Treatment of complex heavy metal wastewater using a multi-staged ferrite process

Yao-Jen Tu [a,*], Chien-Kuei Chang [b], Chen-Feng You [a,*], Shan-Li Wang [c]

[a] Earth Dynamic System Research Center, National Cheng-Kung University, No. 1, University Road, Tainan City 701, Taiwan, ROC
[b] Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Science, No. 415, Chien Kung Road, Kaohsiung 807, Taiwan, ROC
[c] Department of Soil and Environmental Sciences, National Chung Hsing University, 250 Kuo Kuang Rd., Taichung 402, Taiwan, ROC

ARTICLE INFO

ABSTRACT

Complete removal of heavy metal from complex heavy-metal wastewater (CHMW) requires advanced technology. This study investigated the feasibility of a multi-staged ferrite process (MSFP) for treating CHMW, containing Cd, Cu, Pb, Cr, Zn, Ag, Hg, Ni, Sn and Mn. Our experimental results showed that most of the supernatants after conventional single-step ferrite process could conform to the effluent standard of Environmental Protection Administration in Taiwan. However, the sludge could not satisfy the toxicity characteristic leaching procedure (TCLP) limits due to high Cd, Cu, and Pb concentrations. The performance of MSFP in removing heavy metals from wastewater was subsequently investigated and the parameters of three treating steps in MSFP were optimized under 70 °C and 90 °C at pH 9, and 80 °C at pH 10. After the three-staged procedures, all heavy metals in supernatant and sludge could fulfill the contamination levels regulated by law. In addition, the sludge generated from the MSFP was examined by XRD and forms a stable spinel structure, which could be effectively separated by external magnetic field.

1. Introduction

Complex heavy metal wastewater (CHMW) refers to the wastewater with large variation of species and concentrations of heavy metals. Factories with a low volume-high diversity production and plants treating collective wastewater produce significant quantities of CHMW. Treating this kind of wastewater is considerably more difficult than treating industrial wastewater with stable composition.

Conventional technologies for treating wastewater containing heavy metals include chemical precipitation [1–5], membrane separation [6–9], coagulation [10–12], adsorption [13–16] and ion exchange [17,18]. Nevertheless, a sludge containing heavy metals would be generated either through one treatment method or a combination of several methods. One of the major concerns in these processes is the secondary pollution from the release of heavy metals into the environment. Thus, the sludge is often solidified before being disposed in a landfill, which leads to increased treatment costs and environmental loading.

Previous studies confirmed the feasibility of ferrite process (FP) to treat wastewater containing heavy metals effectively [19–23].

Ferrite (Fe_3O_4), a magnetic iron oxide containing Fe^{2+} and Fe^{3+} in the structure, has spinel structure and can be synthesized through the reaction depicted by Eq. (1) [24]:

$$3Fe^{2+} + 6OH^- + 1/2O_2 \rightarrow Fe_3O_4 + 3H_2O \qquad (1)$$
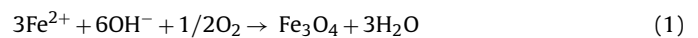
When heavy metal ions coexist with Fe^{2+}, they can be incorporated into the structure through co-precipitation [24]. The principle of FP to treat heavy metals is presented in Eq. (2).

$$xM^{2+} + (3-x)Fe^{2+} + 6OH^- + 1/2O_2 \rightarrow M_xFe_{(3-x)}O_4 + 3H_2O \qquad (2)$$
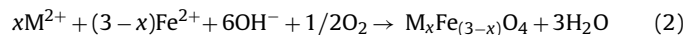
Previous studies have shown that pH, temperature and Fe^{2+} dosage are important factors determining the performance of FP [25–30]. For yielding high quality ferrite and suppressing the formation of the other crystal phases, the solution pH needs to be controlled at 9–11 and reaction temperature over 70 °C. A dosage of Fe^{2+} 5–10 times higher than the gross metal content in solution is required to ensure the removal efficiency.

The $M_xFe_{(3-x)}O_4$ in Eq. (2) is the sludge generated from FP. It is the soft magnetism that allows quick separation from the solution by using an external magnetic field whereupon time and cost are expected to be much less than those of sedimentation or filtration techniques.

The conventional single-step FP cannot efficiently remove some heavy metals, such as Pb, Cd, and Cu, and the resultant sludge cannot pass the toxicity characteristic leaching procedure (TCLP) limits

[23], which underscores the need for the "Extended Reaction Ferrite Process" to solve the problem. However, extending the reaction means that a large amount of $FeSO_4$ dosage would be added in this process.

The behavior of each heavy metal is probably different in FP. In other words, reaction parameters such as pH or temperature may have different effect on each heavy metal. A systematic investigation into the optimal conditions of each heavy metal was initiated and the multi-staged ferrite process (MSFP) combining several reaction conditions was developed to treat the CHMW cost-effectively.

