Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

p-ISSN: 0972-6268 e-ISSN: 2395-3454	Vol. 17	No. 4	pp. 1419-1424	2018

Original Research Paper | Open Access

Study on the Oxidation Process of As(III) in Acidic Wastewater Containing Arsenic by Electrolysis and Ultrasonic Coupling

Linbo Li*†, Zhao Yang*, Zeli Yu, Tao Hong* and Yuhong Tian*†**

*School of Metallurgical Engineering, Xi'an University of Architecture and Technology, Xi'an, 710055, China

**Research Centre on Metallurgical Engineering and Technology of Shaanxi Province, Shaanxi Key Laboratory of Gold and Resource, Xi'an, 710055, China

†Corresponding authors: Yuhong Tian and Linbo Li

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 04-04-2018
Accepted: 04-06-2018

Key Words:
Arsenic
Acid wastewater
Oxidation method
Electrolysis
Ultrasound

ABSTRACT

The ultrasonic and electrochemical combination oxidation technology was used to treat the acid wastewater containing arsenic in this work. To clarify the oxidation process of As(III) to As(V) in the anode region under the electrolysis and ultrasonic coupling, the oxidation process of As(III) under different influence factors (time/electrolysis voltage/arsenic concentration/ultrasonic power) was studied in a sulphuric acid-arsenic mixture system. The results show that trivalent arsenic oxidation efficiency can be increased when ultrasound is added in the process of electrolysis. The oxidation rate of trivalent arsenic is 25.49% higher than that produced by simple electrolysis when the electrolytic time is 120 min. The increase of electrolysis voltage can increase the oxidation efficiency of arsenic when the voltage is less than 6V. Below 1.1540g/L, the increase of arsenic concentration can promote the oxidation of As(III). The increase of ultrasonic power can promote the oxidation of As(III). However, the excessive ultrasonic power will cause the problem of acoustic shielding, resulting in excessive energy consumption and other problems. As a result, the oxidation efficiency of arsenic decreases.

INTRODUCTION

Arsenic is a toxic and harmful substance (Choong et al. 2007). A large amount of acid wastewater containing arsenic is produced after flue gas washing during the high temperature extraction of heavy metal sulfide ore (Wang 2016). This kind of wastewater has the characteristics as heavy pollution source, continuous emission, high concentrations of free acid and arsenic, and complex composition (Basha et al. 2008, Xiaojuan 2012, Guo 2010). At present, the most commonly used arsenic wastewater treatment method in the industry is precipitation (Ahoranta et al. 2016, Peng et al. 2018). The method represented by treatment with lime neutralization-arsenic sulfide/ferrous salt has such disadvantages as large waste emissions, high processing costs, and difficult to effectively meet the standard after treatment compliance (Harper 1992, Mohan & Pittman 2007, Shih & Lin 2003). In view of the characteristics of flue gas washing acid wastewater containing arsenic, the existing treatment methods have high running costs, incomplete treatment and serious pollution of waste residues. And experimental results show that when pH is less than 9.5, most of the trivalent arsenic in water has electrical neutrality, so most of the arsenic treatment methods such as flocculation, sedimentation, and adsorption of trivalent arsenic have little effect on trivalent arsenic (Ahoranta et al. 2016, Guo et al. 2015, Liu et al. 2016). At the same time the toxicity of trivalent arsenic in wastewater is 60 times higher than pentavalent arsenic. So, the oxidation of trivalent arsenic to pentavalent arsenic is a necessary part in the process (Yang et al. 2017).

