Effective Dismantling of Waste Printed Circuit Board Assembly with Methanesulfonic Acid Containing Hydrogen Peroxide

Xiaojiao Zhang,[a] Jie Guan,[a] Yaoguang Guo,[a] Yonghai Cao,[b] Jiang Guo,[b] Hao Yuan,[a] Ruijing Su,[a] Bo Liang,[a] Guilan Gao,[a] Yuan Zhou,[a] Jinqiu Xu,[a] and Zhanhu Guo[b]

[a]Shanghai Cooperative Center for WEEE Recycling, School of Environmental and Materials Engineering, Shanghai Polytechnic University, Shanghai 201209, China; guanjie@sspu.edu.cn (for correspondence)

[b]Integrated Composites Laboratory (ICL), Department of Chemical & Bimolecular Engineering, University of Tennessee, Knoxville, TN 37996

Dismantling of waste printed circuit boards (WPCBs) is of great importance in the recycling chain of electronic wastes (e-wastes), since there are lots of high-value components and toxic substances contained in the WPCBs. In this work, effective dismantling was achieved by dissolving the lead-tin solder into a leachant containing methanesulfonic acid (MSA) and H_2O_2. Different concentrations of H_2O_2 and MSA as well as leaching time were investigated. The final optimization experiment scheme was obtained from the simulation with the help of Design-Expert 8.0.6 software. A leachant containing 3.5 mol/L MSA and 0.5 mol/L H_2O_2 with a reaction time of 45 min was regarded as the optimum conditions for the selective desoldering separation of electronic components (ECs) from the WPCBs. © 2017 American Institute of Chemical Engineers Environ Prog, 36: 873–878, 2017

Keywords: hydrometallurgy, desoldering, orthogonal design

INTRODUCTION

For decades, the exponentially growing demands for electric and electronic equipments (EEEs) lead to the increase of discard waste electrical and electronic equipments (WEEEs), which contain lots of valuable metals and nonmetallic materials. For instance, printed circuit boards (PCBs), typical electronic wastes (e-wastes) accounting for about 3 wt% of all WEEEs [1,2], contain approximately 70% nonmetals and 30% metals [3]. Therefore, WEEEs are called “urban mining” resources [4]. Compared with the natural minerals, the metals grade in WEEEs is much higher, demonstrating that it is a significant urgent issue to recycle the valuable components from WEEEs [5].

Generally, the waste PCBs (WPCBs) are not bare PCBs but PCB assemblies, i.e. PCBs mounted with various functional electronic components (ECs) including resistors, relays, capacitors, integrated circuits, etc., via solder [6]. Therefore, the WPCBs are more complicated and diverse in chemical compositions with many kinds of metal and nonmetal materials, including precious heavy metals, alloys, resins, glass-fiber and halide flame retardant [3]. Therefore, the recycling process of WPCBs is much more complicated. The first step for the pretreatment of WPCBs is to classify PCBs and dismantle ECs of PCBs [4] for the realization of recovering useful materials. And also, the value of the ECs can be partly preserved through dismantling. Among the recently reported industrial dismantling technologies of WPCBs [1,6], the most common way to remove the ECs is to heat PCB assemblies at a temperature above the melting point of solder ($\geq$ 210°C) [4]. However, a certain amount of toxic gases including acetaldehyde, benzene, xylene, styrene and lead fume can be released and cause a secondary pollution [7]. Hence, it is necessary and indispensable to dismantle PCB assemblies environmental-friendly and selectively, targeting at singling out hazardous or valuable components.

