Ultrasound Assisted Method to Increase the Aluminum Dissolve Rate from Acidified Water

Wen Po Cheng, Chi Hua Fu, Ping Hung Chen, Ruey Fang Yu

Abstract—Aluminum salt that is generally presents as a solid phase in the water purification sludge (WPS) can be dissolved, recovering a liquid phase, by adding strong acid to the sludge solution. According to the reaction kinetics, when reactant is in the form of small particles with a large specific surface area, or when the reaction temperature is high, the quantity of dissolved aluminum salt or reaction rate, respectively are high. Therefore, in this investigation, water purification sludge (WPS) solution was treated with ultrasonic waves to break down the sludge, and different acids (1 N HCl and 1 N H_2SO_4) were used to acidify it. Acid dosages that yielded the solution pH of less than two were used. The results thus obtained indicate that the quantity of dissolved aluminum in H_2SO_4-acidified solution exceeded that in HCl-acidified solution. Additionally, ultrasonic treatment increased the rate of dissolution of aluminum and the amount dissolved. The quantity of aluminum dissolved at 60℃ was 1.5 to 2.0 times higher than that at 25℃.

Keywords—Coagulant, Aluminum, Ultrasonic, Acidification, Temperature, Sludge.

I. INTRODUCTION

COAGULATION is an important process in the purification of drinking water. While the production of drinking water, the coagulation and precipitation processes produce a large quantity of sludge. In Taiwan, around 120,000 tons of water purification sludge (WPS) is generated from water treatment plants annually, and about 30% of this sludge is alum salt [1]. Alum sludge is composed of the aluminum coagulant and mineral clay in raw water. Water purification sludge contains less heavy metal and organic contamination than wastewater treatment sludge, because the raw water that is used to purify water is relatively clean and the coagulant that is used for treatment is of relatively high quality. Therefore, recovering aluminum salt from such the large amount of produced water purification sludge is worthwhile.

According to past research, the main approaches for recovering alum from WPS include acidification, basification, membrane separation, and ion exchange [1-9]. Since aluminum hydroxide, $Al(OH)_3$, is an amphoteric compound, it can be dissolved in acid or alkaline solutions. It also reacts with acid to form soluble aluminum ions, and forms soluble $Al(OH)_4^-$ ions in alkali. According to Panswad and Chamnan [10], if the pH of alum sludge is reduced by adding H_2SO_4 to between 1 and 3, then an aluminum recovery rate of approximately 70 to 90% can be achieved. If NaOH or $Ca(OH)_2$ is used to extract and recover the aluminum, then the aluminum recovery rate is highest at a pH between 11.2 and 11.8.

These acidification or basification methods are relatively simple. Therefore, they are commonly used for aluminum recovery and in studies of the regeneration of coagulant. For example, the pH that has recently been found to maximize aluminum dissolution efficiency (in terms of moles of aluminum dissolved per mole of H^+ or OH^- ion) in Taiwan, is 2 and 12 in acidification and basification treatments, respectively [11-13]. However, in the basification process, the humic acid in the alum sludge may easily dissolve in a strong alkaline solution, inhibiting the recovery of the aluminum. Accordingly, the acidification process is generally more convenient and more efficient than the basification process for recovering aluminum from sludge. Additionally, the size of the sludge particles and the dissolution temperature are important factors that influence the dissolution of metal ions. When the sludge particles are small, the ability to form complex bonds between the sludge particles and the metal ions is poor. Such weak bonds may promote the dissolution of the sludge [14]. Therefore, the metal is easily dissolved (pH < 2.5). Additionally, a higher dissolution temperature provides sufficient energy to break the amorphous chemical bonds of the sludge and increase the metal dissolution rate [15]. Accordingly, during the acidification process, increasing the solution temperature may increase the quantity of aluminum dissolved.