In this paper, ultrasonic and electrochemical synergistic oxidation to oxidize trivalent arsenic into pentavalent arsenic was used, which can reduce the toxicity of arsenic, improve the conversion efficiency and provide guarantee for the removal of arsenic. Compared with traditional wastewater treatment process, ultrasound combined with electrochemistry can degrade toxic wastewater under mild reaction conditions (Lakshmipathiraj et al. 2010, Yang et al. 2016, Yang et al. 2014). It has many advantages such as low cost, no pollution, easy and safe operation, and the metal material in the wastewater can also be recycled so as to increase economic benefits. Besides, the combination of ultrasound and electrochemistry has many potential advantages, such as cleaning and degassing of electrode surface, depassivation of electrode surface, accelerating the mass transfer of liquid and accelerating the rate of degradation. The oxidation process of As(III) to As(V) under different influence factors (time/electrolysis voltage/ arsenic concentration/ultrasonic power) has been studied in a sulphuric

acid-arsenic mixture system. The optimum conditions of electrolysis and ultrasonic coupling are determined when As(III) is oxidized to As(V).

EXPERIMENTS

Experimental method: Prepare 20% sulphuric acid, add 0.5 g/L ammonium thiocyanate, then 0 g/L to 4 g/L of sodium arsenite and stir for some time. The solution was moved into an electrolytic cell after sodium arsenite was completely dissolved. The solution should be prepared when to be used. The temperature was controlled at 10°C. Titanium plating platinum as anode and graphite as cathode were taken, and the reaction time was kept at 120 min. 20 mL anode solution was taken every 25 min, and the concentrations of As(III) and As(V) in anodic solutions under different conditions were analysed.

Experimental equipment: In this experiment, the electrolysis and ultrasonic coupling method was used to treat the acidic wastewater containing arsenic. A self-made electrolytic bath system was adopted and the ultrasonic generator was custom made. The experimental equipment is shown in Fig. 1.

Analysis method: Caro's acid in solution was detected by potassium dichromate oxidation reduction titration. The trivalent arsenic and pentavalent arsenic in solution were detected by hydride generation-atomic fluorescence spectrometry.

RESULTS AND DISCUSSION

Effect of ultrasonic sound on oxidation process of anode zone: When added ultrasound, ultrasonic cavitation in aqueous solution can produce hydrogen radicals and hydrogen peroxide radicals, enhance the oxidability of the solution and increase the synthesis rate of Caro's acid. Ultrasound can also increase ionic activity, accelerate the rate of ion migration and reduce the concentration of polarization (Adewuyi 2001). Therefore, the effect of ultrasound and ultrasound time on As(III) oxidation process should be investigated.

***Experimental conditions*:** 2 g/L sodium arsenite was added to the 20% sulphuric acid solution, electrolytic voltage was 6.0 V, the ultrasonic frequency was 40 kHz, the ultrasonic power was 150 W, and the oxidation rate of As(III) in anodic solutions under different ultrasonic conditions were analysed. The experimental results are shown in Fig. 2.

As shown in Fig. 2, the oxidation rate of As(III) in anode zone increases gradually with the increase of electrolysis time, the oxidation rate of As(III) becomes slow and eventually tends to balance with the increase of electrolysis time. This is mainly because the electrolysis process is exothermic; as the electrolysis time is too long, the temperature rise causes the hydrolysis of peroxosulphuric acid and slow down the process of indirect oxidation. Moreover, with the increase of time, the ratio of As(V) and As(III) concentration in anode solution increases gradually. The oxidation potential of trivalent arsenic also increases gradually, which leads to a decrease in the oxidation rate of As(III). The oxidation rate of As(III) is greatly improved by the addition of ultrasound. This is mainly because the ultrasonic cavitation can produce hydrogen radicals and hydrogen peroxide radical, accelerate ion migration, improve the formation rate of oxidant, and promote the indirect electrochemical reaction process. In addition, ultrasonic mechanical agitation can reduce the concentration polarization of solution and increase the