2. Materials and methods

2.1. Preparation of simulated CHMW

The simulated CHMW containing Cd, Cu, Pb, Cr, Zn, Ag, Hg, Ni, Sn, and Mn was prepared by dissolving $Cd(NO_3)_2 \cdot 4H_2O$, $CuSO_4 \cdot 5H_2O$, $Pb(NO_3)_2$, $K_2Cr_2O_7$, $Zn(NO_3)_2 \cdot 6H_2O$, $AgNO_3$, $Hg(NO_3)_2$, $NiSO_4 \cdot 6H_2O$, $SnCl_2 \cdot 2H_2O$, and $KMnO_4$ (Merck, Darmstadt, Germany) in deionized water. The concentration of each heavy metal was 0.002 M and the total metal concentration was 0.02 M. Each stock solution was prepared with the concentration of 1 M and was acidified by HNO_3 for preservation. The simulated CHMW was prepared by mixing 2 mL of each heavy metal stock solution and then diluted to 1 L. To investigate the effects of anions on the removal efficiency, the salts of various anions, including Cl^-, NO_3^-, SO_4^{2-}, MnO_4^- and $Cr_2O_7^{2-}$, were added into the CHMW.

2.2. Treating CHMW by single-step and multi-staged FP

1 L of the simulated CHMW was added into a 2-L stainless steel reactor connected to an automatic temperature controller. A certain amount of $FeSO_4 \cdot 7H_2O$ was then added and dissolved into the CHMW. Air was continuously supplied with a flow rate of 3 L air min^{-1}. The solution pH was maintained at constant (± 0.2 units) throughout the reaction period by adding NaOH or HNO_3. The dosages of $FeSO_4$ were 0.1, 0.14 and 0.2 mol, 5, 7, and 10 times the gross heavy metal concentration respectively (Fe/M = 5, 7, 10) in the systems.

The solution pHs were adjusted to 9, 10 and 11, where temperatures were set to 70, 80, 85, and 90 °C, to study the pH and temperature effects. After 20, 40, 60, 80 and 120 min, the suspensions were cooled down to room temperature and a magnet was applied to separate the solid from the aqueous solution. The collected solid was then dried at 105 °C for 24 h and subjected to the toxicity characteristic leaching procedure (TCLP) test. The concentrations of Hg and Cd in aqueous solutions were determined by ICP-MS (Element II, Thermal Scientific, Germany) and those of the other heavy metals were determined using ICP-AES (ELAN 5000, PerkinElmer, Germany). The detection limit of each heavy metal is as follows: Cu 0.04 mg L^{-1}, Cd 2.1 μg L^{-1}, Pb 0.03 mg L^{-1}, Ni 0.06 mg L^{-1}, Cr 0.08 mg L^{-1}, Zn 0.04 mg L^{-1}, Mn 0.02 mg L^{-1}, Hg 1.2 μg L^{-1}, Ag 0.03 mg L^{-1}, Fe 0.07 mg L^{-1}, and Sn 0.01 mg L^{-1}. The relative standard deviation (RSD) of three replicate analyses was normally lower than 3%.

The removal efficiencies of two-staged and three-staged FP were investigated by varying the pH and reaction temperature. In the two-staged FP, the pH was designed to 7 and 10 and the reaction temperatures were set to 70 and 80 °C (Table 1). In the three-staged FP (Table 2), three of the four following reaction conditions were executed in sequence: A. 70 °C and pH 7 (an economic condition); B. 80 °C and pH 10 (the optimal condition for treating Cu); C. 70 °C and pH 9 (the optimal condition for the formation of ferrite [28]; and D. 90 °C and pH 9 (the particle sizes of ferrite were larger and

Table 1
Two-staged FP reaction procedures.

No.	Reaction procedure	
F1	I. 70 °C, pH = 7	II. 70 °C, pH = 10
F2	I. 80 °C, pH = 7	II. 80 °C, pH = 10
F3	I. 70 °C, pH = 7	II. 80 °C, pH = 10
F4	I. 70 °C, pH = 10	II. 80 °C, pH = 7
F5	I. 80 °C, pH = 10	II. 70 °C, pH = 7
F6	I. 80 °C, pH = 7	II. 70 °C, pH = 10
F7	I. 70 °C, pH = 7	II. 80 °C, pH = 7
F8	I. 70 °C, pH = 10	II. 80 °C, pH = 10
F9	I. 80 °C, pH = 7	II. 70 °C, pH = 7
F10	I. 80 °C, pH = 10	II. 70 °C, pH = 10

$[Fe^{2+}]$ dosage is 5 times the total heavy metal concentration in each stage.
Reaction time of each stage is 40 min.

more stable). In total, 24 sets of the three-staged procedures were investigated in this study (Table 2).

2.3. TCLP test of the sludge

The TCLP test was conducted following the standard method NIEA R201.13C of the Environmental Protection Administration of Taiwan. The extraction reagent was prepared by adding 5.7 mL glacial acetic acid and 64.3 mL 1 M NaOH to 1 L volumetric flask that contained 500 mL de-ionized water. The solution was then diluted to 1 L using de-ionized water. 4 g of dried sludge from the FP was placed in a 100 mL extraction bottle containing 80 g extraction reagent controlled at 4.93 ± 0.05 pH. The extraction bottles were rotated at a frequency 30 rpm for 18 h, and the concentrations of the heavy metals in the extraction liquid were measured subsequently.

