Available online at http://www.journalijdr.com

ISSN: 2230-9926

IJDR

International Journal of Development Research
Vol. 07, Issue, 08, pp.14614-14619, August, 2017

Original Research Article | Open Access

EFFECT OF TEMPERATURE ON REMOVAL OF COPPER FROM ELECTROPLATING INDUSTRIAL SLUDGE VIA BIOSOLUBILIZATION: KINETICS AND THERMODYNAMICS STUDIES

[1]Venkatesa Prabhu, S., [1]Uga Waktole, B., [1]Gizachew Assefa and [2,*]Arulvel, R.

[1]Department of Chemical Engineering, Addis Ababa Science and Technology University, Ethiopia
[2]Department of Biotechnology, K.S.Rangasamy College of Technology, India, 637 215

ARTICLE INFO

Article History:
Received 10th May, 2017
Received in revised form
15th June, 2017
Accepted 22nd July, 2017
Published online 30th August, 2017

Keywords:

Biosolubilization, Rate constant,
Shrinking core model,
Rate-controlling step,
Activation energy,
Gibbs free energy,
Enthalpy Entropy.

***Corresponding author**

ABSTRACT

The industrial sludge with heavy metal poses a severe threat to the environment and human health when it is disposed to a landfill site without proper treatment. In this work, the removal of Cu from electroplating industrial sludge by biosolubilization was studies using adapted *Acidithiobacillus ferrooxidans* as the bacterial agent with due importance for investigating the effect of temperature. The experiments were carried out in 250 mL Erlenmeyer flasks with 5% (w/v) sludge and at the different temperatures between 27 and 39°C. Experimental results showed that the temperature had great impact on biosolubilization, and the ideal temperature was found to be 36°C. The pseudo-first-order kinetic model was used to determine the rate-constant values of Cu solubilization at different temperatures. Using the shrinking core model analysis, the rate-controlling step was identified. In addition, the activation energy, Gibbs free energy, and change in enthalpy and entropy were calculated for the biosolubilization process.

Citation: Venkatesa Prabhu, S., Uga Waktole, B., Gizachew Assefa and Arulvel, R., 2017. "Effect of temperature on removal of copper from electroplating industrial sludge via biosolubilization: kinetics and thermodynamics studies", *International Journal of Development Research*, 7, (08), 14614-14619.

INTRODUCTION

Development of technology and escalation of industrialization result in increase of waste products, such as sludge, those are disposed in huge quantity around the world (Babel and Del, 2006). The disposal of such wastes is the most important part of waste management, and it involves high cost and human effort. In metal-finishing industries like electroplating industry, significant quantity of heavy metal-rich sludge is generated as a waste product during the processes (Kobya *et al*., 2010). So far, this heavy metal-laden sludge has been disposed in landfills. Owing to the recent increase in the consumption of various metals and environmental restrictions, an increasing number of research works concentrating on metal removal from plating sludge have been observed (Wang *et al*., 2003). The heavy metal removal from the sludge can be achieved by several pretreatment methods before its disposal such as alkaline–chlorination–oxidation, evaporative recovery, electrocoagulation, membrane process, reverse osmosis, adsorption, ion exchange, electrochemical treatment, source control (usage of metals), and addition of strong chelating agent mainly EDTA (Ethylene Diamine Tetra Acetic acid) (Tyagi *et al*., 1988). However, these methods are limited by requirement of large amount of chemicals, high process cost, difficulties in the operational procedure, and release of harmful gases in the atmosphere (Bosecker, 1997). Alternatively, bio-based methods such as biosorption, biodegradation, biodeterioration, bioremediation, and biosolubilization are applied for treating the sludge. These methods are encouraged due to their low operating cost, high effectiveness, and ecofriendly nature than other methods mentioned earlier (Villar and Garcia, 2006). Among the bio-based methods, biosolubilization is a quite suitable and proven technique to remove the heavy metal toxics from the sludge (Pathak *et al*., 2008). In biosolubilization, the metals are solubilized and removed as leachate using the sulfur-oxidizing bacteria (Liu *et al*., 2007). Biosolubilization can be represented by the following equations:

$S^0 + H_2O + (3/2) O_2 \rightarrow H_2SO_4$ (by bacterial catalysis) (1)

H_2SO_4 + Sludge-M → Sludge-2H + MSO_4 (by chemical reaction) (2)