Ultrasonic frequencies cover the range from 16 kHz to 10^6 kHz. When an ultrasonic wave with high energy passes through a liquid solution, cold boiling, which is also called cavitation, occurs. In sludge, cold boiling initially causes erosion at points on the surface of the sludge. Particle collisions break up the sludge. Secondly, the diffusion layer at the particle surface is disturbed by this cold boiling effect. Finally, the broken particle may easily absorb solvent by capillary action [16-17]. Therefore, ultrasonic waves are frequently applied to alum sludge to reduce the volume of sludge [18-21]. Therefore, in this investigation, alum sludge is treated with ultrasonic waves to evaluate the recovery rate aluminum coagulant under various conditions of species of acid, size of sludge, reaction time and temperature.

II. EXPERIMENTAL

A. Sludge preparation

Sludge was obtained from the sludge drying bed of Ming-Der water treatment plant at Miao-Li, Taiwan. After the sludge was dried at 60℃ and well mixed, a sludge sample was prepared.

B. Determination of acid dosage

Thirty grams of the sludge sample were added to a beaker with 1000 mL distilled water to prepare 3% (W/W) sludge

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solution. Two of these sludge solutions were separately titrated with 1N HCl and 1N H_2SO_4. In each titration process, 30 mL of acid was added to the test sludge solution. The pH and added volumes of acids (HCl and H_2SO_4) were recorded. If the pH of sludge solution after mixing exceeded two, then another 30 mL acid was added to the solution with mixing until the pH dropped below two, and the total acid dosages were again determined.

C. Sludge acidification experiment

Dried sludge was added to a beaker to prepare 3％(W/W) sludge solution. Then, to two of these sludge solutions was separately added the previously determined volume of 1N HCl and 1N H_2SO_4. Each solution was mixing with a magnetic stirrer. The effects of acid and reaction time on aluminum recovery were studied. The same 3％(W/W) solution was also treated with ultrasonic waves for one hour. To two samples of these ultrasonically treated solutions were separately added equal volumes of 1N HCl and 1N H_2SO_4. The solutions with mixing were tested at 25 and 60°C, respectively. This experiment demonstrated that the sludge size and reaction temperature influences the dissolution of aluminum. During the reaction, a series of solution samples were filtrated and analyzed by atomic absorption spectrometry (Z-5000 HITACHI CO. JAPAN) to obtain aluminum concentration. The SONIFIER 450 (Branson Co. USA) ultrasonic wave generator was used. After the sludge samples had been appropriately diluted, they were analyzed using a Particle Counter (Model 8000A HRLD-400HC and Hiac/Royco MC100S; Pacific Scientific, USA) to obtain particle diameter distribution data.

III. RESULTS AND DISCUSSION

A. Determination of acid dosage

In this investigation, two acids, H_2SO_4 and HCl, were used to recover aluminum ions from sludge, and to regenerate aluminum sulfate or aluminum chloride solutions. At 25°C, 30 mL of the acids (1N HCl and 1N H_2SO_4) were separately added to each sample of sludge solution. The pH was recorded as the acid was added with mixing. No more acid was added when the pH stabilized at less than two. According to Fig. 1, in the initial stage of the addition of acid, the acid reacted with the alkaline carbonate, rapidly reducing the pH. When pH the dropped below three, then the acid initiated the dissolution mechanisms reacting with aluminum and other metal hydroxide compounds in the sludge. In this stage, the pH dropped slowly. When the pH was close to two, the acid dosage was close to the optimal dosage at which aluminum dissolution efficiency was maximal [11-13]. The added acid was consumed as it destroyed the amorphous chemical bonds and released the alum ions. Therefore, even increasing the acid dosage did not significantly reduce the pH values. Since the drop in pH is strongly affected by the contents of the sludge, including the percentages of $CaCO_3$, metal hydroxide compounds and aluminum, determining acid dosages by simple calculation based on chemical reaction equations is difficult. When both 1N HCl and 1N H_2SO_4 were added separately for 120 mL separately, the pHs of the two acidified sludge solutions dropped to close to but

