.24 (Fe/M = 10) to 0.41 (Fe/M = 30) mg/L.

The experimental results clearly demonstrate that Fe/M ratio does not have influence on the Cu concentration in effluent water due to the very low concentration (0.24–0.41 mg/L). Nevertheless,

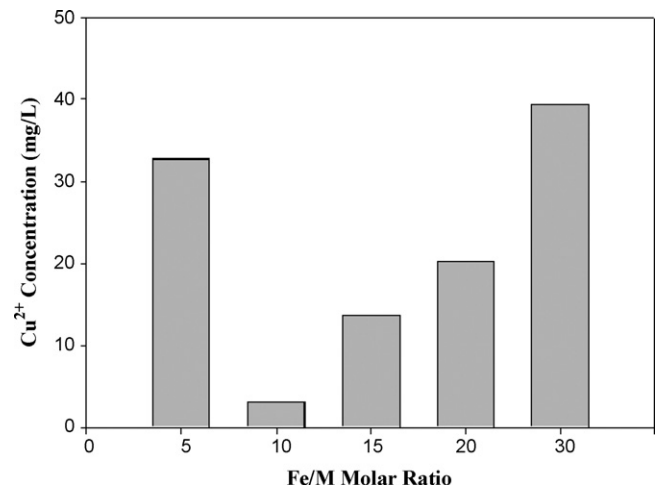


Fig. 6. Effects of Fe/M on Cu concentration in sludge TCLP test.

Table 2

The results of wastewater after treatment.

Parameters ^a	Standard (Taiwan) ^b	After FFP treatment	Removal efficiency of FFP (%)
COD (effluent)	120	81.2	80.0
TOC (effluent)	– ^c	57.5	57.1
Fe (effluent)	–	0.72	
Cu (effluent)	3.0	0.24	99.4
Fe (TCLP)	–	0.52	
Cu (TCLP)	15.0	3.10	

^a All units are “mg/L”.^b The effluent and TCLP standards are legislated by Taiwan Environmental Protection Agency.^c “–” represents “no standards”.

the Fe/M ratio severely affected the experimental results of the sludge TCLP test. According to the Standards for Defining Hazardous Waste in Taiwan, the TCLP standard for Cu is 15 mg/L. The leaching Cu concentrations in TCLP test were 3.1 (Fe/M = 10) to 39.5 (Fe/M = 30) mg/L (Fig. 6). The increase of the Fe/M ratio, from 10 to 30, increased Cu concentration due to the competition between Fe²⁺ and Cu²⁺ captured into the ferrosineral structure (see Eq. (3)). It means that large amount of Fe²⁺ instead of Cu²⁺ might directly enter the ferrosineral structure and then form Fe₃O₄, not CuFe₂O₄, but Cu²⁺ reacts with oxygen to generate CuO which leads to a decline in sludge stability. Based on analytical results, a Fe/M ratio of 10 was chosen as the optimum molar ratio.

3.4. Summarization of FFP treatment efficiency

Table 2 presents results for printed circuit board wastewater treated using FFP, and it clearly indicates that the effluent water quality and the sludge TCLP test results satisfied Taiwan's standards. For example, COD and Cu were greatly reduced to 81.2 and 0.24 mg/L after FFP treatment, respectively. Therefore, the results in Table 2 prove that the FFP can be successfully applied for industrial wastewater treatment under proper operational procedures. The treatment efficiency of FFP is also evaluated in Table 2. It is noted that the Cu removal efficiency is over 99%, and this result also clearly indicates the high effectiveness of the FP.

3.5. SEM/EDS measurement

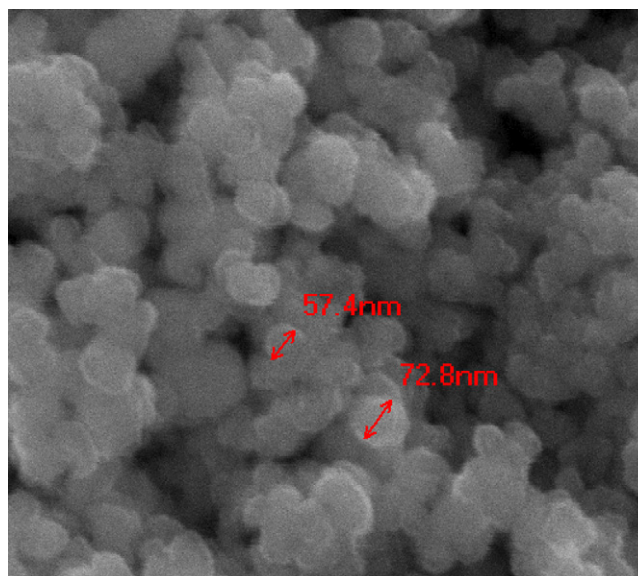
Fig. 7 displays the SEM photograph of sludge generated by the FFP. Through the SEM test, it could be clearly observed that the sludge consisted of granular particles, and the particle size of the sludge was nearly 50–80 nm.

The EDS test results (Table 3) indicate that the major components of the sludge were Cu, Fe and O. However, C and Na were also found in the EDS test results. The source of Na may be the NaOH solution used to adjust pH during reaction. Moreover, to enhance the observation of SEM, all samples were pretreated with carbon coating, and therefore, may explain the existence of C in the EDS test results.