The elemental sulfur (S^0) is used as an energy source for such biosolubilization operation and the bacterial oxidation of S^0 results in the production of sulfuric acid, which aids to metal dissolution. *Acidithiobacillus ferrooxidans*, *A. thiooxidans*, *A. caldus*, and *A. albertensis* are the common S^0-oxidizing microorganisms that can be used in biosolubilization process (Nareshkumar and Nagendran, 2008). Like all biological processes, biosolubilization is also influenced by temperature. Many studies have suggested the possibility of using optimized temperature to improve metal solubilization rate and efficiency (Tyagi *et al*., 1994; Franzmann *et al*., 2005). Thus, the process optimization with respect to temperature and its kinetics is of immense importance in biosolubilization. In this work, experimental studies were carried out with due importance to optimize the temperature on biosolubilization of Cu from electroplating industry sludge using sludge-adapted bacteria, *A. ferrooxidans*. In addition, the rate kinetics and determination of rate-controlling step for Cu solubilization were determined using the pseudo-first-order model and shrinking core model (SCM). Further, this study extended to calculate the thermodynamic parameters such as change in Gibbs free energy, enthalpy, and entropy for biosolubilization reaction.

MATERIALS AND METHODS

Characterization of electroplating sludge

Sludge was obtained from an effluent treatment plant of electroplating industry, Chennai, India. It was collected from different depths (10 100 cm) along the sludge bed in the effluent treatment plant section and stored at 4 °C using sterilized polythene bags. It was then air-dried overnight at room temperature. To determine the total heavy metal content in the sludge, the sample was digested with nitric acid/perchloric acid/sulfuric acid at the ratio of 8:1:1. Dissolved heavy metals were analyzed by atomic absorption spectrometry (AA200 model; PerkinElmer). The ion activity was analyzed using dry sludge/water extract (10:25) through a calibrated pH meter (Eutech Instruments, Singapore). The organic matter present in the sludge was determined by Walkely–Black method (using standard 1 N $K_2Cr_2O_7$ and ferroin indicator). Micro–Kjeldahl distillation was used to analyze the total nitrogen content. Total available phosphorus content in the sludge was estimated by using micro-vanadate-molybdate method after extraction with 0.5 M sodium bicarbonate. Calcium, magnesium, and potassium contents were determined using flame photometry (CL378 model; Elico) after ammonium acetate extraction. The procedures for sludge characterization were followed as outlined in the American Public Health Association (APHA) standard (Wang *et al*., 2007). Five replicates were used for sludge characterization and the mean values are taken into consideration.

Bacterial culture and sludge adaptation

The bacterial strain, *A. ferrooxidans*, was obtained from National Collection of Industrial Microorganism (NCIM 5371), Pune, India. The culture was grown in 9K medium (pH 4) with S^0 as the energy source. The medium had following chemical composition: S^0 (sterilized by tyndallization), 10 g/L; $MgSO_4.7H_2O$, 0.5 g/L; $(NH_4)_2SO_4$, 3 g/L; K_2HPO_4, 0.5 g/L; $Ca(CO_3)_2$, 0.01 g/L; and KCl, 0.1 g/L. To adapt the culture to sludge, the culture was developed in 80 mL sterilized 9K media supplemented with 0.2% (w/v) of sludge along with 20% (v/v) of inoculum for 2 weeks. From this culture, 20 mL inoculum was transferred to 80 mL fresh 9K media containing 0.6% (w/v) sludge. From this culture, a subculture was prepared using the fresh media containing sludge level 1.0% (w/v). It can be considered as sludge-adapted culture which behaves with improved resisting activity against sludge toxicity. This sludge-adapted bacterial culture was used as inoculums for the biosolubilization experiments.