less than two. Therefore, the acid volume was determined to be 120 mL. This acid volume was in the experiments herein.
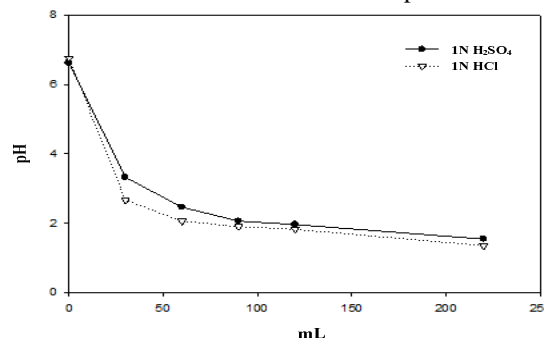

Fig. 1 Relationship between sludge solution pH and dosages of 1N HCl and 1N H_2SO_4

B. Acid species affects quantity of dissolved aluminum

When the reaction temperature was 25°C, 30 g sludge was added to 1 L distilled water. To two of the test sludge solutions were separately added 120 mL 1N HCl and 120 mL 1N H_2SO_4. Then the test solutions were then mixed suing magnetic stirrers for 120 minutes. During the mixing, water samples were extracted every 30 minutes for aluminum concentration analysis. According to the data in Fig. 2, for a particular acid dosage, the dissolved aluminum concentration in the solution that was acidified using H_2SO_4 clearly exceeded that in the solution that was acidified using HCl. When the solution was mixed for ten minutes, the aluminum concentration in the H_2SO_4-acidified solution was 206.4 mg/L. This concentration was 68.7% higher than that the aluminum concentration found in the HCl-acidified solution, which was 122.38 mg/L. When the experiment was terminated at 120 minutes, the aluminum concentration in H_2SO_4-acidified solution was 262.4 mg/L, which was 21.3% higher than the concentration of 216.35 mg/L in the HCl-acidified solution.
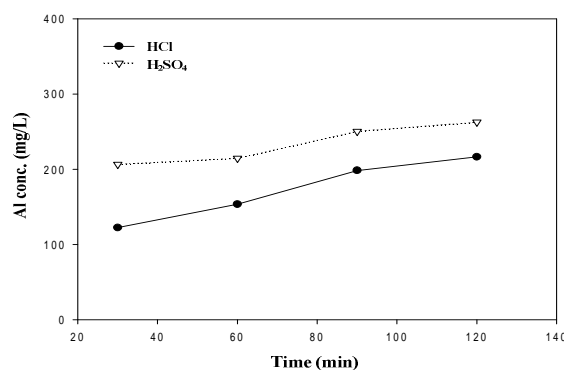

Fig. 2 Relationship between dissolved aluminum concentration and reaction time

These results indicate that adding H_2SO_4 is more efficient in dissolving aluminum than adding HCl. The main reason is that the chemical affinity between SO_4^{2-} and the aluminum ion exceeds that between Cl^- and the aluminum ion, and aluminum sulfate complexes are therefore significantly stronger than aluminum chloride complexes [22-23]. Accordingly, H_2SO_4

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relatively easily dissolves the aluminum ions into the solution. Hence, H_2SO_4 is traditionally used to recover aluminum from sludge.