2.4. Saturation magnetization of the sludge

Superconducting Quantum Interference Device (MPMS-XL7, Quantum Design, USA) was commissioned to reveal the saturation magnetization of the sludge generated from the FP.

2.5. XRD analysis of the sludge

The crystal phases in the sludge were assayed by an X-ray diffractometer (D8 Advance, Bruker, Germany) with Cu Kα radiation ($\lambda = 0.15406$ nm) while XRD patterns were obtained in 2θ range of 10–80° with a scanning rate 0.5° min^{-1} and a step size 0.02°.

3. Results and discussion

3.1. The optimal conditions for various heavy metals

Tables S1 and S2 in the Supplementary Information section summarize the heavy metal concentration in supernatant and TCLP after single-step FP where 27 single-step FP reactions with varying pH, temperature and $FeSO_4$ dosage were investigated. The results show that almost all supernatants could fulfill the effluent standards while Cu, Cd and Pb did not conform to the TCLP limit in all conditions. The average extracted concentrations of Cu, Cd and Pb in single-step FP were 71.83 mg L^{-1}, 94.40 mg L^{-1}, and 54.13 mg L^{-1}, respectively, far surpassing the limited values.

Figs. 1–3 show the treatment efficiency for Cu, Cd, and Pb, respectively, as the functions of pH, reaction time, temperature, and Fe^{2+} dosage. Unless the parameters are specifically mentioned in the text, the operated pH, reaction time, temperature, and Fe^{2+} dosage (Fe/M) were generally set to be 9, 80 min, 80 °C, and Fe/M = 5 respectively. The results reveal that the most important factor for fulfilling the requirement of TCLP was pH (Fig. 1). The optimal Cu treatment efficiency was yielded at high pH (pH 10), high
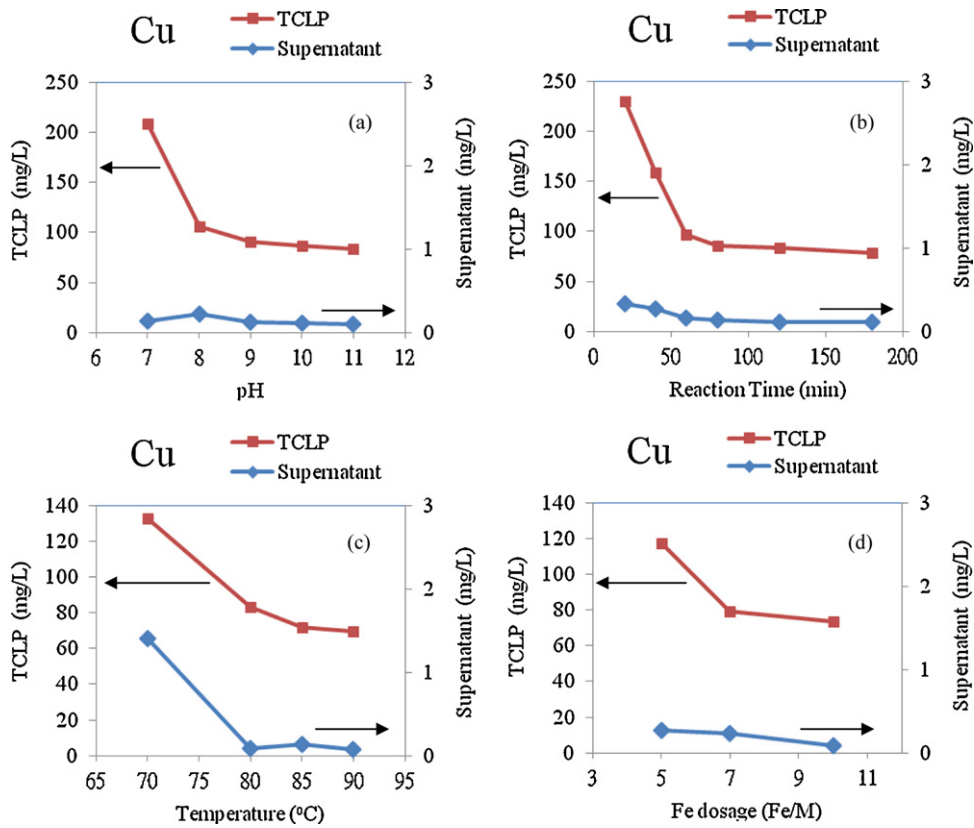
Fig. 1. Treatment efficiency of single-step FP for Cu as a function of (a) pH, (b) reaction time, (c) temperature, and (d) Fe dosage.
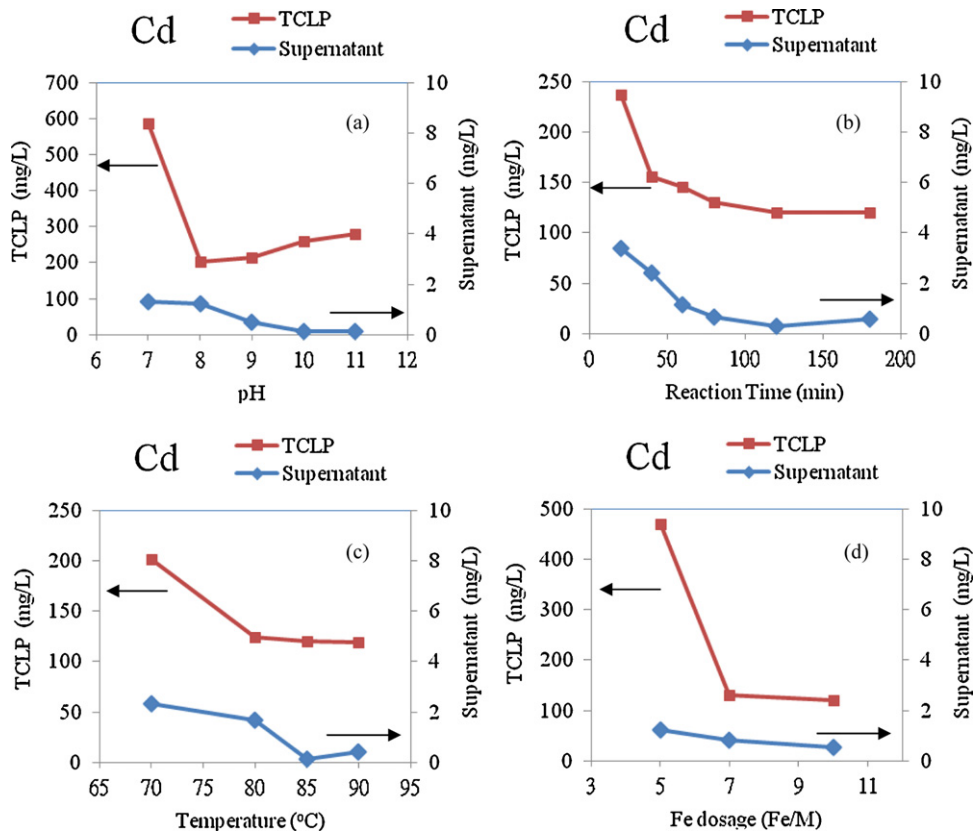

