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Effect of Temperature on Removal of CR (VI) From Tannery Sludge through Bioleaching: Studies and Kinetics

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Abstract: Tannery industries generally produce huge quantity of Cr(VI) laden sludge that poses a serious threat to the environment while disposing it in landfill without proper treatments. Bioleaching is found to be the attractive technology for treating this kind of sludge to remove heavy metals because of its environmentally friendly nature and cost benefits. But, there are several process parameters including temperature play vital role for efficient bioleaching due to microbial sensitivity with temperature. In the present study, the influence of temperatures on the removal efficacy of Cr(VI) from tannery sludge was investigated using the bacteria, Acidithiobacillus ferrooxidans in the shake flask. Results showed that the maximum of 91.2% Cr was removed from the sludge under the temperature maintained at 310 K. The obtained bioleaching data were subjected to kinetic studies for rate-controlling step. It was found that the analysis using shrinking core model on bioleaching data indicated that the chemical reaction control model holds good. This study gives a design strategy with respect to temperature for treating tannery sludge to remove toxic Cr by bioleaching.
Keywords: Bioleaching, Chromium(VI), Rate controlling step, *Acidithiobacillus ferrooxidans*,Shrinking core model.

I. INTRODUCTION

Tanning is a process in which the animal skins are treated to produce leather that is more durable and susceptible to decomposition. Tanning can be performed with either vegetable or mineral methods. Cr is used in this process in order to produce stretchable leather that has extensive applications in the industries[1].Now a day, 80−90% of leather processing in the world is tanned by chrome tanning. In the tannery industry, only 60% of the Cr is used and the rest is dropped as sludge. Not only Cr, the heavy metals, Cd, Pb, Cu, Zn, and Niare also found in tannery sludge due the further processing [2, 3].Compared to various heavy metals present in the sludge, Cr is found to be rich in different forms, which can be toxic and carcinogenic [4]. It is the 21st abundant element in the Earth's crust and the most important in commercial products and the environment.

Almost all the sludge that is generated in the industries is disposed of in open fields due to lack of appropriate disposal facilities[5]. In order to get rid of various health hazards caused due to thistannery sludge disposal, it is necessary to give more importance for Cr(VI) removal from the sludge. Several studies have shown that,there are various physical and chemical methods available for removal of metals from sludge. Though,they have been widely applied in practice,they also possess several limitations such as high cost and low efficiency[4].Alternatively, biological method that employs microbes as the leaching catalyst for removing metals which known as bioleaching. It is proven to be more economical and environmentally acceptable. Bioleaching process was originally developed for recovery of metals from low quality ores by the mining industry[6]. Bioleaching processes are based on the sulphur oxidation or iron oxidation bychemolithotropic bacteria or filamentous fungi.The intensively used microorganism in the bioleaching processes is seemed to be *Acidithiobacillus ferrooxidans*[7].They obtain energy by oxidizing elemental sulphur (S^0) [8]. It is been reviewed from the literature that indirect leaching was found to be more efficient than the direct method[6]. In indirect mechanism, elemental sulfur (S^o) is oxidized first to sulfuric acid (Eq. 1) by the action of bacteria and then sulfuric acid aids the dissolution of metals. (Eq. 2) [8]:

$$S^o + H_2O + 1.5O_2 \xrightarrow{Bacteria} H_2SO_4 \qquad \text{---------}(1)$$
$$H_2SO_4 + Sludge\text{-}M \xrightarrow{} Sludge\text{-}2H + MSO_4 \qquad \text{--------} (2)$$

Here M is the bivalent metal. There are different works have been carried out on different parameters on sludge bioleaching, but only a few demonstratebioleaching kinetics[9]. In the present study, the influence of temperature in the bioleaching of chromium from tannery sludge and rate controlling-kinetics of leaching process using the procured culture *A. ferrooxidans*has been carried out.

II. MATERIALS AND METHODS

2.1. Sludge sample and characterization:

Sludge has been collected from a tannery industry located atKumarapalayam,Erode. Samples were collected in polypropylene bottles and the sludge was air-dried at room temperature overnight.Available phosphorus in the sludge was determined using micro-vanadate-molybdate method after extracting the total amount with 0.5 M sodium bicarbonate using spectrophotometry.Metal content in the sludge were determined after acid digestion (HNO_3/H_2O_2) [10]. The dissolved metal concentration in the sludge was determined after membrane filtration and quantified using atomic absorption spectrometer (AA200 model; PerkinElmer).Using the flame photometer (CL378 model; Elico; India),concentration of sodium, potassium and calcium were determined[11]. Soluble sulfate estimation was done by the barium sulfate precipitation method using UV-visible spectrophotometer (U2900 model; Hitachi; Japan).