C. Effect of size of sludge particles on aluminum dissolution

Four sets of test sludge solutions, formed by adding 30 g sludge to 1 L distilled water, were prepared. Two of these test solutions were treated with 166 W ultrasonic for one hour. To both those solutions that had been ultrasonically treated and to those that had not, 120 mL 1N HCl and 120 mL 1N H_2SO_4 were separately added. Then, the solutions were mixed using stirrers for 120 minutes. During mixing, sample water was extracted to analyze the distribution of sizes of the sludge particles. According to Fig. 3, the aluminum concentrations in the ultrasonically treated HCl and H_2SO_4-acidified exceed those in the untreated solutions. Additionally the aluminum concentrations in H_2SO_4-acidified solutions, both treated and untreated, exceeded those in the HCl-acidified solutions. The aluminum concentration rose rapidly to 525.25 mg/L for 40 minutes after H_2SO_4 was added to the solution (with ultrasonic pretreatment). Then, the dissolution rate decreased with increasing reaction time. These results indicate that the dissolution rate can be increased by ultrasonic pretreatment of the acidified solution. The results also indicate that after H_2SO_4 was added for 120 minutes, the aluminum concentration in the ultrasonically treated solution was 593.25 mg/L, which was 2.26 times the concentration (262.4 mg/L) in the untreated solution. Additionally, after HCl was added for 120 minutes, the aluminum concentrations in the ultrasonically treated solutions was 311.3 mg/L, which was 1.44 times the concentration (216.35 mg/L) in the solution without ultrasonic pretreatment. These results indicate that both ultrasonic pretreatment and H_2SO_4 acidification can increase the quantity of dissolved aluminum in the test solutions.
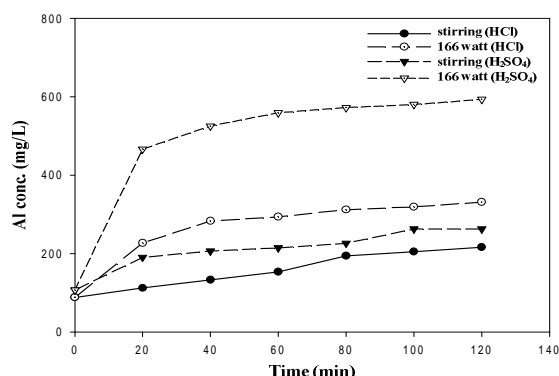

Fig. 3 Effect of ultrasonic pre-treatment on concentrations of dissolved aluminum
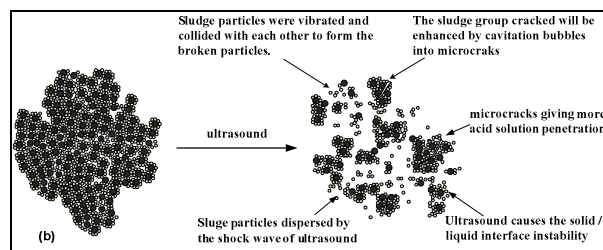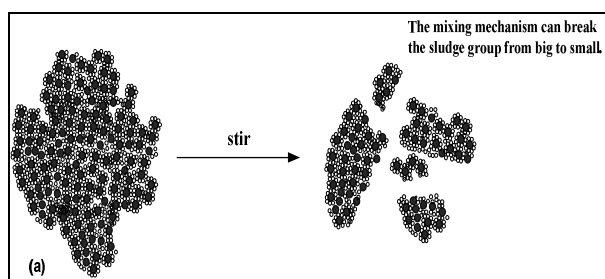

Fig. 4 Coagulation sludge diagram, where ● represents sludge particles, and ○ represents aluminum hydroxide. (a) Mixing effect. (b) Splitting of sludge by ultrasound
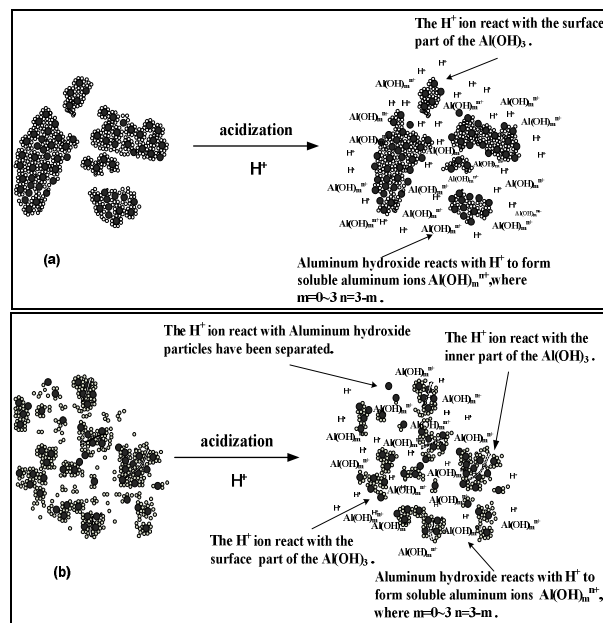