Fig. 2. Treatment efficiency of single-step FP for Cd as a function of (a) pH, (b) reaction time, (c) temperature, and (d) Fe dosage.

Table 2
Three-staged FP reaction procedures.

No.	Reaction combination	Reaction procedures		
G1	ABC	I. 70 °C, pH = 7	II. 80 °C, pH = 10	III. 70 °C, pH = 9
G2	ACB	I. 70 °C, pH = 7	II. 70 °C, pH = 9	III. 80 °C, pH = 10
G3	BAC	I. 80 °C, pH = 10	II. 70 °C, pH = 7	III. 70 °C, pH = 9
G4	BCA	I. 80 °C, pH = 10	II. 70 °C, pH = 9	III. 70 °C, pH = 7
G5	CAB	I. 70 °C, pH = 9	II. 70 °C, pH = 7	III. 80 °C, pH = 10
G6	CBA	I. 70 °C, pH = 9	II. 80 °C, pH = 10	III. 70 °C, pH = 7
G7	ABD	I. 70 °C, pH = 7	II. 80 °C, pH = 10	III. 90 °C, pH = 9
G8	ADB	I. 70 °C, pH = 7	II. 90 °C, pH = 9	III. 80 °C, pH = 10
G9	BAD	I. 80 °C, pH = 10	II. 70 °C, pH = 7	III. 90 °C, pH = 9
G10	BDA	I. 80 °C, pH = 10	II. 90 °C, pH = 9	III. 70 °C, pH = 7
G11	DAB	I. 90 °C, pH = 9	II. 70 °C, pH = 7	III. 80 °C, pH = 10
G12	DBA	I. 90 °C, pH = 9	II. 80 °C, pH = 10	III. 70 °C, pH = 7
G13	ACD	I. 70 °C, pH = 7	II. 70 °C, pH = 9	III. 90 °C, pH = 9
G14	ADC	I. 70 °C, pH = 7	II. 90 °C, pH = 9	III. 70 °C, pH = 9
G15	CAD	I. 70 °C, pH = 9	II. 70 °C, pH = 7	III. 90 °C, pH = 9
G16	CDA	I. 70 °C, pH = 9	II. 90 °C, pH = 9	III. 70 °C, pH = 7
G17	DAC	I. 90 °C, pH = 9	II. 70 °C, pH = 7	III. 70 °C, pH = 9
G18	DCA	I. 90 °C, pH = 9	II. 70 °C, pH = 9	III. 70 °C, pH = 7
G19	BCD	I. 80 °C, pH = 10	II. 70 °C, pH = 9	III. 90 °C, pH = 9
G20	BDC	I. 80 °C, pH = 10	II. 90 °C, pH = 9	III. 70 °C, pH = 9
G21	CBD	I. 70 °C, pH = 9	II. 80 °C, pH = 10	III. 90 °C, pH = 9
G22	CDB	I. 70 °C, pH = 9	II. 90 °C, pH = 9	III. 80 °C, pH = 10
G23	DBC	I. 90 °C, pH = 9	II. 80 °C, pH = 10	III. 70 °C, pH = 9
G24	DCB	I. 90 °C, pH = 9	II. 70 °C, pH = 9	III. 80 °C, pH = 10

