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Kinetics on Biosolubilization of Copper from Electro Plating Sludge: Effect of Agitation Speed

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Abstract: In this present study, typical characteristics and kinetics of biosolubilization of copper from the electro plating industrial sludge using microorganism, *Acidithiobacillus ferrooxidans* was investigated. Since agitation speed is one of the key factor influence the biosolubilization process, hence it is necessary to study the effect of agitation speed on biosolubilization method. The experiments were carried out in 250 mL Erlenmeyer flasks with agitation speed varying from 100 to 300 rpm at temperature 30 °C. The attainment of Cu biosolubilization was inspected for the period of 20 days. It was observed that the high pH reduction, absence of lag phase and improved Cu solubilization were obtained in the experiment with 200 rpm. At this agitation speed, the efficiency of biosolubilization of Cu from the sludge was 56.85 % after 20 days. The pseudo-first order kinetic equation was used to determine the rate-constant of Cu solubilization. The kinetic study indicated that the rate-constant of Cu solubilization was observed to be maximum at the agitation speed of 200 rpm. Using shrinking core model kinetics, it was also observed the rate of solubilization was controlled by the chemical reaction step.
Keywords : Biosolubilization, agitation, pseudo-first order, rate constant, shrining core model.

Introduction

The hazardous consequences of heavy metals arise from the metal interaction with proteins (enzymes) and metabolic processes getting inhibition in humans, plants and animals. It may cause serious threat to life of plants, aquatic organisms, animals and humans being. The heavy metal concentration in the wastes sludge can be reduced by several pretreatment methods such as alkaline-chlorination-oxidation, electro coagulation, adsorption, membrane process, reverse osmosis, evaporative recovery, ion exchange, and electrochemical treatment[1]. The main drawback of these methods are need of chemicals in large amount, high operating cost, difficulties in the working procedure and release of toxic gases in the atmosphere[2]. Hence suitable remediation techniques are required to alter the treatment of wastes for removing heavy metals[3].

Biosolubilizationis a process, which employs the microorganisms to transform solid insoluble compounds into soluble and extractable elements. Usually, biosolubilization is used to leach the metals from its sulfide ores. Hence, it is called as bioleaching. This process has several advantages for leaching the metals such as less energy requirement, environmentally friendly, and no need of sophisticated control instruments. Even though this process is originally developed for metal extraction from its ore, in last decade, lot of work have been concentrated for sludge detoxification to remove the heavy metals. In bioleaching, acidophilic sulfur-oxidizing microorganisms are employed for the recovery of metals[4].The oxidation of elemental sulfur or reduced sulfur compounds leads to generation of H_2SO_4 by the acidophilic bacteria[5] (Equation1 and Equation 2). Then the bacterially produced H_2SO_4 is responsible for the metal biosolubilization.

$S^0+H_2O+1.5O_2 \rightarrow H_2SO_4$………………………………………………….. (1)

H_2SO_4+Sludge-M →Sludge-2H+MSO_4(where M is a bivalent metal)…. (2)

The efficiency of bioleaching is predominantly influenced by different physical, chemical and biological factors of bioleaching system such as material nature, concentration of solids, temperature, pH, agitation, oxidation-reduction potential (ORP),medium composition, strains of bacteria and concentration of cell. Among these factors agitation is one of the main factors that influencing the process quite reasonably[6].It is also required to find the optimal velocity of agitation to attain proper aeration, suspension of solids in homogenous form, uniformity in pH and temperature, transfer of heat and mass (nutrients, oxygen and carbon di oxide).

The objective of this study was to optimize the bioleaching process with due respect to agitation speedfor evaluating the efficiency of solubilization of Cu from electroplating industrial sludge using the bacteria *Acidithiobacillus ferrooxidans*. In addition, the rate kinetics and determination of rate-controlling step of Cu solubilization were studied using the pseudo-first order model and shrinking core model (SCM), respectively.