Fig. 5 Alum sludge acidification. (a) Effect of mixing on acidified sludge. (b) Effect of ultrasound on acidified sludge

The above results can be explained by the change of sludge size. The mixing and ultrasonic vibration mechanisms will be separately considered. In Fig. 4(a), the stirring mechanism can only break up the large sludge particles to form small particles. The sludge particles are attached to, and combined with $Al(OH)_3$. During the acidification process, the H^+ ions can react only at the surface of $Al(OH)_3$ and cannot acidify the interior the $Al(OH)_3$ particles in the sludge (Fig. 5(a)). The data in Fig. 4(b) indicate that the cold boiling by the ultrasonic vibration energy may create erosion points on the surfaces of the particles. Sludge particles vibrated and collided with each other, causing them to break up. Hence, by the capillary effect, H^+ ions may react with the surface and the interior of the $Al(OH)_3$ during the acidification process (Fig. 5(b)). Therefore, the H^+ ions in the ultrasonically treated solution have more opportunities to react with the aluminum than do those in the untreated solution. The above claims are verified by the data on the distribution of particle diameters that are plotted in Fig. 6. After 166 W ultrasonic was applied, the number of particles with a diameter of less than 5 μm was five times the number without ultrasonic pretreatment. Ultrasonic treatment may have shrunk the sludge particles.

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The small particles may have allowed enough of the acid to come into contact with Al(OH)$_3$ to accelerate aluminum dissolution. Therefore, ultrasonic treatment makes particles smaller, enhancing acidification.
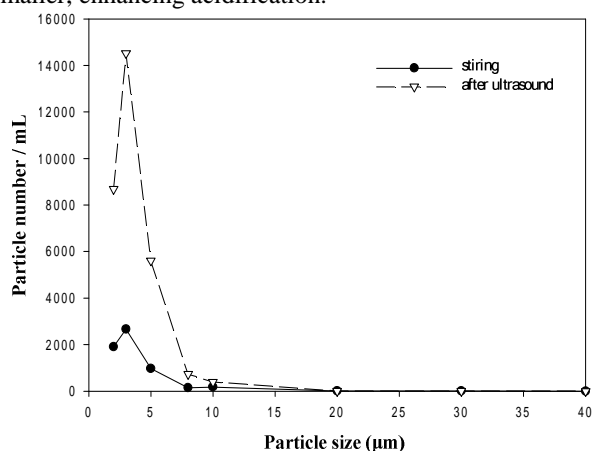

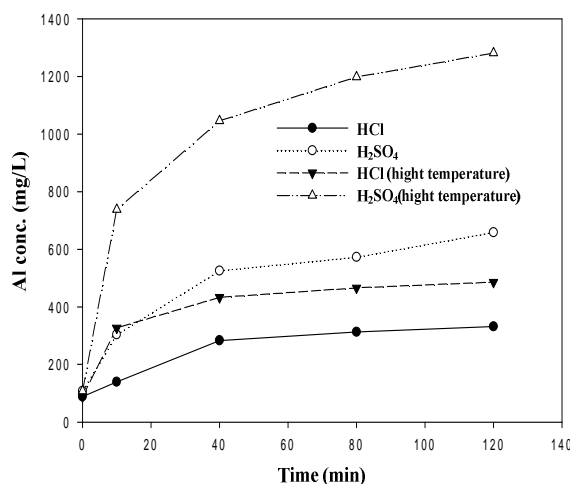Fig. 6 Effects of mixing and ultrasonic vibration on sludge size distribution

Fig. 7 Effect of reaction temperature on concentration of dissolved aluminum

D. Effect of temperature on acidification process

Four sets of test sludge solutions were prepared were prepared by adding 30 g sludge to 100 mL distilled water. All of the test solutions were treated with 166 W ultrasonic for one hour. At 25°C, two of these test solutions were separately acidified by adding 120 mL 1N HCl and 120 mL 1N H$_2$SO$_4$ and mixing for 120 minutes. The other two test solutions were acidified under the same experimental conditions but at 60°C.