Biosolubilization assays

Biosolubilization experiments were performed in 250 mL Erlenmeyer flasks, each flask contained working 100 mL volume, 90% (v/v) 9K medium, and 10% (v/v) inoculum along with 5% (w/v) sludge loading. The pH value of the media was initialized to 4.05 using the 1 N H_2SO_4, and the flasks were shaken at 200 rpm. To investigate the influence of temperature on biosolubilization, the experiments were carried out at different predetermined temperatures ranging from 27 to 39 °C. A control experiment without inoculum was carried out to compare with the biosolubilization efficiency. During the biosolubilization, the media pH was assessed every day by a calibrated pH meter (Eutech Instruments). At every 2-day intervals, the samples (5 mL) were periodically collected from the flasks and were centrifuged at 3000 rpm for 20 minutes. The supernatants were collected from the centrifuge and the dissolved Cu concentration was analyzed by atomic absorption spectrometry (AA200 model; PerkinElmer). The losses in working volume due to the sample collection and evaporation were compensated by adding the fresh nutrient solution (9K medium without elemental sulfur). Cu removal efficiency by biosolubilization, denoted by E_{Cu} (%), was calculated as the ratio between the solubilized Cu and the total Cu present in the original sludge, which can be calculated from the following equation:

$E_{Cu} (\%) = [(M^{t}_{sol}) \times 100]/(M_T)$ (3)

where, M^t is the solubilized Cu concentration at time t during the biosolubilization and M_T the total Cu concentration present in the original sludge.

Kinetic procedures

The pseudo-first-order kinetic model can be applied to figure out the rate of biosolubilization of metal. In this study, the rate of biosolubilization Cu can be deduced from pseudo-first-order model, as given in equation (4).

Rate of solubilization of Cu = $\frac{dC}{dt} = k(C \quad C_t)$ (4)

where (dC/dt) is the rate of solubilization of Cu and k is defined as the rate constant of solubilization that refers the speed of the reaction. By integrating equation (4) between respective limits of Cu concentration (at $t = 0$, $C_t = 0$ and $t = td$, $C_t = C_t$) the following equation can be obtained:

$$\ln\left(\frac{C}{C - C_t}\right) = kt \qquad (5)$$

where C and C_t are the total available Cu concentration in the original sludge and solubilized Cu concentration in aqueous phase at time t during biosolubilization, respectively. Equation (5) is the simple linear model. It was used to determine reaction rate constant as the slope obtained from the plot of $\ln[C/(C - C_t)]$ versus time. To get a better understanding of the mechanism of biosolubilization, the rate-controlling step was identified by the kinetic studies based on the Shirking Core Model (SCM) of fluid–particle reaction (Younesi *et al*., 2006). According to SCM, the controlling step, ash layer diffusion, or chemical reaction may control the rate of Cu solubilization. The developed equations for the mentioned rate-controlling steps are $1+2(1 - X_{Cu}) - 3(1 - X_{Cu})^{2/3} = F_o t$ and $1 - (1 - X_{Cu})^{1/3} = F_o t$, respectively, where X_{Cu} is the fraction of solubilized Cu present in the aqueous phase at time t and F_o is the observed kinetic constant applicable to the respective model. On the basis of the linear regression correlation from the plots of $[1 + 2(1 - X_{Cu}) - 3(1 - X_{Cu})^{2/3}]$ versus time and $[1 - (1 - X_{Cu})^{1/3}]$ versus time, the rate-controlling step was determined.

Determination of activation energy

The activation energy is the minimum amount of energy required to promote the reaction. The Arrhenius equation [Equation (6)], which correlates the activation energy and rate constant, can be used to calculate activation energy (Mehta *et al*., 2003):

$$\ln k = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \qquad (6)$$

where E is the activation energy (cal/mol), A the frequency factor, k the rate constant of biosolubilization, R the gas constant (J/mol K), and T the absolute temperature (K). Based on equation (6), an Arrhenius plot [lnk versus $(1/T)$] was prepared. Using this plot, activation energy was calculated from the slope.

Determination of thermodynamic parameters

The Gibbs free energy is a thermodynamic potential that measures process-initiating work obtainable from a thermodynamic system at isothermal and isobaric processes. In this study, the change in Gibbs free energy (ΔG°) was determined using the correlation, $\Delta G^\circ = -RT\ln K_c$ (Adesola *et al*., 2012), where R is the gas constant (8.314 J/mol/K), T the absolute temperature (K), and K_c the equilibrium constant. The equilibrium constant (K_c) was calculated as the ratio of concentration of solubilized Cu present in the aqueous solution to the concentration of Cu present in leach, the residue after attaining the saturated solubilization. ΔG° can be correlated with thermodynamic parameters, change in entropy (ΔS°), and enthalpy (ΔH°) by van't Hoff equation as given next (Pradhan *et al*., 2010).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (7)$$

Replacing ΔG° by ($-RT\ln K_c$) and rearranging, equation (7) can be written as follows:

$$\frac{\Delta S}{R} - \frac{\Delta H}{RT} = \ln K_c \qquad (8)$$

Using the relationship given in equation 8, ΔH° and ΔS° were determined from the slope and intercept of the linear plot ($\ln K_c$) versus (1/T).