Experimental

Characterization of Electro plating sludge

Electro plating sludge was obtained from effluent treatment plant of plating industry situated in Chennai, India. It was collected from the sludge bed using sterilized polythene bags and stored at 4°C to avoid any changes in its property. It was air dried for overnight at room temperature. In order to estimate the total heavy metal content in the sludge, the sample was digested with concentrated nitric acid/per chloric acid/sulfuric acid which prepared at the ratio 8:1:1. The digested heavy metals from the aqueous solution were analyzed by atomic absorption spectrometry (Perkin Elmer, AA200 model). Using calibrated pH meter (Eutech Instruments, Singapore), the ion activity was analyzed afterpreparing dry sludge/water extract (10:25). Walkely-Black method (using standard 1N $K_2Cr_2O_7$ and Ferroin indicator) was used to determine the organic matter present in the sludge. The total nitrogen content was determined by Micro-Kjeldahl distillation method. After extracting the sludge sample with 0.5M sodium bicarbonatethe total available phosphorus was determined by Micro-vanadate-molybdate method. Calcium, magnesium and potassium contents of the sludge sample were determined after extracting with ammonium acetate solution by flame photometry (Elico, CL378 model). Sludge characterization was followed according tothe protocols outlined in the American Public Health Association (APHA) standard[7].

Bacterial cultureand sludge adaptation

The bacterial strain, *A. ferrooxidans* (NCIM 5371) used in biosolubilization process was obtained from National Collection of Industrial Microorganism, Pune, India. Prior to prepare inoculum, the bacterial culture was enriched in 9K medium (pH 4) with S^0 as energy source. The composition of medium had: S^0 (sterilized by tyndallization), 10 g/L; MgSO4.7H_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. For preparing the inoculum, adaptation of the culture to sludge was carried out to enhance the resistance against sludge toxicity. For that,20% (v/v) of bacterial culture was inoculated in 80 mL sterilized 9K media containing 0.2% (w/v) of sludge. From this culture, 20 mL was transferred to 80 mL the fresh 9K media containing 0.6% (w/v) of sludge. It was sub-culturedagain using the fresh media contained sludge level of1.0% (w/v). This can be considered as the sludge adapted culture and it was used as inoculums for the further biosolubilization experiments.

Biosolubilization assays

The biosolubilizationwere performed in 250 mL Erlenmeyer flasks. Each flask had the 100 mL of working volume which contained 90% (v/v) of 9K medium, 10% (v/v) of inoculum and 5% (w/v) of sludge loading. To study the effect of agitation speed on biosolubilization, the experiments were carried out at different agitation speed ranging from 100 to 300 rpm.Initial value of pH of the media was adjusted to 4 using the 1N $H_2SO_4$for stimulating the bacterial activity. The flasks were maintained at30°C. A control experiment, without inoculum, was also carried outto compare the biosolubilization efficiency with inoculated experiments. During the biosolubilization process, the media pH was measured every day by calibrated pH meter (Eutech Instruments, Singapore). Oxidation reduction potential (ORP) of the medium was monitored every day using of calibrated ORP meter (Eutech Instruments, Singapore).The samples (5 mL) were periodically collected from the flasks for every two day intervals and subjected to centrifuge at 3000 rpm for 20 minutes. The supernatants were subjected for the determination of dissolved Cu concentration by Atomic Absorption Spectrometry (Perkin Elmer, AA200 model).In order to compensate the volume losses, fresh nutrient solution (9K medium without elemental sulfur) was added. The removal efficiency of Cu [E(%)] by biosolubilization was calculated as the ratio between the solubilized Cu and the total Cu present in the original sludge. It can be calculated from the following equation.

$E(\%) = [(C^t)/ (C_T)] \times 100$(3)

Here, $C^t$is solubilized Cu concentration at the time t during the biosolubilization and C_T is the total Cu concentration present in the original sludge.