$[Fe^{2+}]$ dosage is 5 times the total heavy metal concentration in each stage.
Reaction time of each stage is 40 min.
Reaction combination: A: 70 °C, pH 7; B: 80 °C, pH 10; C: 70 °C, pH 9; D: 90 °C, pH 9.

temperature (90 °C), high Fe^{2+} dosage (Fe/M = 10), and longer reaction time (80 min). Meanwhile, it is the formation of CuO on the surface of ferrite instead of into the spinel structure that results in high Cu extraction concentration from TCLP test [29].

Fig. 2 shows that the optimal Cd treatment efficiency yielded at pH 8, >80 °C, Fe/M > 7, and reaction time 80 min. Kiyama [25]

suggested that the first step for heavy metals captured into the spinel structure is to form $M(OH)^+$. The hydrolysis constant of $Cd(OH)_2$ is rather small ($\log K = -10.1$), leading to the difficulty for further formation of $Cd(OH)^+$. Subsequently, $Cd(OH)_2$ was formed under alkaline environments [29]. With the superior solubility of $Cd(OH)_2$ than that of ferrite, the occurrence of $Cd(OH)_2$ in the
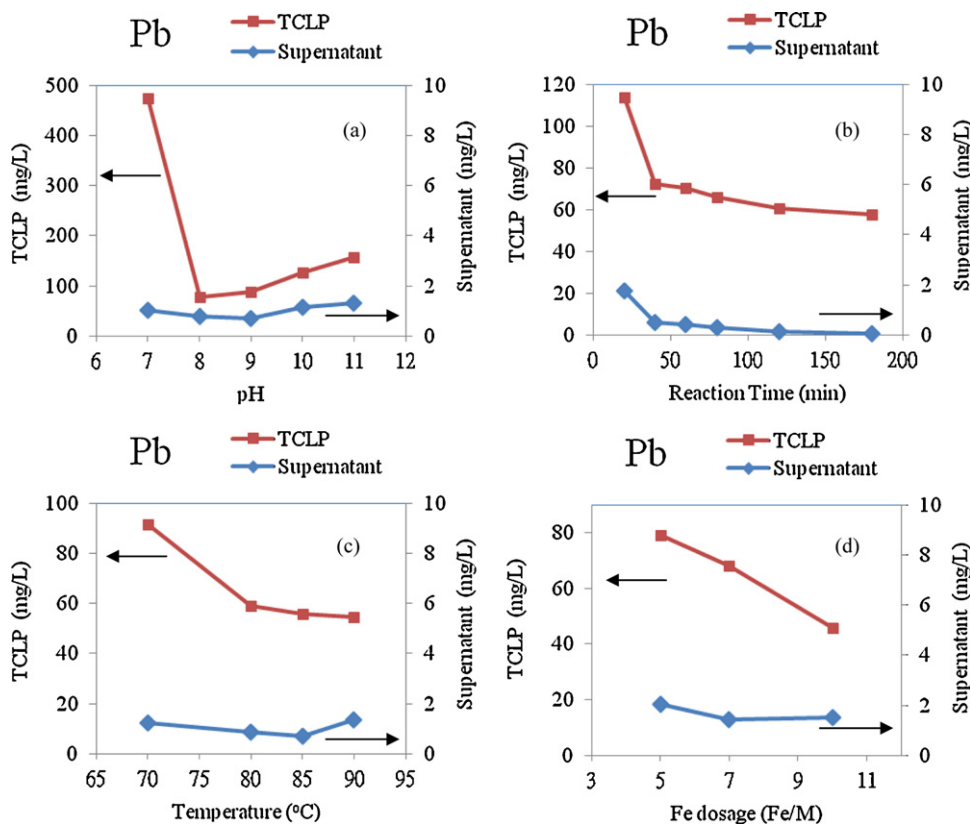

Fig. 3. Treatment efficiency of single-step FP for Pb as a function of (a) pH, (b) reaction time, (c) temperature, and (d) Fe dosage.

Table 3
Heavy metal concentrations in supernatants and TCLP in the optimal two-staged FP.

	Cu	Cd	Pb	Ni	Cr	Zn	Mn	Hg	Ag	Fe	Sn
Supernatant (mg L^{-1})	0.087	0.050	B.D.	0.321	2.779	B.D.	0.030	0.027	0.049	0.230	0.015
Effluent standard [a] (mg L^{-1})	3.0	0.03	1.0	1.0	2.0	5.0	10.0	0.005	0.5	10.0	–
TCLP (mg L^{-1})	8.493	9.205	7.482	1.616	0.132	0.059	3.930	0.073	0.123	1.540	0.151
TCLP limit [b] (mg L^{-1})	15.0	1.0	5.0	–	5.0	–	–	0.2	5.0	–	–

The optimal conditions of two-staged FP is the F8 shown in Table 1: I. 70 °C, pH = 10; II. 80 °C, pH = 10. –: No limited standard at present; B.D.: below detection limit.