2.2.Bacterial strain and media:

Strain,*A.ferroxidans*(NCIM 5371) was procured from National Collection for Industrial Microorganism, Pune. They were grown in 9Ksyntheticmedium with composition: $(NH_4)_2SO_4$(3 g /L), $MgSO_4.7H_2O$ (0.5 g /L), K_2HPO_4 (0.1 g /L), $Ca(CO_3)_2$ (0.01 g /L), S^o (10 g/L), and KCl (0.1 g/L).The media pH was adjusted to 3 using 1N $H_2SO_4$to stimulate the bacterial growth.It was cultivated in an orbital shaker at 150rpm for two weeks.They were routinely sub cultured every 10 days for further activation.

2.3. Experimental:

Bioleaching experiments were carried out in 250mL capacity Erlenmeyer flasks with 100 mL working volume and supplemented with 5g of sludge.The flasks were inoculated with 10%(v/v) bacterial culture and the flasks were incubated at different temperatures such as 301, 304, 307, 310, 313K.The initial pH was set to 3 for the bioleaching experiments. The flasks were maintained at different temperatures and rotated at 180 rpm. The changes in the media pH and ROP were monitored every two days during the bioleaching course. The 5 ml of samples were drawn from the flasks to determine the concentration of solubilized Cr from the sludge. Solubilized Cr was determined using UV-Visible Spectrophotometer (U2900 model; Hitachi; Japan).

Metal bioleaching efficiency of Cr, denoted by η(%), was calculated using the following equation:

$$\eta\ \% = \left(\frac{Cr_0 - Cr_{soln}}{Cr_T}\right) \times 100 \quad \text{------------------ (3)}$$

WhereCr_0 andCr_{soln} are the solubilized Cr concentration present in the aqueous phase at zero time and time *t*, respectively. Cr_T is the total Cr concentration present in the primary sludge. All experiments were conducted in triplicate and mean values with standard deviation of parameters have been expressed as results.

2.4. Kinetic Studies:

The analysis of sludge bioleaching mechanism is of immense importance for designing and further application of the process. So, shrinking core model (SCM)of fluid–particle reaction kinetics was used for the analysis of rate controlling step[12,13].The mathematical model for the controlling step is shown in (Table.1).X_{Cr} represents the fraction of Cr leached in the aqueous phase and Cis observed kinetic constant ($time^{-1}$).

III. RESULTS AND DISCUSSION

3.1.Characteristics of tannery sludge:

The physico-chemical characteristics of the sludge revealed that the sludge was found to be alkaline in nature. Nitrogen and phosphorus content in the sludge was estimated to be 4,364 and 2617mg/Kg,respectively. The estimated levels of sodium, potassium and calcium were313,224,20650mg/Kg, respectively. It was observed from the analysis that the heavy metal, Cr was abundantly present in sludge.The concentration of total chromium present in the sludge was found to be 11850mg/kgwhich poses highly toxic and hazardous to the environment when it disposed without treatment.

3.2.Changes in pH and ROP during the process:

In the inoculated experiment changes in pH and ROP show significant changes whereas, no changes were observed in control without bacteria. This is due to the conversion of elemental sulfur to metal sulphuric acid by bacterial catalysis. It was observed that at 301,304,307,310,and 313 K the pH values decreased from 3 to 2.86, 2.53, 2.44, 2.36, 2.02, and 2.23, respectively. Among the experiments, 310 K showed a tremendous decrease in pH, thereby facilitating bacterial growth.The variation in pH during the bioleaching process is shown in Figure 1.

The sludge ROP of the control increased slowly as compared to those with inoculums. The variation in ROP during bioleaching process is shown in Figure 2.In the control experiment, the change in ROP was from

245 to 257 mV. Significant change in ROP of the bioleaching medium was observed in experiments with varying temperatures (from 301 Kto 313 K).At the end of 20^{th} day, the flask maintained at 310 K showed considerable increase in ROP (from 268 to 625 mV). It was also observed that ROP increased from 256, 261, 248,and 255mV to 545, 554, 590, and 595 mV for the respective experiments with 301, 304, 307, and 313 K temperature. The increase in ROP showed a similar trend as decrease in pH with respect to different temperatures. The rate of ROP increase took place in the order of 310 K>313 K>307 K>307 K>301 K, and it is well supported by the pH profiles.The results showed that the culture had rapid growth at the temperature of 310 K with low pH levels and high ROP. That indicated the presence of good oxidizing environment in leaching media at this temperature.

3.3.Effect of temperature on removal of chromium:

Figure 3. shows the bioleaching of Cr from the sludge at different temperatures such as 301,304, 307, 310,313 K. The experimental results revealed that Cr bioleaching is greatly influenced by the temperature. Cr solubilization was reached the maximum in a relatively short period of time at 310 K. After 30 days of treatment, the bioleaching efficiencies of Cr were 79.16%, 80.14%, 84.57%, 91.52%and 85.62% at the experiments at 301, 304, 307, 310, and 313 K, respectively.It has been reported that the bioleaching behavior of metals strongly depends on their chemical forms in the original sludge. The experimental data show that the removal efficiencies of heavy metal with respect to temperature took place in the order of 310 K>313 K>307 K> 304 K>301 K.Therefore, the better heavy metal solubilization requires treatment preferably an optimum temperature of 310 K.