Kinetic approaches

The pseudo-first order kinetic model can be used to figure out the rate of biosolubilization of copper. In this study, the rate of Cu biosolubilization (k) can be deduced from pseudo-first order model whichis given in equation4.

$$\ln\left(\frac{C}{C - C_t}\right) = kt \qquad (4)$$

Here C and C_t are the total available Cu concentration in the original sludge and solubilized Cu concentration respectively, in aqueous phase attime't'. Using equation 4,the slope obtained from the plot of $\ln[C/(C- C_t)]$ versus time was prepared to determine reaction rate constant. In order to get a clear outline of biosolubilization mechanism, the rate-controlling step was determined based on the shrinking core model (SCM) of fluid-particle reaction[8]. According to SCM, the rate may be controlled either by ash layer diffusion or chemical reaction step. The developed equationsfor the above mentioned rate-controlling steps are $1+2(1-X_{Cu}) -3(1-X_{Cu})^{2/3} = F_ot$ and $1- (1-X_{Cu})^{1/3} = F_ot$, respectively. Where, X_{Cu} is the fraction of solubilized Cuat time 't' in the aqueous phase and F_o is the observed kinetic constant for the respective model. The rate-controlling step was determinedfrom the linear regression correlation of the plots,$[1+2(1-X_{Cu})-3(1-X_{Cu})^{2/3}]$ versus time and $[1-(1-X_{Cu})^{1/3}]$ versus time.

Results and Discussion

Sludge characteristics

The characteristics of electro plating sludge sample are listed in the table 1. The characterization of sludge revealed that the sludge was in alkali condition (pH 9.1). The total available Kjeldahl Nitrogen in the sludge was about2505 mg kg^{-1}, 1,509 mg kg^{-1} of phosphorus, and moderate level of potassium (356 mg kg^{-1}). During biosolubilization these nutrients could be utilized as by*A. ferrooxidans*. Calcium and magnesium (20210 and 8610 mg kg^{-1}, respectively) were also found in high level. The level of organic carbon in the sludge was observed to be low (0.9 mg kg^{-1}). Hence, the adverse effect caused by the organic source can be neglected. The analysis of heavy metal presentin the sludge revealed that the copper content in the sludge was about 3540 mg kg^{-1}. It is extremely high and causes a serious threat to the environment when it disposed in land without proper treatment.

Table 1.Physico-chemical properties of soil sample

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

± indicates the standard deviation of data represent mean value of five samples

Effect of agitation speed on media pH during biosolubilization

The oxidation of sulfur by *A. ferrooxidans* results in production of sulfuric acid which causes the pH reduction in the media during biosolubilization. This bio-acidification can be assessed by monitoring the pHdecrement. The profiles of pH change in media during biosolubilization at different agitation speed were depicted in figure 1. In the control, there was no effective change in the pH value was observed. The chemical oxidation of S^0 created a minimum drop in pH value (from 4.06 to 3.6) in control experiment. In the inoculated flasks at different agitation speeds, significant decrement in the pH value wasrecorded within two weeks.It revealed that therapid growth and good adaptation of microorganism. During 20 days of period, the pH value of the media was dropped from the initial values 4.06 to 2.58, 2.45, 2.06, 2.33 and 2.39 at 100, 150, 200, 250, and 300 rpm, respectively. Therefore, 200 rpm of the agitation speed, would be beneficial to reduce the pH of the media approximately to 2.0which suitable for the effective biosolubilization[9,10].

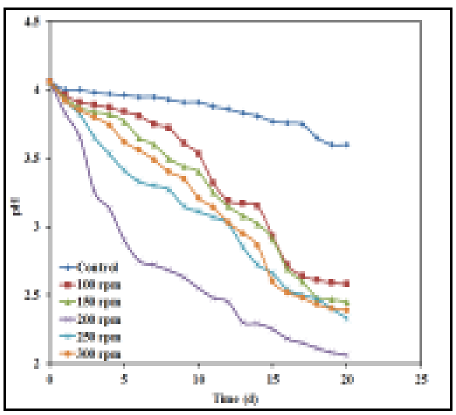

Figure 1.Change in pH value during biosolubilization of Cu at different agitation speeds

Effect of agitation speed on ORP of the medium

The change in ORPat different agitation speed during biosolubilization is presented in figure 2. Due to the absence of bacterial activity in the control experiment, the ORP was found to be constant about 195 mV. The ORP values were attained as 236, 241, 461, 389 and 328 mV in the experiments at 100,150,200,250, and 300 rpm, respectively, after 20^{th} day. A maximum evolution in ORP from165 to 461 mV was found in the experiment at 200 rpm. It clearly showed that the rpm of 200helps the effective oxidizing environment for the type of sludge and microorganism used. This resultsare in line with other reports which suggested that 400-500 ORP range is suitable for the improved biosolubilization[11,12].