Table 3

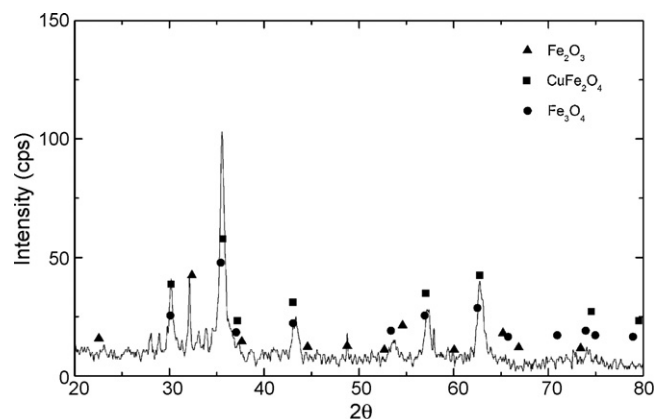
EDS test results of the sludge generated from the FFP.

Element	Sludge from FFP Atomic (mol%)
C	9.9
O	54.72
Na	1.18
Fe	33.29
Cu	0.91
Total	100

**Fig. 7.** SEM photograph of the sludge generated by the FFP.

3.6. XRD measurement

The structural determination of the sludge was investigated by using XRD, and the pattern is shown as Fig. 8. It is easily found that the sludge is crystallized with diffraction peaks around 30°, 36°, 57° and 62° which were the characteristic peaks of CuFe₂O₄ and Fe₃O₄. The characteristic diffraction peaks of CuFe₂O₄ and Fe₃O₄ are very similar due to the same spinel structure, and therefore it can be only proposed that the composition of sludge may contain CuFe₂O₄ and Fe₃O₄.

**Fig. 8.** XRD pattern of the sludge.

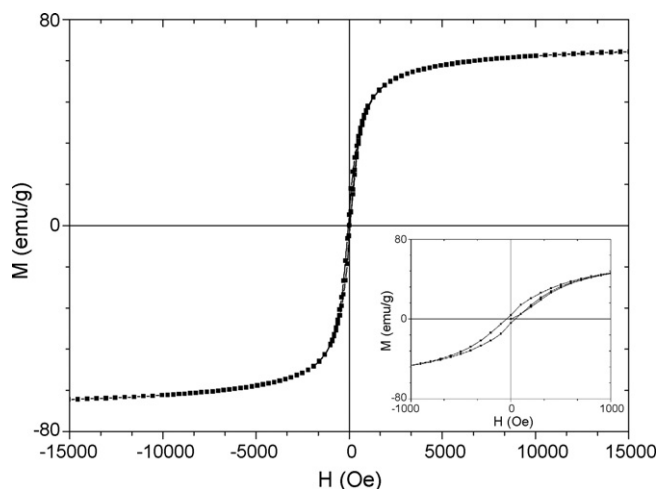


Fig. 9. M – H curve of the sludge measured with SQUID.

It is very interesting that there is an extra diffraction peak around 32° which is the characteristic peak of hematite Fe_2O_3 . During the multi-stage FP reaction, the pH and reaction temperature were not consistent, which means some of the reaction conditions may not be the optimum ones for the formation of Fe_3O_4 ; moreover, the great overdose of Fe^{2+} was added due to capturing Cu into the structure of CuFe_2O_4 , and this might lead to other side reactions and inhibit the Eq. (1). With the addition of alkali to the solution of Fe^{2+} , $\text{Fe}(\text{OH})_2$ is also formed but it rapidly absorbs O_2 which is greatly added in the reaction to promote the FP and then turns to the product Fe_2O_3 [31].

3.7. SQUID measurement

Magnetization of the sludge was measured using SQUID at the room temperature (300 K). Since it is a function of the magnetic field, an M – H curve is illustrated in Fig. 9, and here M and Oe in the figure represent magnetization intensity and magnetic field strength. The test result reveals that the saturation magnetization (M_s) of sludge is 67.5 emu/g, which is lower than nanopowder Fe_3O_4 (92 emu/g) [32] but higher than CuFe_2O_4 (26 emu/g) [33].

4. Conclusions

This study applied a sequential FFP procedure to treat printed circuit board wastewater. The optimum conditions for the Fenton method of FFP were: pH of 2, Fe^{2+} dosage of 500 mg/L, H_2O_2 dosage of 3000 mg/L, reaction time of 1 h and the H_2O_2 batch dosing type. To completely remove metal ions from wastewater, the multi-stage FP can be applied. The reaction parameters of each stage were: temperature = 70°C and pH 9, temperature = 90°C and pH 9, and temperature = 80°C and pH 10, respectively, and the Fe/ M molar ratio for each stage was 10.

In this study, the effluent water and sludge treated using the FFP successfully met Taiwan's standards. Meanwhile, the sludge generated from wastewater treatment can be recycled as magnetic material and catalysts to improve sludge value, as compared with conventional chemical precipitation. Therefore, these procedure can be significantly applied to treat industrial wastewater and are worthy of further investigation.

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