The data in Fig. 7 indicate that following ultrasonic treatment, H$_2$SO$_4$ acidification for 120 minutes at 25°C yielded an aluminum concentration of 658.7 mg/L. At 60°C, the aluminum concentration was 1281.4 mg/L. The aluminum concentration at 60°C was 1.95 times that at 25°C. When HCl was used in acidification, the aluminum concentration at 25°C was 331.3 mg/L. At 60°C, the concentration was 486 mg/L. The aluminum concentration at 60°C was 1.47 times that at 25°C. Based on the above results, increasing the reaction temperature

increased the aluminum concentration in the solution, independently of the acid used. At 10 minutes and 60°C, the aluminum concentration in H$_2$SO$_4$-acidified solution was 783 mg/L. That in the HCl-acidified solution was 303.2 mg/L. After 10 minutes of the acidification reaction, the aluminum concentration increased slowly, indicating that when enough acid was added to the test solutions, increasing the temperature may also have increased the reaction rate, causing the aluminum to be dissolved rapidly. However, at both 25 and 60°C, the aluminum recovery efficiency in H$_2$SO$_4$-acidified solution exceeded that in HCl-acidified solution. This result is consistent with that in the previous discussion concerning the effect of the acid species [19-20]. It is also consistent with thermodynamic theory. The rate of dissolution of a chemical compound depends on the solubility product constant, K$_{sp}$, which depends on reaction temperature. For most compounds, the heat or enthalpy change of the dissolution reaction is positive, so the dissolution reaction is endothermic. Therefore, the value of K$_{sp}$ for the dissolution of Al(OH)$_3$ is temperature-dependent and increases with temperature. A higher temperature provides more heat energy to break the amorphous Al(OH)$_3$ chemical bonds, increasing the dissolution rate of the aluminum.

IV. CONCLUSION

The acidification method was used in this investigation to recover alum salts from the sludge of a water treatment plant. The effects of acid species, sludge size, and reaction temperature on aluminum recovery were discussed. Experimental results revealed that ultrasonic treatment could break up the sludge particles and increase the quantity of aluminum dissolved. Also, the quantity of aluminum dissolved increased with the reaction temperature. The concentration of aluminum dissolved at 60°C solution was around 1.5 to 2.0 times higher that at 25°C. The aluminum dissolving efficiency in H$_2$SO$_4$-acidified solution exceeded that in HCl-acidified solution.

REFERENCES

[1] A.O. Babatunde, Y. Q. Zhaoa, Constructive approaches toward water treatment works sludge management: an international review of beneficial reuses. Journal of Critical Reviews in Environmental Science and Technology, 37(2) (2007), pp. 129 – 164.
[2] D.J. Wozniak, J.Y.C. Huang, Variables affecting metal removal from sludge. Journal of Water Pollut. Control Fed., 54 (1982), pp. 1574-1580.
[3] I.G. Shimko, E.K. Chernetskii, A.M. Gens, N.I. Biryukova, Regeneration of coagulant from aluminum hydroxide containing precipitates from water-softening stations of viscose fibre plants. Journal of Fibre Chemistry, 18(4) (1987), pp. 326-328.
[4] P. Prakash, D. Hoskins, A.K. SenGupta, Application of homogeneous and heterogeneous cation-exchange membranes in coagulant recovery

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from water treatment plant residuals using donnan membrane process. Journal of Membrane Science, 237(1-2) (2004), pp. 131-144.

[5] B. Jiménez, M. Martínez, M. Vaca, Alum recovery and wastewater sludge stabilization with sulfuric acid. Water Sci. Technol., 56(8) (2007), pp. 133-141.