RESULTS AND DISCUSSION

Sludge characteristics

The selective physicochemical characteristics of electroplating sludge sample are listed in Table 1.

Table 1. Physicochemical properties of sludge sample (all values are expressed mg/kg of dry sludge)

Sl. No	Selected parameters	Compositions
1	pH	9.1 ± 0.14
2	Total nitrogen	2,505 ± 67
3	Total available phosphorus	1,509 ± 46
4	Sulfate	520 ± 68
5	Organic mater	0.9± 0.14%
6	Calcium	20,210± 176
7	Magnesium	8,610± 243
8	Potassium	356 ± 38
9	Copper	3,540± 72

±The standard deviation of data represents mean value of five samples.

The sludge characterization revealed that the sludge was in alkali condition (pH 9.1). The sludge contained 2505 mg kg^{-1} total available Kjeldahl nitrogen, 1509 mg kg^{-1} phosphorus, and moderate level of potassium (356 mg kg^{-1}). These nutrients could be used by the culture, *A. ferrooxidans*, during biosolubilization. Calcium and magnesium contents were also found to be high (20,210 and 8610 mg kg^{-1}, respectively). Organic carbon present in the sludge was observed to be quite low (0.9 mg kg^{-1}). Hence, the adverse effect due to organic inhibition can be ignored. The heavy metal analysis showed that Cu was retained in the sludge (approximately 3540 mg kg^{-1}). It indicated that the Cu content in the sludge is too high and posing a serious threat to the environment when it disposed on land without proper treatment.

Effect of temperature on media pH during biosolubilization

The S^0 oxidation by *A. ferrooxidans* results in production of sulfuric acid, which is associated with reduction of media pH in biosolubilization (Chen and Lin, 2001; Couillard *et al*., 1994). This bioacidification can be assessed by monitoring the decrease in pH. The profiles of change in media pH during biosolubilization experiments at different temperatures are presented in Figure 1. In the control, there was no significant change in pH value. However, a mild drop in pH value (from 4.05 to 3.6) occurred due to chemical oxidation of S^0. In the inoculated experiments at different temperatures, a sharp decrease in the pH value was observed within 2 weeks. It showed that the good adaptation and rapid growth of microorganism are accompanied by better S^0 oxidation. Though there is a decrease in pH value with increasing temperature, further drop in pH was not observed beyond 36 °C. After the 20th day, the pH values of the media were dropped from the initial value of 4.05 to 2.59, 2.45, 2.4, and 2.35 at 27, 30, 33, and 39 °C, respectively. In the experiment conducted at 36 °C, the pH value dropped to 2.06 after the 20th day, which was the least among the experiments at different temperatures. Therefore, it is apparent that 36 °C is the appropriate temperature for bringing down the media pH by approximately 2.0, which supports the published data about temperature sensitiveness of *A. ferrooxidans* (Pathaka *et al*., 2009; Liu *et al*., 2003).

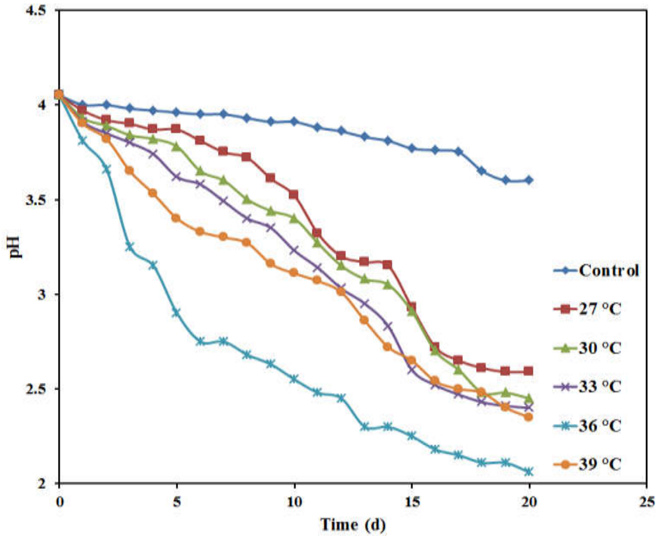

Figure 1. Change in media pH during biosolubilization of Cu at different temperatures