In this work, environmental-friendly and widely used methanesulfonic acid (MSA) electrolyte for industrial lead-tin alloy electroplating [8] was used together with hydrogen peroxide (H_2O_2) as a novel chemical leachant to dissolve solder selectively for dismantling ECs from WPCBs. Through the exploratory trials, the MSA solution without H_2O_2 was unable to achieve desoldering separation of tin-lead alloy for dismantling of ECs from WPCBs dramatically. After the addition of H_2O_2 into the MSA solution, the welded ECs significantly fell off the PCBs. In the MSA-H_2O_2 aqueous system, H^+ and $CH_3SO_3^-$ are ionized by MSA, and the differences of the standard electrode potential between hydrogen peroxide/tin (1.912 V) and hydrogen peroxide/lead (1.902 V) [9] are so close that they can be considered to be stripped down easily from the PCBs with almost the same ratio at room temperature (1). Furthermore, the thermodynamic calculations of (1) using the *HSC Chemistry* Version 5.0 software demonstrated that the change of Gibbs free energy (-181.5 kcal/mol at 20°C) of the redox reaction (1) was much lower than the boundary of -10.1 kcal/mol [10]. Thus, this phenomenon can occur spontaneously. After the leaching process, the constituents of the leachant are similar to the solution that was used to electroplate lead-tin alloy. Therefore, tin and lead in the leachant may be directly electrolyzed to reclaim the solder rather than to undergo a purification process.

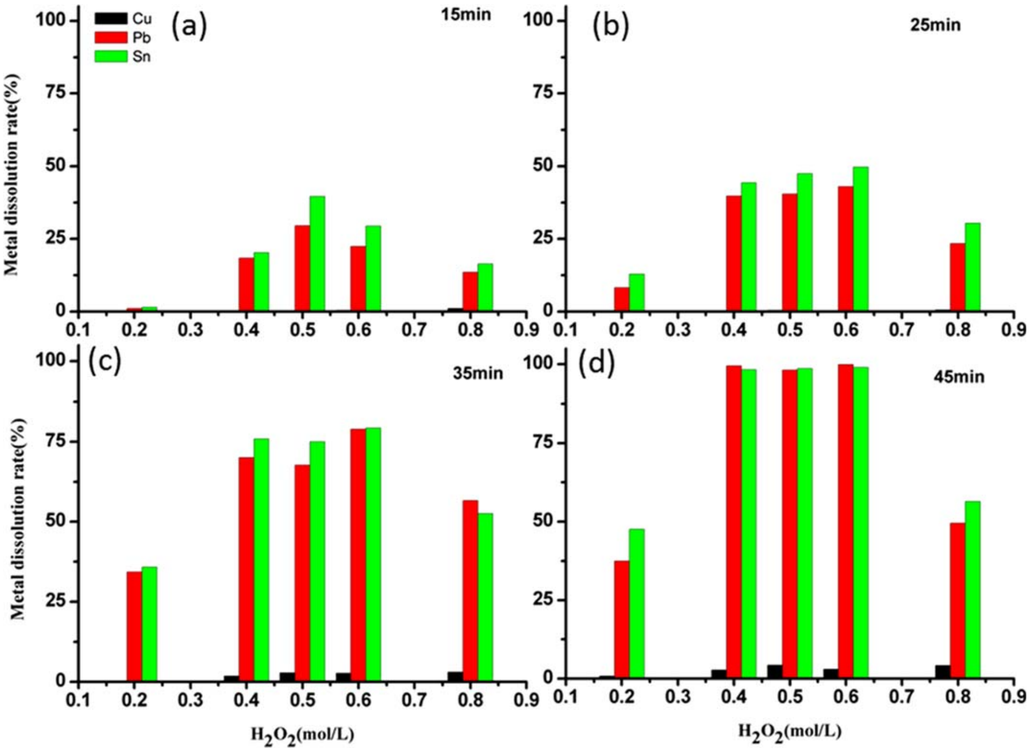

Figure 1. Effect of H_2O_2 concentration on the dissolution rate of Sn, Pb and Cu at (a) 15, (b) 25, (c) 35 and (d) 45 min. Conditions: [MSA] =3.0 mol/L, $T = 20 \pm 2°C$. [Color figure can be viewed at **wileyonlinelibrary.com**]