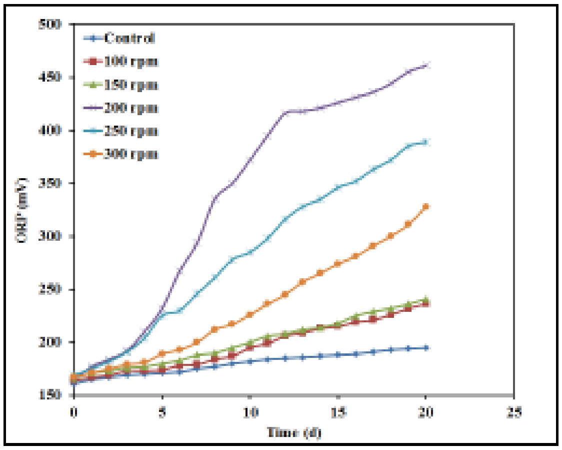

Figure 2. Change in ORP value during biosolubilization of Cu at different agitation speed

Effect of agitation speed on Copper solubilization

Figure 3 shows the Cu solubilization efficiency with time at different agitation speeds. Due to the absence of bacterial activity, the control experiment showed only5.35% of Cu solubilization at the end of 20th day. This solubilization was due to the sulfuric acid added for the initialization of pH value to the 4.05.For the experiments at different agitation speeds, the Cu solubilization efficiencies were found to be 30%, 54.57% and 56.85%respectively at 100,150, and 200 rpm. When agitation speed is further increased beyond 200 rpm, the solubilization of Cu reduced to 36.33% and 31.99% at 250 rpm and 300 rpm, respectively. It proved that 200 rpm of agitation speed is ideal for the achievement of enhanced Cu solubilization.Though the biosolubilization of Cu ranging 80–90% is reported somewhere else, that may be dependent on the sludge type, solid concentration, and type of bacteria used. The profile of Cu solubilization observed was suitably assisted by the pH decrement coupled with ORP increment.

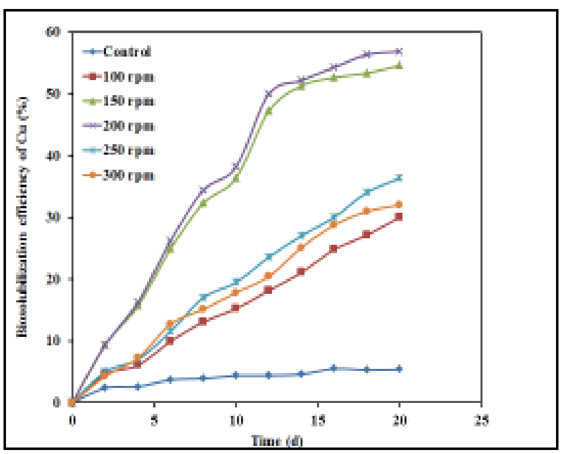

Figure 3. Biosolubilization efficiency of Cu at different agitation speeds

Kinetics of rate and rate-controlling step

The empirical equation (Equation 4) of pseudo-first order was used to determine the solubilization rate of Cu. Figure 4 show a plot based on pseudo-first-order rate kinetic model. The kinetic result indicated that the rate constant value increases with agitation speed up to 200 rpm. At 100 rpm the rate constant value of Cu solubilization was calculated to be 0.0174 d^{-1}. With further increase in agitation speed of150rpm, the values of rate constant increased to 0.0451d^{-1}. The rate constant value attained as maximum of 0.0479d^{-1} at 200 rpm. When the agitation speed increased beyond 250 rpm and 300 rpm, the rate constant value dropped to 0.0225 $d^{-1}$and 0.0199 d^{-1}. This decline was due to the adverse effect of agitation speed to bacterial growth.