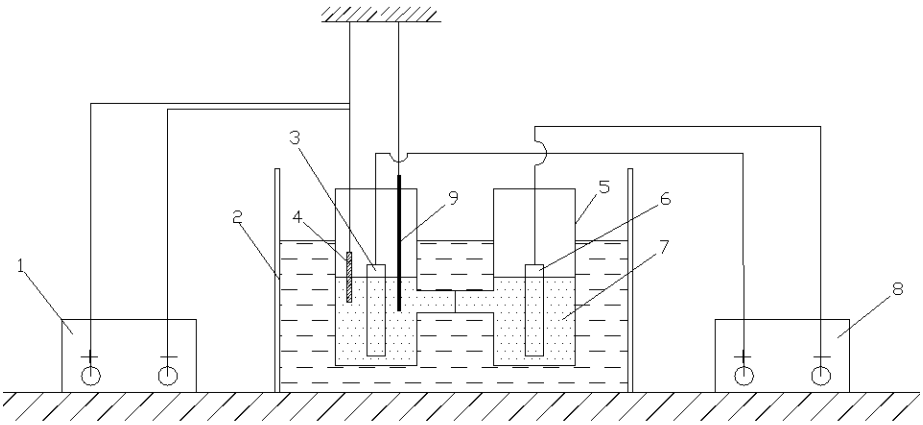

Fig. 1: Diagram of ultrasonic enhanced electrolytic equipment.
(1-ultrasonic generator, 2-thermostatic bath, 3-platinum plated titanium anode, 4-transducer probe, 5-electrolytic tank, 6- graphite cathode, 7-electrolyte, 8-DC power supply, 9-thermometer)

mass transfer rate in the solution. Cavitation effects of ultrasound can remove bubbles on the surface of the anode and prevent anodic passivation, thus improving the current efficiency and increasing the rate of electrochemical oxidation. When the electrolysis time reaches 120 min, the oxidation rate of trivalent arsenic is 60.84% without ultrasound, while the oxidation rate of trivalent arsenic reaches 86.33% when the ultrasound is added. It can be seen that the ultrasonic effect greatly improves the oxidation efficiency of trivalent arsenic. Therefore, it is feasible to use ultrasound and electrolysis to oxidize trivalent arsenic.

Effect of electrolysis voltage on oxidation of anode zone: Because both, direct electrochemical oxidation and indirect electrochemical oxidation, exist in the electrochemical oxidation process of As(III), therefore, it is necessary to investigate the effect of electrolysis voltage on the oxidation of As(III) in the sulphuric acid-arsenic mixing system under ultrasonic conditions.

The electrolysis voltage is composed of theoretical voltage and overpotential. Overpotential is caused by the polarization of the electrode. With the addition of ultrasound to the electrolysis process, the concentration polarization can be reduced and the diffusion mass transfer can be enhanced, thus the anodic electrode potential and anodic oxygen evolution overpotential are increased, the side reaction is suppressed, the formation rate of peroxosulphuric acid and the oxidation rate of As(III) are increased.

***Experimental conditions*:** 2 g/L sodium arsenite was added to the 20% sulphuric acid solution, the ultrasonic frequency was 40 kHz, and the ultrasonic power was 150 W, and the oxidation rate of As(III) in anodic solutions under different electrolysis voltage (4V, 5V, 6V and 7V) were analysed respectively. The experimental results are shown in Fig. 3 and Table 1.

As shown in Fig. 3, with the increase of electrolysis time, the oxidation rate of As(III) in the anode solution increases continuously. When the electrolysis time is constant, the oxidation rate of trivalent arsenic tends to be stable, this is because with the continuous progress of the electrolytic process, the concentration of As(V) in the solution is more and more higher. The oxidation potential of trivalent arsenic increases as the concentration ratio of As(V)/As(III) in the solution increases, so the oxidation rate of trivalent arsenic gradually slows down. The oxidation rate of trivalent arsenic increases with the increase of voltage when the voltage is less than 6 V. When the voltage is more than 6 V, the oxidation rate of trivalent arsenic decreased significantly. The reason is that at the higher voltage, both, the anodic overpotential and the energy consumption increase, which accelerate the decomposition of Caro's acid and weaken