Moreover, H_2O_2 is relatively stable in the acidic medium, and its final product is environmental-friendly H_2O, hardly affecting the recycling of the leachant. Therefore, MSA-H_2O_2 aqueous system can be regarded as environmental-friendly desoldering separation of tin-lead alloy for dismantling ECs from WPCBs. However, the Cu metallization in the PCBs is covered by the lead-tin solder, with the dissolution of solder into the leachant, the leaching of the copper layer may also occur partly at room temperature (Eq. (2)), since the difference of standard electrode potential between hydrogen peroxide and copper is 1.439 V [9]. Therefore, it is critical to control the leaching of copper to be least for the achievement of environmental-friendly desoldering separation of tin-lead alloy for dismantling ECs from WPCB by the MSA-H_2O_2 aqueous system.

$$2H_2O_2 + Sn + Pb + 4H^+ = Sn^{2+} + Pb^{2+} + 4H_2O \tag{1}$$

$$H_2O_2 + Cu + 2H^+ = Cu^{2+} + 2H_2O \tag{2}$$

Hence, the objective of the present research is to further explore and optimize the operating conditions. The influences of the concentrations of MSA and H_2O_2, and leaching time on the dissolution concentrations of lead, tin and copper were investigated. At last, the effect trend of the factors was explored by calculations with the help of Design-Expert 8.0.6 software, and the final optimization experiment scheme was obtained.

EXPERIMENTAL

Materials

Methanesulphonic acid (CH_4SO_3, MSA, 98–101%), and hydrogen peroxide (H_2O_2, 30%) were both purchased from Sinopharm Chemical Reagent, China and were directly used without any further treatment. In order to make sure negligible difference among each other and to be representative, the PCB samples were all customer-made and underwent the basic process of copper and tin plating. The ECs were mounted by solder connection. The contents of metals contained in the examined PCBs were 37.0 mg for lead, 70.0 mg for tin, and 68.0 mg for copper.

EXPERIMENTAL PROCEDURES

All the experiments were conducted in 250 mL beakers containing 100 mL mixed solution of certain concentrations of MSA and H_2O_2. The beakers are immersed in a constant water bath to keep the temperature at 20 ± 2°C. Prior to each experiment, the PCB samples and certain aliquots of chemicals were transferred to the reactor vessel to obtain the desired concentrations. To study the effect of H_2O_2 concentration, the concentration of MSA was maintained at 3.0 mol/L. The H_2O_2 concentration was changed in the range from 0.2 to 0.8 mol/L. In order to examine the influence of MSA concentration, the acid concentration was changed in the range from 1.5 to 3.5 mol/L with the H_2O_2 concentration being at 0.5 mol/L. About 1 mL leaching sample was withdrawn after 15, 25, 35, and 45 min, respectively, and followed by adding 50 mL 2% HNO_3 solution. After 30 min, the sample solutions were detected with an iCAP 6300 inductively coupled plasma-atomic emission spectrometry (ICP-AES), purchased from Thermo Scientific.

EVALUATION INDEX

The dissolution rates of lead and tin in the solder are the most important index to evaluate the dismantling effect of the leachant. The evaluation equations are presented as Eq. (3).

$$\text{Metal dissolution rate} = \frac{m}{m_0} \times 100\% \tag{3}$$

where m_0 is the total mass of metals, mg; m is the dissolved mass of metals, mg.