[6] S. Ishikawa, N. Ueda, Y. Okumura, Y. Iida, K. Baba, Recovery of coagulant from water supply plant sludge and its effect on clarification. Journal of Material Cycle and Management, 9(2) (2007), pp. 167-172.

[7] G.R. Xu, Z.C. Yan, Y.C. Wang, N. Wang, Recycle of Alum recovered from water treatment sludge in chemically enhanced primary treatment. Journal of Hazardous Materials, 161 (2009), pp. 663-669.

[8] T. Yu, D.G. Shen, C.N. Yang, Q.N. Shao, P.S. Song, L.N. He, W.X. Pan, S.P. Bi, Technical development of Aluminum salt recovery from alum sludge. Journal of The Administration and Technique of Environmental Monitoring, 21(2) (2009), pp. 45-52.

[9] Z. Liu, S.M. Zhu, Y.H. Li, A new regeneration approach to cation resins with aluminum salts: application of desalination by its mixed bed. Frontiers of Environmental Science& Engineering in China, 2011, DOI: 10.1007/s11783-010-0262-6.

[10] T. Panswad, P. Chamnan, Aluminum recovery from industrial aluminum sludge. Water Supply, 10(4) (1992), pp. 159-166.

[11] C.W. Li, J. L. Lin, S.F. Kang, C.L. Liang, Acidification and alkalization of textile chemical sludge: volume/solid reduction, dewaterability, and Al(III) recovery. Journal of Separation and Purification Technology, 42(1) (2005), pp. 31-37.

[12] W.L. Peng, Effect of acidification/alkalization on water treatment plant sludge reduction and dewaterability. master's thesis, Tankang University, Taiwan R.O.C, 2009.

[13] S.H. Huang, J.L. Chen, K.Y. Chiang, H.C. Wu, Effects of acidification on dewaterability and aluminum concentration of alum sludge. Journal of Separation Science and Technology, 45(8) (2010), pp.1165-1169.

[14] D.L. Lake, P.W. Kirk, J.N. Lester, Heavy metal solids association in sewage sludge. Journal of Water Res., 23(3) (1989), pp. 285-291.

[15] A. Tessier, P. Gampbell and M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals. Journal of Anal. Chem., 51 (1979), pp. 844-851.

[16] Y.J. Chen, H.Y. Teng, P.S. Wei, Y.C. Dung, Monitoring and analysis of acoustic cavitation behaviors in liquid. Journal of Advanced Engineering, 2(3) (2007), pp. 157-161.

[17] T.J. Mason, Ultrasound in Environmental Engineering II (Ed. Neis, U.), 2002, 35, 1.

[18] K.Y. Show, T. Mao, J.H. Tay, D.J. Lee, Effects of ultrasound pretreatment of sludge on anaerobic digestion. Journal of Residuals Science & Technology, 3(1) (2006), pp. 51-60.

[19] H.T. Zhuang, Q.C. Yin, S.Q. Ding, D.T. Wang, Research about recovery of aluminum in sludge from water supply plant. Journal of Bohai University, 30(3) (2009), pp. 202-206.

[20] A. Grönroos, Ultrasonically enhanced disintegration, Polymers, Sludge, and Contaminated Soil, 2010, VTT Publications, p. 734.

[21] J. Bien, M. Kowalczyk, T. Kamizela, M. Mrwiec, The influence of ultrasonic disintegration aided with chemicals on the efficiency of sewage sludge centrifugation. Environmental Protection Engineering, 36(1) (2010), pp. 35-43.

[22] M.K. Ridley, D.J. Wesolowski, D.A. Palmer, B. Pascale, R.M. Kettler, Effect of sulfate on the release rate of Al^{3+} from gibbsite in low-temperature acidic waters. Journal of Environ. Sci. Technol., 31 (1997), pp. 1922-1925.

[23] C.H. Huang, L. Chen, C.L. Yang, Effect of anions on electrochemical coagulation for cadmium removal. Journal of Separation and Purification Technology, 65(2) (2009), pp. 137-146.