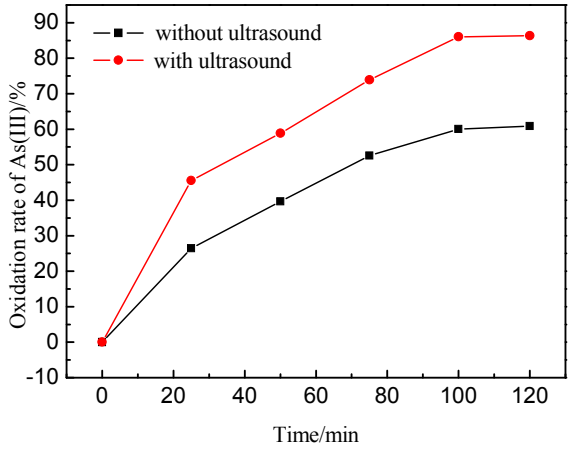

Fig. 2: Effect of ultrasound on anodic oxidation.

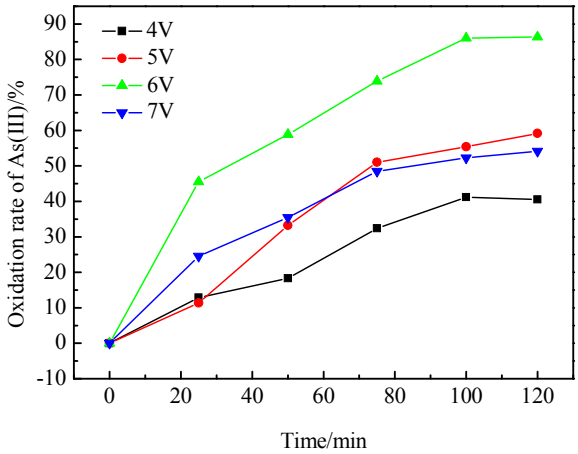

Fig. 3: Effect of electrolysis voltage on anodic oxidation.

the indirect electrochemical oxidation process. As given in Table 1, when the electrolysis time is 120 min and the electrolytic voltage is 6 V, the oxidation rate of trivalent arsenic is up to 86.34%, indicating that 6 V is the most suitable electrolysis voltage for ultrasonic and electrolytic oxidation of trivalent arsenic.

Effect of arsenic concentration on oxidation of anode zone: According to the research (Compton et al. 1997, Tudela et al. 2014), the oxidation potential of As(III) is influenced by the concentration ratio of As(V) and As(III) in the solution, therefore, the influence of trivalent arsenic content in electrolyte solution on arsenic oxidation process should be considered. The addition of ultrasound in the solution can enhance the diffusion mass transfer, reduce the concentration polarization of the solution and increase the oxidation rate of arsenic, but the effects on the oxidation rate of As(III) are different when the initial arsenic solution is different in the ultrasonic environment.

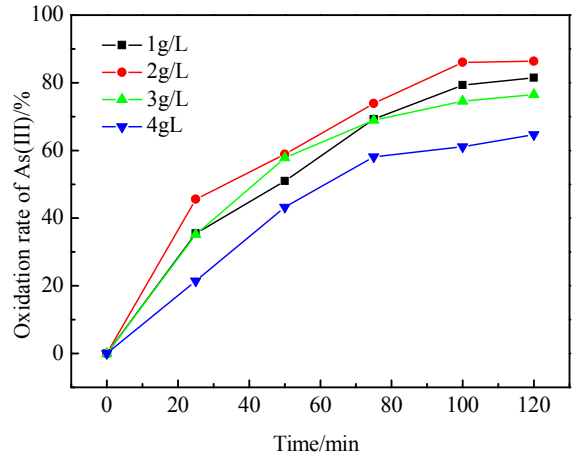

Fig. 4: Effect of arsenic concentration on anodic oxidation.