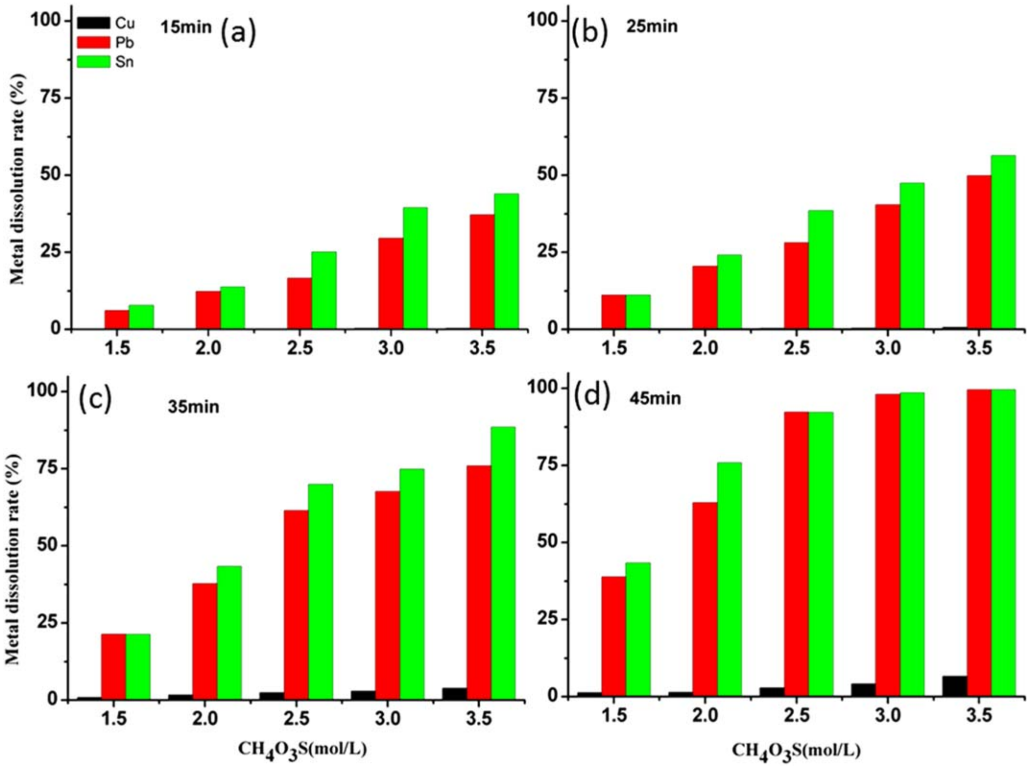

Figure 2. Effect of MSA concentration on the dissolution rate of Sn, Pb, and Cu at (a) 15, (b) 25, (c) 35, and (d) 45 min. Conditions: [H_2O_2] =0.5 mol/L, $T = 20 \pm 2$°C. [Color figure can be viewed at **wileyonlinelibrary.com**]

RESULTS AND DISCUSSION

Influence of H_2O_2 Concentration

In order to explore the optimal concentration of H_2O_2, the concentration of H_2O_2 ranging from 0.2 to 0.8 mol/L was investigated. The reaction between solder and leachant was obviously observed after 15 min and the ECs were all dismantled from the boards at around 45 min. The dissolution rate of lead-tin solder increased with prolonging the reaction time (Figure 1). However, the dissolution rate of lead-tin solder increased rapidly with increasing the H_2O_2 concentration, when the H_2O_2 concentration was below 0.4 mol/L. The leaching rate of lead and tin was approximate 100% with the condition of 0.4∼0.6 mol/L H_2O_2 at 45 min, while the dissolution rate was decreased when the H_2O_2 concentration exceeded 0.6 mol/L. However, the dissolution rate of copper was only less than 3% when less than 0.4 mol/L of H_2O_2 was added, which could be negligible relative to almost all leaching of the solder, and all separated ECs.

Influence of Acid Concentration

Figure 2 shows the influence of MSA concentration. The dissolution rate of metals increased with the increase of MSA concentration. Furthermore, the leaching concentrations of metals increased gradually with the extension of leaching time from 15 to 45 min. When the concentration of MSA exceeded 3.0 mol/L at 45 min, the solder was almost removed from the PCBs (Figure 2d). Moreover, with the increase of MSA concentration and the extension of the reaction time, the leaching of copper was also unexpectedly increased (Figure 2). However, the total copper dissolution rate was less than 5% when 3.0 mol/L MSA was added after the reaction time of 45 min, which could be regarded as negligible on the dismantling of ECs from PCBs.

Table 1. Factor levels of experiment.

Factor Level	H_2O_2 (mol/L) A	CH_4O_3S (mol/L) B	Time (min) C
(1)	0.3	1.5	25
(2)	0.5	2.5	35
(3)	0.7	3.5	45

Orthogonal Experiment

Based on the aforementioned discussion of single-factor experiment, an orthogonal experiment was carried out to study the influence of multiple factors. Orthogonal experiment is a kind of high efficiency, rapid and economic experiment design method [11]. According to the results obtained in the single-factor experiments, the experiment design for three factors and three levels was shown in Table 1. The orthogonal experiment was designed by the software of Design-Expert 8.0.6 and the results were shown in Table 2.