Effect of temperature on Cu solubilization

Figure 2 shows the efficiency of Cu solubilization with time at different temperatures. In the control experiment, without inoculum, 6.05% of Cu was found to be solubilized after 20th day. It might be due to the sulfuric acid added for initializing pH value to 4. In the experiments at 27, 30, 33, and 36 °C, the efficiencies of Cu solubilization were found to be 40.99%, 50.28%, 56.85%, and 58.69%, respectively. With further increase in temperature to 39 °C, the solubilization of Cu reduced to 37.41%. It showed that 36 °C is the ideal temperature to achieve enhanced Cu solubilization for the type of microbe and sludge used in this process. Though the biosolubilization of Cu ranging 80% 90% is reported elsewhere, that depends on the sludge type, solid concentration, and type of bacteria used in the process. The observed profiles of Cu solubilization were well supported by the decrease in pH coupled with increase in ORP.

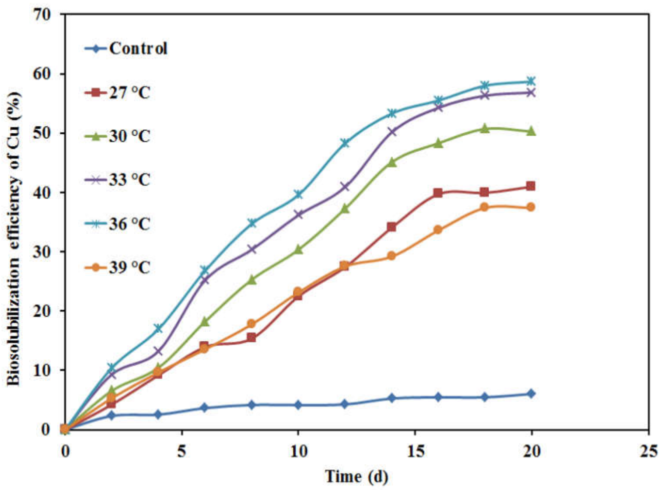

Figure 2. Biosolubilization efficiency of Cu at different temperatures

Kinetics of rate and rate-controlling step

The pseudo-first-order empirical equation [equation (5)] was used to analyze the rate kinetics of Cu solubilization. Figure 3 shows a plot using solubilization data based on equation (5). The linear regression analysis revealed that the pseudo-first-order rate kinetic model is well fitted to the experimental data. The kinetic result showed that the rate constant value increases with temperature up to 36°C. The rate constant value of Cu solubilization at 27°C was calculated to be 0.0124 d^{-1}. With further increase in temperature to 30 and 33°C, the values of rate constant increased to 0.0163 and 0.0188 d^{-1}, respectively. The rate constant value attained to be maximum (0.0201 d^{-1}) at 36°C. However, at temperature beyond 36°C (at 39°C), the rate constant value dropped to 0.0113 d^{-1}. This decline was due to the adverse effect of temperature on bacterial growth.

The rate-controlling step was determined using the SCM. Figures 4a and 4b show the graphical fitting to examine the significance of mathematical linear equation of controlling steps. The correlation coefficient obtained from the graphs gives the evidence that solubilization data fit better to the model of chemical reaction control step. It is clear that the rate-controlling step is a chemical reaction between bacterially produced sulfuric acid and metal components present in the sludge. It was observed that there was no effect of temperature on the rate-controlling step for Cu solubilization.

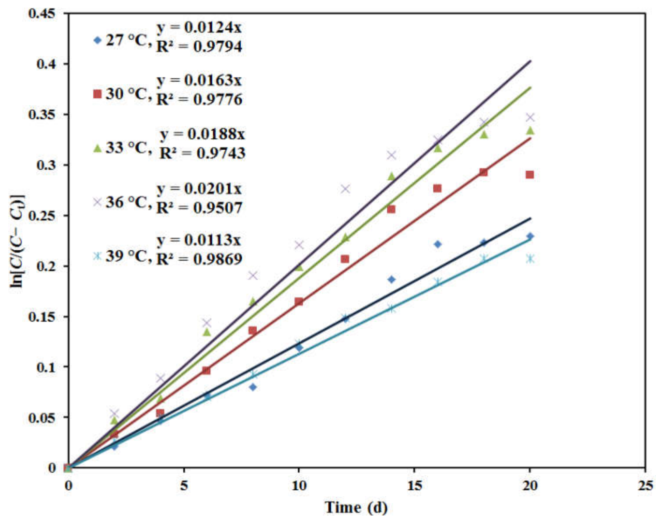

Figure 3. Pseudo-first order kinetic plot for Cu solubilization at different temperatures