[a] Effluent standard in Taiwan.

[b] The identification criteria for hazardous industrial wastes in Taiwan.
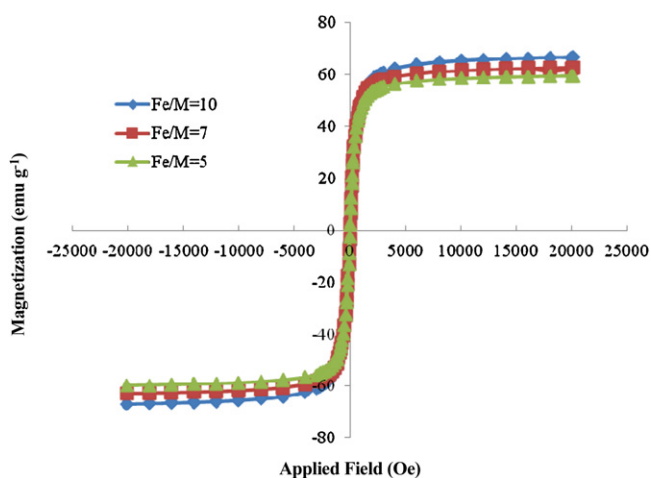
Fig. 4. Magnetization curve of FP sludge.

sludge contributed to the high Cd extraction efficiency in the TCLP tests.

Fig. 3 indicates similar Pb and Cd behaviors under same optimal conditions of pH, temperature, Fe^{2+} dosage, and reaction time. Two potential reasons for the observed high leaching Pb concentration in the TCLP test are: (1) precipitations of PbSO$_4$ and PbCrO$_4$ may potentially occur in the simulated heavy metal wastewaters, but the possibility of forming PbCrO$_4$ was low as revealed by the low leaching concentration of Cr in the TCLP test. PbSO$_4$ is the more likely to be precipitated in the sludge of FP. (2) Radius of Pb^{2+} (1.12 Å) is much larger than Fe^{2+} (0.77 Å) [31]. If the lattice position of Fe^{2+} in ferrite is replaced by Pb^{2+}, the resultant spinel structure of PbFe$_2$O$_4$ is less stable and thus Pb is easier to be dissolved in the TCLP test.

3.2. Performance of multi-staged FP

The single-step FP cannot be applied to treat CHMW because the quality of the sludge cannot fulfill the environmental laws. The multi-staged FP, combination of several stages with different reaction conditions including two or three-staged FP, are investigated for their efficiencies in removing heavy metals from CHMW.

3.3. Two-staged FP

The two-staged FP can indeed enhance the treatment efficiency substantially (see Table 3). More detailed results are shown in Tables S3 and S4 in the Supplementary Information. The results demonstrate that the optimal supernatants after the two-staged FP can fulfill the effluent standard. Only Cd, Cr and Hg exceed slightly the effluent standards. The optimal TCLP specifically indicates that the difficult treatment of heavy metals (Cu, Cd, Pb) have been reduced 10 times, from approximately 100 mg L^{-1} to nearly 10 mg L^{-1}. Nevertheless, the performance is still unsatisfactory. Hence, the three-staged FP is essential for further tests in treating CHMW.

3.4. Three-staged FP

Table 4 shows the optimal conditions of the three-staged FP for fully treating CHMW. The results demonstrate that the three-staged reaction strongly increases the effectiveness of the FP, all heavy metals in supernatants and TCLP fulfilling the environmental rules through the optimal procedures (Table 2): 70 °C, pH = 9; 90 °C, pH = 9; and 80 °C, pH = 10.

Each heavy metal has its optimal treatment condition as mentioned in Section 3.1. Proper combination of these processes may satisfy the need for effectively removing different heavy metals in CHMW. The extended reaction FP proposed by Lou and Chang [23], a typical representative of multi-dosage concept, however, cannot obtain the best economic efficiency of repeated dosage in fixed conditions of extended reaction FP. This study shows that multi-dosage can be a cost-effective treatment method by changing the reaction conditions at different stages which results in the conspicuous reduction of the FeSO$_4$ dosage.