Model Analysis

The results were analyzed by the software of Design-Expert with the ANOVA (Analysis of variance, ANOVA) model. The analysis results of ANOVA model show the influence of multiple factors on the dissolution rate of lead-tin solder.

Model Analysis for Dissolution Rate of Lead

The results of model analysis for leaching of lead are shown in Table 3, and the model *F*-value is 23.40, indicating the significance of the model. The value of "Prob > F" less than 0.0500 indicates that the model terms are significant.

The selected factor patterns are summarized in Table 4. "Adeq Precision" measures the signal to noise ratio, and the ratio with the value greater than 4 is desirable. The model

Table 2. Orthogonal experiment results.

	Factor			Evaluation index		
Number	H_2O_2 (mol/L)	CH_4O_3S (mol/L)	Time (min)	Response Pb (%)	Response Sn (%)	Response Cu (%)
1	0.3	1.5	25	12.08	14.97	0.34
2	0.3	2.5	35	56.45	58.21	4.32
3	0.3	3.5	45	90.19	94.73	6.42
4	0.5	1.5	35	27.57	29.04	1.67
5	0.5	2.5	45	93.26	96.45	11.27
6	0.5	3.5	25	57.75	59.14	8.45
7	0.7	1.5	45	32.87	33.26	9.71
8	0.7	2.5	25	25.35	25.94	5.42
9	0.7	3.5	35	59.76	60.88	10.46

Table 3. ANOVA for selected factorial model.

Source	Sum of squares	df	Mean square	*F* Value	*P* Prob > *F*	
Model	6430.99	6	1071.83	23.40	0.0415	Significant
A-A	636.28	2	318.14	6.95	0.1258	
B-B	3317.05	2	1658.53	36.22	0.0269	
C-C	2477.66	2	1238.83	27.05	0.0356	
Residual	91.59	2	45.80			
Cor Total	6522.58	8				

df = degrees of freedom.

Table 4. Summary of selected factor pattern.

Std. Dev.	6.77	R^2	0.9860
Mean	50.59	Adj R^2	0.9438
C.V. %	13.38	Pred R^2	0.7156
PRESS	1854.73	Adeq Precision	14.316

PRESS = predicted residual sum of squares; CV = coefficient of variation.

Table 5. Reliability analysis of selected factor pattern.

Term	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High
Intercept	50.59	1	2.26	40.88	60.29
A	2.32	1	3.19	−11.41	16.05
A^2	8.94	1	3.19	−4.79	22.67
B	−26.41	1	3.19	−40.14	−12.69
B^2	7.77	1	3.19	−5.96	21.49
C	−18.86	1	3.19	−32.59	−5.13
C^2	−2.66	1	3.19	−16.39	11.07

Table 6. ANOVA for selected factorial model.

Source	Sum of squares	df	Mean square	*F* Value	*P* Prob> *F*	
Model	6787.31	6	1131.22	20.74	0.0467	Significant
A-A	748.22	2	374.11	6.86	0.1272	
B-B	3416.01	2	1708.00	31.32	0.0309	
C-C	2623.09	2	1311.54	24.05	0.0399	
Residual	109.06	2	54.53			
Cor Total	6896.38	8				

ratio of 14.316 indicates an adequate signal. This model can be used to navigate the design space.

The reliability analysis of selected factor pattern is summarized in Table 5. From the results, the equation of lead dissolution rate in the scale of parameters set in the experiments could be obtained. The final equation in terms of coded factors is shown as below.

$$\text{Dissolution rate of lead} = 50.59 + 2.32 \times A + 8.94 \times A^2 - 26.41 \times B + 7.77 \times B^2 - 18.86 \times C - 2.66 \times C^2 \tag{4}$$

Model Analysis for Dissolution Rate of Tin

Table 6 shows the analysis of variance for selected factorial model. The model *F*-value of 20.74 implies the model is valid. The value of "Prob > F" indicates only a 4.67% chance for this model to be invalid. The selected factor patterns are summarized in Table 7. The model ratio of 13.403 indicates an adequate signal. This model can be used to navigate the design space.