Activation energy and thermodynamic properties

The activation energy was determined using Arrhenius equation, as given in equation 5. Following equation (6), an Arrhenius plot of ln$k$ versus $(1/T)$ was prepared (Figure 5). From the slope, the activation energy was calculated to be 40.99 kJ/mol. The values of G˚ for biosolubilization at 27, 30, 33, 36, and 39°C were found to be −912.128, −22.420, −699.877, −708.280, and −1336.152 J/mol, respectively. The negative values of G˚ indicate the spontaneity in the biosolubilization process. The values of H˚ and S˚ were calculated by plotting (1/T) and (lnK_c) according to equation 8 and the same is presented in Figure 6. It was found that the values of H˚ and S˚ were 61.62 kJ/mol and 202.89 J/mol/K, respectively.

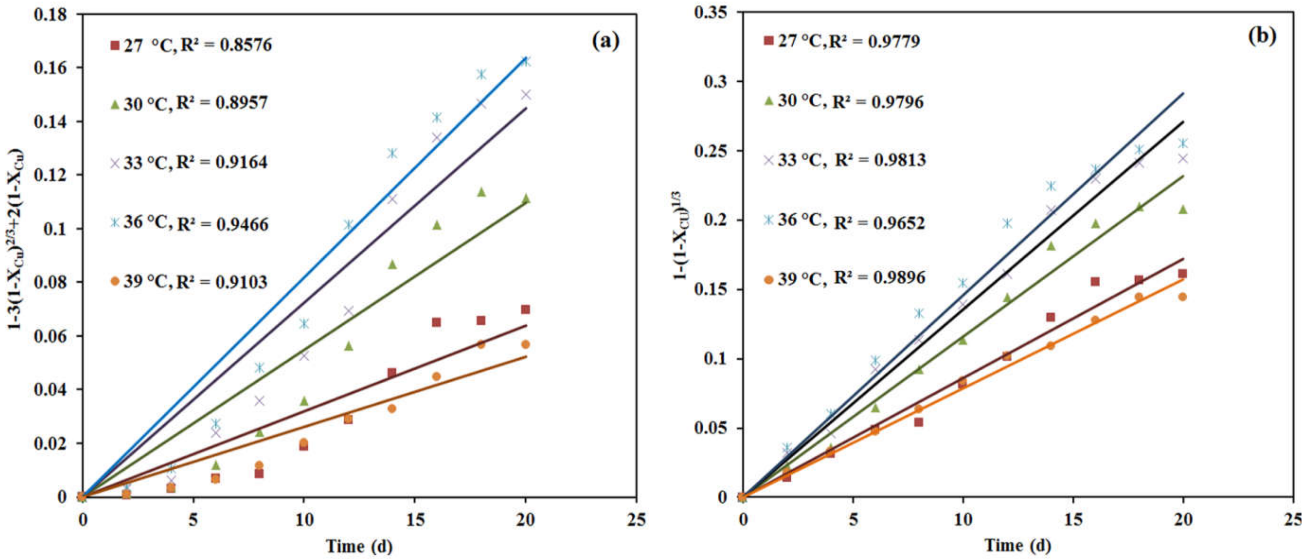

Figure 4. Plot for determination of rate controlling-step for Cu solubilization (a) Ash layer diffusion control (b) Chemical recation control