3.5. Rapidly magnetic separation for the FP sludge

Solid–liquid separation is usually an arduous and costly issue in industrial plants. Compared with traditional solid-liquid separation methods such as precipitation, filtration and centrifugation, magnetic separation is more effective and rapider. In order to investigate its magnetic behavior, the FP sludge was measured using Superconducting Quantum Interference Device at 27 ± 1 °C. The saturation magnetizations of the sludge generated from FP with different Fe/M ratio were found to range from 59.64 to 66.45 emu g^{-1}
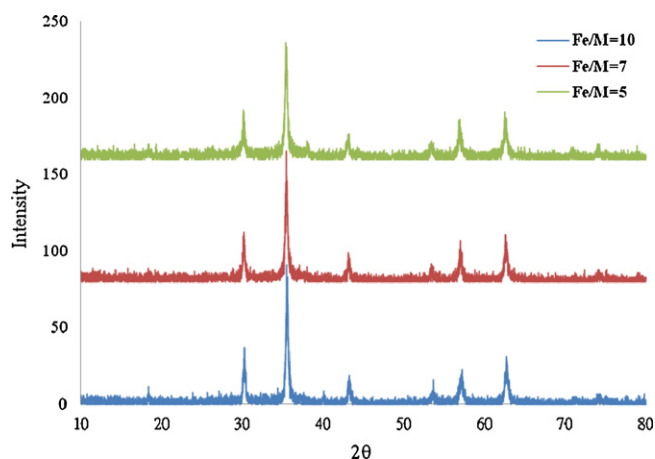
Table 4
Heavy metal concentrations in supernatants and TCLP in the optimal three-staged FP.

	Cu	Cd	Pb	Ni	Cr	Zn	Mn	Hg	Ag	Fe	Sn
Supernatant (mg L^{-1})	0.047	B.D.	0.250	0.389	0.569	B.D.	0.091	B.D.	0.043	0.600	0.011
Effluent standard [a] (mg L^{-1})	3.0	0.03	1.0	1.0	2.0	5.0	10.0	0.005	0.5	10.0	–
TCLP (mg L^{-1})	2.70	0.821	0.050	0.496	0.419	0.066	2.935	0.062	0.037	5.196	0.102
TCLP limit [b] (mg L^{-1})	15.0	1.0	5.0	–	5.0	–	–	0.2	5.0	–	–

The optimal conditions of three-staged FP is the G22 shown in Table 2: I. 70 °C, pH = 9; II. 90 °C, pH = 9; III. 80 °C, pH = 10. –: No limited standard at present; B.D.: below detection limit.

[a] Effluent standard in Taiwan.

[b] The identification criteria for hazardous industrial wastes in Taiwan.

Fig. 5. X-ray diffraction patterns of FP sludge.

(Fig. 4) and the saturation magnetization was increased with increasing Fe/M. The low remanence and coercivity were detected in these samples, showing the FP sludge were paramagnetic. Furthermore, these magnetic FP sludge could be separated by an external magnet within 30 s.

3.6. XRD analysis

The XRD spectrum of the FP sludge displays main diffraction peaks at the d-spacings of 4.8353, 2.9610, 2.5252, 2.0938, 1.6118, and 1.4805 Å (Fig. 5), matching the spinel ferrite structure standard well. The expected species of CuO, Cd(OH)$_2$, and PbSO$_4$ were not detected in the FP sludge because the amounts were too low to be detected by XRD.

4. Conclusions

A novel method improved from conventional FP has been investigated to treat CHMW in this study. This method not only ensures that the supernatant complies with effluent standards but also yields stable sludge, which can pass the TCLP limits to be regarded as a general industrial waste. For the CHMW in this system, the optimum operating parameters in a three-staged FP are: 70 °C, pH = 9; 90 °C, pH = 9; and 80 °C, pH = 10. Furthermore, with its high saturation magnetizations (66.45 emu g^{-1}), the FP sludge could be effectively and rapidly separated by an external magnetic field, which confirms an advantageous and practical technique in solid–liquid separation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.01.050.