Table 8 shows the reliability analysis of the selected factor pattern. From Eq. (5), the scale of parameters set in the experiments can be reached. The final equation in terms of coded factors is shown as follows:

$$\text{Dissolution rate of tin} = 52.51 + 3.46 \times A + 9.03 \times A^2 - 26.76 \times B + 7.69 \times B^2 - 19.16 \times C - 3.14 \times C^2. \tag{5}$$

Model Analysis for Dissolution Rate of Copper

According to the analysis results in Table 9, the "Model F-value" of 2.00 implies that the model is not significant relative to the errors. Therefore, there are no significant model terms. Therefore, this model cannot be used to analyze the influence of multiple factors on the dissolution rate of copper, possibly because that the copper layer is covered by solder, leading to hardly any contact between the leachant and copper at the beginning of the reaction. However, there is a 37.02% chance of the value of "Prob > F," indicating this model is significant, mainly attributed to the reaction between the exposed copper and the leachant after the solder dissolved in the leachant. Therefore, the contact area between copper and the leachant, and the reaction time might cause this model insignificant.

Table 7. Summary of selected factor pattern.

Std. Dev.	7.38	R^2	0.9842
Mean	52.51	Adj R^2	0.9367
C.V. %	14.06	Pred R^2	0.6798
PRESS	2208.54	Adeq precision	13.403

Table 8. Reliability analysis of selected factor pattern.

Term	Coefficient estimate	df	Standard error	95% CI Low	95% CI High
Intercept	52.51	1	2.46	41.92	63.10
A	3.46	1	3.48	−11.52	18.43
A^2	9.03	1	3.48	−5.95	24.01
B	−26.76	1	3.48	−41.73	−11.78
B^2	7.69	1	3.48	−7.29	22.66
C	−19.16	1	3.48	−34.14	−4.19
C^2	−3.14	1	3.48	−18.11	11.84

Optimal Design

With the help of Design-Expert software [12], the results of orthogonal experiment are well analyzed to explore the optimal design for the dismantling of printed circuit board in MSA-H_2O_2 system. The optimization of dissolution rate is shown in Table 10. To obtain the optimum condition, the dissolution rate of lead and tin should reach the maximum value so that the solder can be completely dissolved and achieve the dismantling. The optimal parameters are shown in Table 11.

From the optimal parameters in Table 11, it can be concluded that the optimum concentrations of H_2O_2 and MSA are 0.5 and 3.5 mol/L, respectively, and the reaction time is 45 min. Under the optimum condition, the dissolution rates of lead and tin calculated with the equations are 99.68% and 102.91%, respectively, with the R^2 of 0.995.

CONCLUSIONS

More and more attention has been paid to the dismantling and recycling of WPCBs recently. Proper dismantling of PCBs is beneficial to conserve scarce resources, reuse the components and hazardous materials safely. In the present study, the dismantling of PCBs are investigated on the laboratory-scale. It can be concluded that the leachant containing MSA and H_2O_2 can selectively desolder the tin-lead alloy for dismantling of ECs from WPCBs. The concentrations of H_2O_2 and MSA have distinct effects on the leaching of solder. With the assistance of Design-Expert software, the optimum concentration of H_2O_2 and MSA is determined to be 0.5 and 3.5 mol/L, respectively. The optimum reaction time for the samples used in the experiments is 45 min. The

Table 9. ANOVA for selected factorial model.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F	
Model	102.62	6	17.10	2.00	0.3702	insignificant
A-A	37.16	2	18.58	2.17	0.3151	
B-B	32.24	2	16.12	1.89	0.3465	
C-C	33.21	2	16.61	1.94	0.3399	
Residual	17.10	2	8.55			
Cor Total	119.72	8				

Table 10. Optimization of dissolution rate.

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
A	in range	0.3	0.7	1	1	3
B	in range	1.5	3.5	1	1	3
C	in range	25	45	1	1	3
Response 1 (Pb)	maximum	70	100	1	1	3
Response 2 (Sn)	maximum	70	100	1	1	3

Table 11. Optimal parameters.