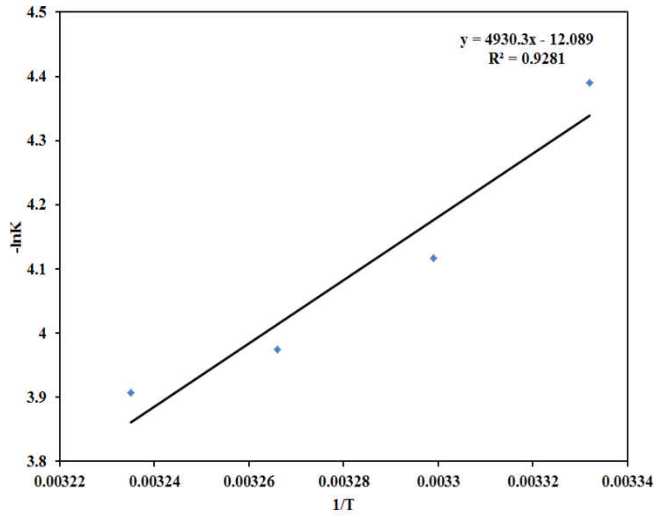

Figure 5 Arrhenius plot for activation energy determination

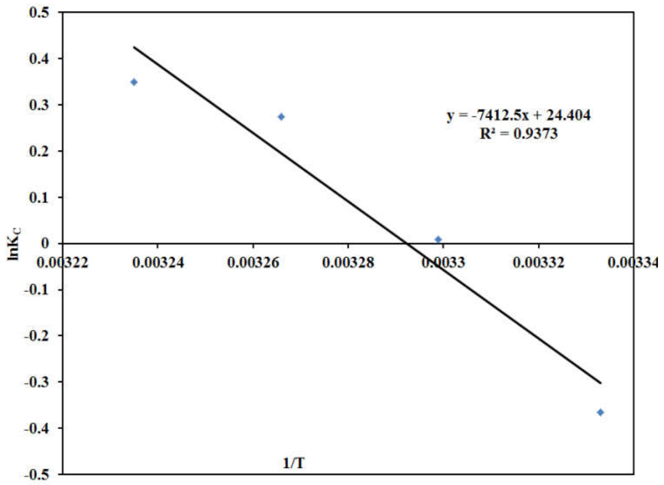

Figure 6. Thermodynamic Plot for determination of H° and S°

The positive value of ΔH° denotes endothermic nature of the biosolubilization process. The positive value of ΔS° denotes increment in randomness for Cu ions at the sludge–solution interface during biosolubilization.

Conclusion

An investigation on the removal of Cu from the electroplating industrial sludge via biosolubilization with due importance to optimize the temperature was carried out. The experiments were performed in shake flasks using adapted *A. ferrooxidans*. The experimental conditions were 100 mL of working volume, 90% (v/v) of 9K medium, 10% (v/v) of inoculum, 5% (w/v) of sludge loading, and temperature range of 27 39°C. The results from the experiments proved that 36°C is the ideal temperature for better Cu solubilization. At this temperature a maximum of 58.69% Cu was solubilized. The kinetic study revealed that the solubilization rate constant is considerably influenced by temperature. It was observed that the maximized value of rate constant, 0.0201 d^{-1}, was obtained at 36 °C. Using SCM, the rate-controlling step was identified as chemical reaction. From the Arrhenius equation, activation energy was calculated to be 40.99 kJ/mol. The values of thermodynamic parameters, H°, and S° were calculated to be 61.62 kJ/mol and 202.89 J/mol/K, respectively.

REFERENCES

Adesola Babarinde, N.A., Oyebamiji Babalola, J., Adegoke, J., Maraizu, U., Ogunbanwo, T. and Ogunjinrin, F. 2012. “Kinetic, equilibrium and thermodynamic studies of the biosorption of Ni(II), Cr(III) and Co(II) from aqueous solutions using banana (*Musa acuminata*) leaf “, *Int. J. Phys. Sci.*, Vol. 7, No. 9, pp. 1376–1385.

Babel S. and Del Mundo Dacera, D. 2006. “Heavy metal removal from contaminated sludge for land application”, *Waste Manage.*, Vol. 26, No. 9, pp. 988–1004.

Bosecker, K. 1997. “Bioleaching: metal solubilizations by microorganisms”, *FEMS Microbiol. Rev.*, Vol. 20, Nos. 3–4, pp. 591–604.

Chen, S.Y. and Lin, J.G. 2001. “Effect of substrate concentration on bioleaching of metal-contaminated sediment”, *J. Hazard. Mater*. Vol. B82, pp. 77–89.

Couillard, D., Chartier, M. and Mercier, G. 1994. “Major factors influencing bacterial leaching of heavy metals (Cu and Zn) from anaerobic sludge”, *Environ. Pollut.*, Vol 85, pp. 175–184.