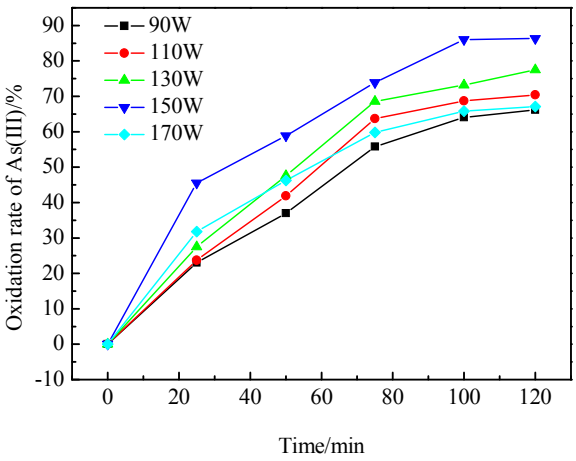

Fig. 5: Effect of ultrasonic power on anodic oxidation

***Experimental conditions*:** With the electrolysis voltage 6.0 V, the ultrasonic frequency 40 kHz and the ultrasonic power 150 W, the oxidation rate of As(III) in anodic solutions under different concentrations of sodium arsenite (1 g/L, 2 g/L, 3 g/L and 4 g/L) were analysed respectively. The experimental results are shown in Fig. 4 and Table 2.

According to Fig. 4, with the increase of electrolysis time, the increasing trend of the oxidation rate of As(III) in the anodic liquid gradually decreases. This is because the concentration ratio of the As(V) and As(III) in the solution increases gradually and the As(III) oxidation potential rises, which leads to slow the oxidation rate of As(III). The oxidation effect of trivalent arsenic increases with the increase of concentration when the initial concentration is less than 2 g/L. When the initial concentration is more than 2 g/L, the oxidation effect of trivalent arsenic becomes weak with the increase of concentration. When the electrolytic time is 120 min, the oxidation effect of four different initial arsenic concentration solutions is given in Table 2. It can be seen that the oxidation rate of arsenic increases first and then decreases when the concentration of sodium arsenite is in the range of 1 g/L to 4 g/L. When the concentration of sodium arsenite is 2 g/L, the oxidation rate of arsenic is as high as 86.34%. This is mainly because the initial concentration of As(III) increases, which leads to solution conductivity to increase, cell voltage to decrease and voltage efficiency to increase. However, at the too high initial concentration of As(III), the density, viscosity and surface tension of the solution increase, the ionic activity reduces, and the oxidation rate of arsenic decreases eventually. Therefore, the most suitable initial arsenic concentration for oxidation of trivalent arsenic is 2 g/L.

Effect of ultrasonic power on anodic oxidation: Ultrasonic power is one of the important factors that affect cavitation (Tzanakis 2015). The magnitude of power directly influences the reaction temperature and reaction rate. Therefore, it is very important to investigate the effect of ultrasonic power on the electrolytic oxidation process.

***Experimental conditions*:** 2 g/L sodium arsenite was added to the 20% sulphuric acid solution, the electrolysis voltage was 6.0 V, the ultrasonic frequency was 40 kHz, and the oxidation rate of As(III) in anodic solutions under different ultrasonic power (90 W, 110 W, 130 W, 150 W, 170 W) was analysed respectively. The experimental results are shown in Fig. 5 and Table 3.

As shown in Fig. 5, with the increase of electrolysis time, the oxidation rate of As(III) in anode solution increases gradually and tends to be smooth at last. After a certain period of electrolysis, the oxidation effect of trivalent arsenic under different ultrasonic power shows that when the ultrasonic power is at 90 W-150 W, the oxidation effect of trivalent arsenic becomes stronger with the increase of ultrasonic power, and the oxidation effect becomes weaker when the ultrasonic power exceeds 150 W. This is mainly because the increase of ultrasonic power can enhance the degree of cavitation, enhance the mechanical agitation of the solution, accelerate the mass transfer of the solution, eliminate concentration polarization and anode passivation, and thus improve the current efficiency and accelerate the reaction rate. However, when the ultrasonic power is too high, the cavitation bubble will become large in the ultrasonic phase of the negative phase and form the acoustic shielding. Moreover, a large number of cavitation bubbles are activated and it has a strong scattering effect on ultrasonic sound velocity. Thus, the sound field energy of the system can be reduced. When the ultrasonic power is too

Table 1: Effect of electrolytic voltage on arsenic oxidation rate when electrolysis for 120 min.