Number	A	B	C	Response 1 (Pb) %	Response 2 (Sn) %	Reliability	
1	0.5	3.5	45	99.69	102.91	0.995	Selected
2	0.3	3.5	45	93.07	97.34	0.837	
3	0.5	2.5	45	88.81	91.53	0.671	
4	0.3	2.5	45	82.19	85.96	0.465	

present study might be helpful for industrial-scale application with the aim of realizing dismantling ECs from WPCBs.

ACKNOWLEDGMENTS

The authors acknowledge the financial supports from National Natural Science Foundation of China (51678353), Shanghai Natural Science Foundation (Nos.15ZR1416800), Shanghai "Chenguang" Program (15CG60), Shanghai Sailing Program (15YF1404300), Shanghai University Youth Teacher Funding Program (ZZZZEGD15011), and Scientific Research Fund Project of Shanghai Second Polytechnic University (EGD15XQD02), Cultivate discipline fund of Shanghai Second Polytechnic University (XXKPY1601) and Eastern Scholar Program of Shanghai. The authors also acknowledge the project supported by Shanghai Cooperative Centre for WEEE Recycling (ZF1224), Shanghai Pudong New Area of Science and Technology Development Fund (PKJ2015-C07 & PKJ2015-C14), and Qingpu "Industry-University-Institute" Cooperation Development Fund (Qing Industry-University-Institute 2015-9).

LITERATURE CITED

1. Hadi, P., Xu, M., Lin, C.S., Hui, C.W., & McKay, G. (2015). Waste printed circuit board recycling techniques and product utilization, Journal of Hazardous Materials, 283, 234–243.
2. Marques, A.C., Cabrera, J.M., & de Fraga Malfatti, C. (2013). Printed circuit boards: A review on the perspective of sustainability, Journal of Environmental Management, 131, 298–306.
3. Huang, K., Guo, J., & Xu, Z. (2009). Recycling of waste printed circuit boards: A review of current technologies and treatment status in China, Journal of Hazardous Materials, 164, 399–408.
4. Xiang, D., Pang, Z.F., Long, D.F., Mou, P., Yang, J.P., & Duan, G.H. (2014). In the disassembly process and apparatus of waste printed circuit board assembly for reusing the components, applied mechanics and materials, Trans Tech Publication, 474–485.
5. Li, P.L., Shi, Y.F., & Liu, D.W. (2014). In status and prospect of disassembly process of electronic components on waste PCBs, Applied Mechanics and Materials, Trans Tech Publication, 1989–1992.
6. Duan, H., Hou, K., Li, J., & Zhu, X. (2011). Examining the technology acceptance for dismantling of waste printed circuit boards in light of recycling and environmental concerns, Journal of Environmental Management, 92, 392–399.
7. Zhao, M., Li, J., Yu, K., Zhu, F., & Wen, X. (2006). Measurement of pyrolysis contamination during crushing of waste printed circuit boards, Journal of Tsinghua University (Science & Technology), 46, 1995–1998.
8. De Greef, R., & Janssen, L. (2001). Electrochemical dissolution of tin in methanesulphonic acid solutions, Journal of Applied Electrochemistry, 31, 693–702.
9. Robert, G., Derek, F., Garry, S., & Dalrymple, I. (2003). Electrochemical Society Proceeding, 18, 346–354.
10. Ma, E., Lu, R., & Xu, Z. (2012). An efficient rough vacuum-chlorinated separation method for the recovery of indium from waste liquid crystal display panels, Green Chemistry, 14, 3395–3401.
11. Islam, M., Beg, M., & Mina, M. (2014). Fibre surface modifications through different treatments with the help of design expert software for natural fibre-based biocomposites, Journal of Composite Materials, **2014**, 48, 1887–1899.
12. Dashti, A., & Nasab, M.E. (2013). Optimization of the performance of the hydrodynamic parameters on the flotation performance of coarse coal particles using design expert (DX8) software, Fuel, 107, 593–600.