Franzmann, P.D., Haddad, C.M., Hawkes, R.B., Robertson, W.J. and Plumb J.J. 2005. "Effects of temperature on the rates of iron and sulfur oxidation by selected bioleaching *Bacteria* and *Archaea*: application of the Ratkowsky equation", *Miner. Eng*., Vol. 18, Nos. 13–14, pp. 1304–1314.

Kobya, M., Demirbas, E., Parlak, N.U. and Yigit, S. 2010. "Treatment of cadmium and nickel electroplating rinse water by electrocoagulation", *Environ. Technol.*, Vol. 31, No. 13, pp. 1471–1481.

Liu, H.L., Chiu, C.-W. and Cheng, Y.C. 2003. "The effects of metabolites from the indigenous *Acidithiobacillus thiooxidans* and temperature on the bioleaching of cadmium from soil", *Biotechnol. Bioeng.,* Vol. 83, No. 6, pp. 638–645.

Liu, Y.G., Zhou, M., Zeng, G.-M., Li, X., Xu, W.-H. and Fan T. 2007. "Effects of solids concentration on removal of heavy metals from mine tailings via bioleaching", *J. Hazard. Mater.*, Vol. 141, No. 1, pp. 202–208.

Mehta, K.D., Pandey, B.D. and Mankhand, T.R. 2003. "Studies on kinetics of biodissolution of metals from Indian Ocean nodules", *Miner. Eng.*, Vol. 16, No. 6, pp. 523–527.

Nareshkumar, R. and Nagendran R. 2008. "Changes in nutrient profile of soil subjected to bioleaching for removal of heavy metals using *Acidithiobacillus thiooxidans*", *J. Hazard. Mater.*, Vol. 156, Nos. 1–3, pp.102–107.

Pathak, A., Dastidar, M.G. and Sreekrishnan, T.R. 2008. "Bioleaching of heavy metals from anaerobically digested sewage sludge", *J. Environ. Sci. Health*, Vol. 43, No. 4, pp. 402–411.

Pathaka, A., Dastidara, M.G. and Sreekrishnan, T.R. 2009. "Bioleaching of heavy metals from sewage sludge using indigenous iron-oxidizing microorganisms: Effect of substrate concentration and total solids", *World Acad. Sci., Eng. Technol.*, Vol. 3, No.10, pp. 519–524.

Pradhan, D., Kim, D.J., Ahn, J.G., Chaudhury, G.R. and Lee S.W. 2010. "Kinetics and statistical behavior of metals dissolution from spent petroleum catalyst using acidophilic iron oxidizing bacteria", *J. Ind. Eng. Chem.*, Vol. 16, No. 5, pp. 866–871.

Tyagi, R.D., Couillard, D. and Tran, F. 1988. "Heavy metals removal from anaerobically digested sludge by chemical and microbiological methods", *Environ. Pollut.*, Vol. 50, No. 4, pp. 295–316.

Tyagi, R.D., Sreekrishnan, T.R., Blais, J.F. and Campbell, P.G.C. 1994. "Kinetics of heavy metal bioleaching from sewage sludge—III. Temperature effects", *Water Res.*, Vol. 28, No. 11, pp. 2367–2375.

Villar, L.D. and Garcia, O, Jr. 2006. "Effect of anaerobic digestion and initial pH on metal bioleaching from sewage sludge", *J. Environ. Sci. Health A Tox. Hazard Subst. Environ. Eng.*, Vol. 41, No. 2, pp. 211–222.

Wang, L., Chua, H., Wong, P.K., Lo, W.H. and Yu, P.H.F. 2003. "Ni^{2+} removal and recovery from electroplating effluent by *Pseudomonas putida* 5-x cell biomass", *J. Environ. Sci. Health*, Vol. A38, No. 3, pp. 521–531.

Wang, Y.-S., Pan, Z.-Y., Lang, J.-M., Xu, J.-M. and Zheng, Y.-G. 2007. "Bioleaching of chromium from tannery sludge by indigenous *Acidithiobacillus thiooxidans*", *J. Hazard. Mater.*, Vol. 147, Nos. 1–2, pp. 319–324.

Younesi, S.R., Alimadadi, H., Keshavarz Alamdari, E. and Marashi, S.P.H. 2006. "Kinetic mechanisms of cementation of cadmium ions by zinc powder from sulphate solutions", *Hydrometallurgy*, Vol. 84, Nos. 3–4, pp. 155–164.

****