Electrolytic voltage (V)	4.0	5.0	6.0	7.0
Arsenic oxidation rate (%)	40.54	59.18	86.34	54.16

Table 2: Effect of As(III) initial concentration on arsenic oxidation rate after electrolysis for 2 h.

Initial concentration of As(III) ($g \cdot L^{-1}$)	0.577	1.154	1.731	2.308
Arsenic oxidation rate (%)	81.47	86.34	76.55	64.69

Table 3: Effect of ultrasonic power on arsenic oxidation rate when electrolysis for 120 min.

Ultrasonic power (W)	90	110	130	150	170
Arsenic oxidation rate (%)	66.18	70.44	77.47	86.34	67.12

large, it increase the energy consumption, raise the temperature of the solution and weaken the indirect oxidation process. Therefore, if the ultrasonic power is too large, it will lead to low oxidation efficiency.

As can be seen from Table 3, when the ultrasonic power is 150 W and the electrolysis time is 120 min, the oxidation rate of trivalent arsenic can reach 86.34%. Therefore, 150 W should be the best ultrasonic power of the ultrasonic electrolysis coupling for oxidation of trivalent arsenic.

CONCLUSIONS

The oxidation procedure of anodic zone in the sulphuric acid-arsenic mixing system has been studied, and the effects of different influencing factors on anodic oxidation were compared. The optimum conditions of electrolysis and ultrasonic coupling were determined when As(III) is oxidized to As(V). The results show:

1. When arsenic containing wastewater is treated by ultrasonic and electrochemical combination oxidation, the oxidation rate of As(III) in the anode region is 25.49% higher than that electrolysis without ultrasonic when the electrolysis time is 120 min. It shows that ultrasound has a great effect on the electrolysis of trivalent arsenic.
2. Adding ultrasound to the electrolysis process can reduce the concentration polarization and enhance the diffusion mass transfer, thus increasing the anodic electrode potential and anodic oxygen evolution overpotential, inhibiting the side reaction, and increasing the formation rate of peroxosulphuric acid and the oxidation rate of As(III).
3. The oxidation rate of As(III) increases with the increase of the electrolysis voltage, but when the electrolysis voltage is too high, the anodic overpotential, the energy consumption and the solution temperature increase, resulting in the decomposition of Caro's acid, thus reducing the oxidation efficiency of the trivalent arsenic. So the most suitable voltage is 6 V.
4. The increase of arsenic concentration can promote the oxidation of As(III), but when the concentration of arsenic is too high, the density, viscosity and surface tension of solution increase, and the ionic activity of solution decreases, which ultimately leads to the reduction of arsenic oxidation rate. Therefore, the optimum concentration is 2 g/L.
5. The increase of ultrasonic power can promote the formation of As(V), but when the ultrasonic power is too high, it forms the acoustic shielding, reduce the sound field energy of the system, and increase the energy consumption. So the ultrasonic power should be controlled at 150 W appropriately.

ACKNOWLEDGMENTS

The authors acknowledge the financial support by National Natural Science Foundation of China (Grant No. 51374167).

REFERENCES

Adewuyi, Y.G. 2001. Sonochemistry: Environmental science and engineering applications. Industrial and Engineering Chemistry Research, 40(22): 4681-4715.

Ahoranta, S.H., Kokko, M.E., Papirio, S., Ozkaya, B. and Puhakka, J. A. 2016. Arsenic removal from acidic solutions with biogenic ferric precipitates. Journal of Hazardous Materials, 306: 124-132.

Basha, C.A., Selvi, S.J., Ramasamy, E. and Chellammal, S. 2008. Removal of arsenic and sulphate from the copper smelting industrial effluent. Chemical Engineering Journal, 141(1-3): 89-98.