Figure 5 shows the graphical fit for examine the significance of mathematical linear equation of the rate controlling steps.From the results, it was found that solubilization data fit better to the model of chemical reaction control step. It cleared that the rate controlling factor is chemical reaction between bacterially produced sulfuric acid and metal components present in the sludge. It was also observed that there was no effect of agitation speed on the rate-controlling step in Cu solubilization.

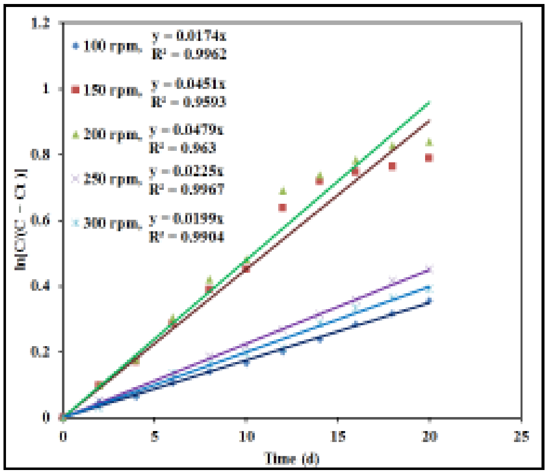

Figure 4. Pseudo-first order kinetic plot for Cu solubilization at different agitation speed

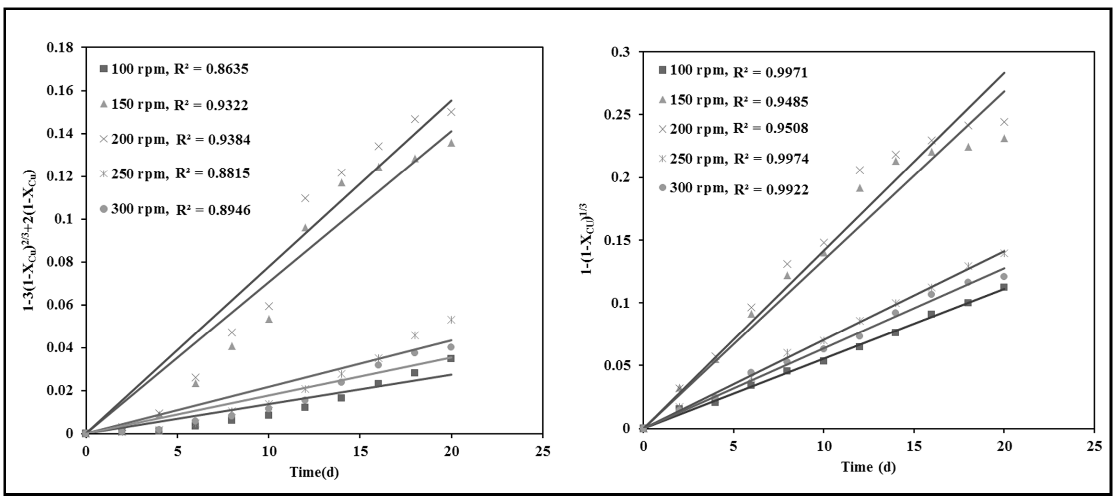

Figure 5. Plot for determination of rate controlling-step for Cu solubilization.

Conclusions

An investigation on the removal of Cu from the electro plating industrial sludge via biosolubilization was carried out under different agitation speeds (from 100 to 300 rpm). The experiments were performed in shake flask using adapted *A. ferrooxidans*. The experimental conditions were 100 mL of working volume have 90% (v/v) of 9K medium, 10% (v/v) of inoculum, and 5% (w/v) of sludge load and at 30°C.From the results, the following conclusions were drawn:

1. Agitation speed of 200 rpm is ideal for efficient Cu biosolubilization.
2. The kinetic study indicates that the solubilization rate constant is considerably influenced by different agitation speed. It was observed that the maximized value of rate constant $0.0479 d^{-1}$ was obtained at 200rpm.
3. The rate-controlling step of Cu biosolubilization was identified as chemical reaction.

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