References

[1] A.E. Lewis, Review of metal sulphide precipitation, Hydrometallurgy 104 (2010) 222–234.
[2] M.M. Matlock, B.S. Howerton, D.A. Atwood, Chemical precipitation of heavy metals from acid mine drainage, Water Res. 36 (2002) 4757–4764.
[3] R.M. Perez, G. Cabrera, J.M. Gomez, A. Abalos, D. Cantero, Combined strategy for the precipitation of heavy metals and biodegradation of petroleum in industrial wastewaters, J. Hazard. Mater. 182 (2010) 896–902.
[4] N. Meunier, P. Drogui, C. Montane, R. Hausler, J.F. Blais, G. Mercier, Heavy metals removal from acidic and saline soil leachate using either electrochemical coagulation or chemical precipitation, J. Environ. Eng. 132 (2006) 545–554.
[5] M.J. González-Muñoz, M.A. Rodríguez, S. Luque, J.R. Álvarez, Recovery of heavy metals from metal industry waste waters by chemical precipitation and nanofiltration, Desalination 200 (2006) 742–744.
[6] L.M. Ortega, R. Lebrun, J.F. Blais, R. Hausler, Removal of metal ions from an acidic leachate solution by nanofiltration membranes, Desalination 227 (2008) 204–216.
[7] S. Velixarov, J.G. Crespo, M.A. Reis, Removal of inorganic anions from drinking water supplies by membrane bio/process, Rev. Environ. Sci. Biotechnol. 3 (2004) 361–380.
[8] B. Gabor, N. Endre, Removal of zinc and nickel ions by complexation-membrane filtration process from industrial wastewater, Desalination 240 (2009) 218–226.
[9] N. Hilal, M. Al-Abri, H. Al-Hinai, Enhanced membrane pre-treatment processes using macromolecular adsorption and coagulation in desalination plants: a review, Sep. Sci. Technol. 41 (2006) 403–453.
[10] M. Al-Abri, A. Dakheel, C. Tizaoui, N. Hilal, Combined humic substance and heavy metals coagulation, and membrane filtration under saline conditions, Desalination 253 (2010) 46–50.
[11] F. Akbal, S. Camci, Comparison of electrocoagulation and chemical coagulation for heavy metal removal, Chem. Eng. Technol. 33 (2010) 1655–1664.
[12] J.R. Parga, D.L. Cocke, J.L. Valenzuela, J.A. Gomes, M. Kesmez, G. Irwin, H. Moreno, M. Weir, Arsenic removal via electrocoagulation from heavy metal contaminated groundwater in La Comarca Lagunera Mexico, J. Hazard. Mater. 124 (2005) 247–254.
[13] M. Ozmen, K. Can, G. Arslan, A. Tor, Y. Cengeloglu, M. Ersoz, Adsorption of Cu(II) from aqueous solution by using modified Fe$_3$O$_4$ magnetic nanoparticles, Desalination 254 (2010) 162–169.
[14] Y.F. Zhou, R.J. Haynes, Sorption of heavy metals by inorganic and organic components of solid wastes: significance to use of wastes as low-cost adsorbents and immobilizing agents, Crit. Rev. Environ. Sci. Technol. 40 (2010) 909–977.
[15] Y.H. Wang, S.H. Lin, R.S. Juang, Removal of heavy metal ions from aqueous solutions using various low-cost adsorbents, J. Hazard. Mater. 102 (2003) 291–302.
[16] J. Aguado, J.M. Arsuaga, A. Arencibia, M. Lindo, V. Gascón, Aqueous heavy metals removal by adsorption on amine-functionalized mesoporous silica, J. Hazard. Mater. 163 (2009) 213–221.
[17] D.A. Clifford, Ion-exchange inorganic adsorption, in: Water Quality and Treatment: A Handbook of Community Water Supplies, 5th ed., American Water Works Association, McGraw-Hill, New York, 1999.
[18] A. Smara, R. Delimi, E. Chainet, E. Chainet, J. Sandeaux, Removal of heavy metals from diluted mixtures by a hybrid ion-exchange/electrodialysis process, Sep. Purif. Technol. 57 (2007) 103–110.
[19] Y. Tamaura, T. Katsura, S. Rojarayanont, T. Yoshida, H. Abe, Ferrite process: heavy metal ions treatment system, Water Sci. Technol. 23 (1991) 1893–1900.
[20] B. Demirel, O. Yenigün, M. Bekbölet, Removal of Cu, Ni, and Zn from wastewaters by the ferrite process, Environ. Technol. 20 (1999) 963–970.
[21] W. Wang, Z. Xu, J. Finch, Fundamental study of an ambient temperature ferrite process in the treatment of acid mine drainage, Environ. Sci. Technol. 30 (1996) 2604–2608.
[22] M. Erdem, F. Tumen, Chromium removal from aqueous solution by ferrite process, J. Hazard. Mater. 109 (2004) 71–77.
[23] J.C. Lou, C.K. Chang, Completely treating heavy metal laboratory waste liquid by an improved ferrite process, Sep. Purif. Technol. 57 (2007) 513–518.
[24] J.C. Lou, Y.J. Tu, Incinerating volatile organic compounds with ferrospinel catalyst MnFe$_2$O$_4$: an example with isopropyl alcohol, J. Air Waste Manage. Assoc. 55 (2005) 1809–1815.
[25] M. Kiyama, Conditions for the formation of Fe$_3$O$_4$ by the air oxidation of Fe(OH)$_2$ suspensions, Bull. Chem. Soc. Jpn. 47 (1974) 1646–1650.
[26] Y. Tamaura, P.V. Buduan, T. Katsura, Studies on the oxidation of iron(II) ion during the formation of Fe$_3$O$_4$ and α-FeOOH by air oxidation of Fe(OH)$_2$ suspensions, J. Chem. Soc., Dalton Trans. (1981) 1807–1811.
[27] E. Barrado, F. Prieto, F.J. Garay, J. Medina, M. Vega, Characterization of nickel-bearing ferrites obtained as by-products of hydrochemical wastewater purification processes, Electrochim. Acta 47 (2002) 1959–1965.
[28] Y.J. Tu, Treatment of heavy metal waste-liquid in laboratory by multi-stage ferrite process, Master's thesis, National Sun Yat-sen University, Taiwan, 2002.
[29] W.Q. Chen, A study on the treatment of heavy metal ions by ferrite process, Master's thesis, National Cheng Kung University, Taiwan, 1992.
[30] J.C. Lou, Y.J. Huang, J.Y. Han, Treatment of printed circuit board industrial wastewater by ferrite process combined with Fenton method, J. Hazard. Mater. 170 (2009) 620–626.
[31] J.E. Huheey, Inorganic Chemistry: Principles of Structure and Reactivity, Baker & Taylor Books, 1983.