Choong, T.S.Y., Chuah, T.G., Robiah, Y., Gregory Koay, F.L. and

Azni, I. 2007. Arsenic toxicity, health hazards and removal techniques from water: An overview. Desalination, 217(1-3): 139-166.

Compton, R.G., Eklund, J.C., Marken, F., Rebbitt, T.O., Akkermans, R.P. and Waller, D.N. 1997. Dual activation: Coupling ultrasound to electrochemistry - an overview. Electrochimica Acta, 42 (19): 2919-2927.

Guo, H. 2010. Smelting contains the arsenie wastewater disposal experiment and applied research including the arsenic dirt acid and the acidity. Department of Environmental Municipal Chang'an University, Xi'an.

Guo, L., Du, Y., Yi, Q., Li, D., Cao, L. and Du, D. 2015. Efficient removal of arsenic from "dirty acid" wastewater by using a novel immersed multi-start distributor for sulphide feeding. Separation and Purification Technology, 142: 209-214.

Harper, T.R.K. and Neville, W. 1992. Removal of arsenic from wastewater using chemical precipitation methods. Water Environment Federation, 64(3): 200-203.

Lakshmipathiraj, P., Prabhakar, S. and Raju, G.B. 2010. Studies on the electrochemical decontamination of wastewater containing arsenic. Separation and Purification Technology, 73(2): 114-121.

Liu, R., Yang, Z., He, Z., Wu, L., Hu, C., Wu, W. and Qu, J. 2016. Treatment of strongly acidic wastewater with high arsenic concentrations by ferrous sulfide (FeS): Inhibitive effects of S(0)-enriched surfaces. Chemical Engineering Journal, 304: 986-992.

Mohan, D. and Pittman Jr, C.U. 2007. Arsenic removal from water/wastewater using adsorbents - a critical review. Journal of Hazardous Materials, 142(1-2): 1-53.

Peng, X., Chen, J., Kong, L. and Hu, X. 2018. Removal of arsenic from strongly acidic wastewater using phosphorus pentasulfide as precipitant: UV-light promoted sulfuration reaction and particle aggregation. Environmental Science & Technology, 52(8): 4794-4801.

Shih, C.J. and Lin, C.F. 2003. Arsenic contaminated site at an abandoned copper smelter plant: Waste characterization and solidification/stabilization treatment. Chemosphere, 53(7): 691-703.

Tudela, I., Zhang, Y., Pal, M., Kerr, I. and Cobley, A.J. 2014. Ultrasound-assisted electrodeposition of composite coatings with particles. Surface and Coatings Technology, 259(PC): 363-373.

Tzanakis, G.S.B.L., Eskin, D.G. and Pericleous, K. 2015. Effect of input power and temperature on the cavitation intensity during the ultrasonic treatment of molten aluminium. Transactions of the Indian Institute of Metals, 68(6): 1023-1026.

Wang, D. 2016. Purification and reuse of highly acidic wastewater with high arsenic concentration and the mechanism of arsenic removal. Enviromental Engineering, East China University of Technology, NanChang.

Xiaojuan, G., Fan, W. and Qinian, W. 2012. Advances in the research on arsenic-bearing wastewater treatment. Industrial Water Treatment, (2): 004.

Yang, B., Zuo, J., Li, P., Wang, K., Yu, X. and Zhang, M. 2016. Effective ultrasound electrochemical degradation of biological toxicity and refractory cephalosporin pharmaceutical wastewater. Chemical Engineering Journal, 287: 30-37.

Yang, B., Zuo, J., Tang, X., Liu, F., Yu, X., Tang, X., Jiang, H. and Gan, L. 2014. Effective ultrasound electrochemical degradation of methylene blue wastewater using a nanocoated electrode. Ultrasonics Sonochemistry, 21(4): 1310-1317.

Yang, J.Q., Chai, L.Y., Li, Q.Z. and Shu, Y.D. 2017. Redox behavior and chemical species of arsenic in acidic aqueous system. Transactions of Nonferrous Metals Society of China (English Edition), 27(9): 2063-2072.