3.4. Kinetic studies:

The models of ashlayer diffusion,chemical reaction, and diffusion through liquid film which were applied on the observed bioleaching data. Figures 4, 5, and 6show the fitting of the experimental data to above said models.On comparison of regression coefficients (given in Table 2) of linear best fit among the plots, $[1-(1-X_{Cr})^{1/3}]$ *vs* time was observed to be the best.It is apparent that the chemical reaction–controlled SCM fits well. The rate-controlling factor is a chemical reaction between sludge components and bacterially produced sulfuric acid.

IV. CONCLUSION

The present study showed that the bioleaching using sulfur-oxidizing bacteria, *A.ferrooxidans* was effective in removing chromium from the tannery sludge. Cr solubilization efficiencies were observed for experiments carried out at different temperatures. Maximum bioleaching efficiency of Cr was achieved to be 91.2% at 310 K. It is very obvious that the values of bioleaching rate constant were high in the treatment at 310 K. The analysis based on SCM revealed that chemical reaction between bacterially catalyzed sulfuric acid and sludge componentsreaction controlsthe overall bioleaching reaction rate of Cr. This study clearly demonstratesthe practicability and design strategy of detoxificationsystem for tannery sludge to remove Cr using bioleaching process, which thereby provides a solution to control the toxicity levels in the environment.

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Table 1. Mathematical models of rate controlling steps

Controlling step	Mathematical model
Diffusion through the ash layer	$1+2(1-X_{Cr})-3(1-X_{Cr})^{2/3}= C$
Chemical reaction	$1-(1-X_{Cr})^{1/3}= C$
Diffusion through liquid film	$X_{Cr}= C$

Table 2. Values of regression coefficient of the graphical fit for different controlling step models

Temperature (K)	Ash layer diffusion control model	Chemical reaction control model	Diffusion through liquid film Model
	Value of R^2	Value of R^2	Value of R^2
301	0.806	0.9643	0.9448
304	0.8473	0.9573	0.8796
307	0.8579	0.9512	0.8368
310	0.8837	0.9539	0.7636
313	0.877	0.9698	0.8669

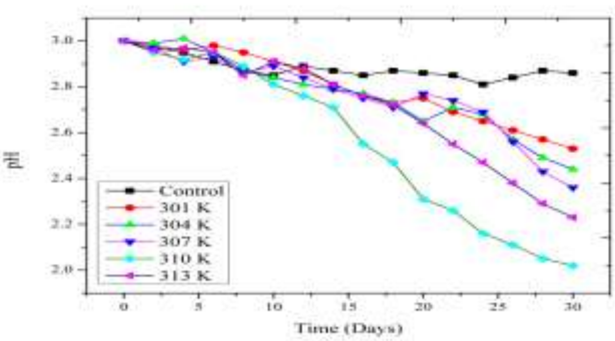

Figure 1. The variation of pH at different temperatures during bioleaching process

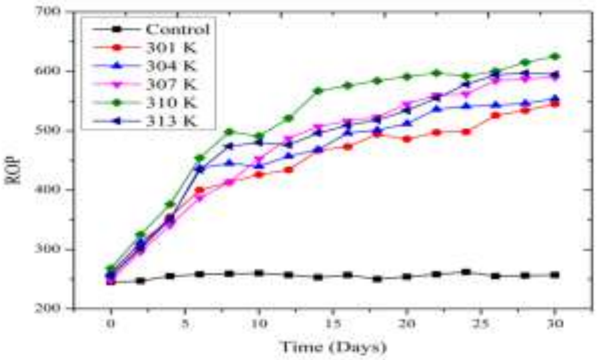

Figure 2. The variation of ROP at different temperatures during bioleaching.

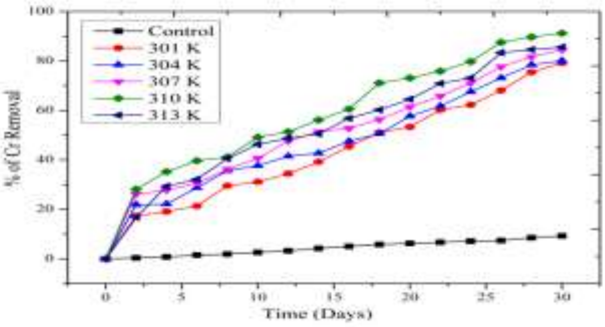

Figure 3. Bioleaching efficiency of chromium at different temperatures.

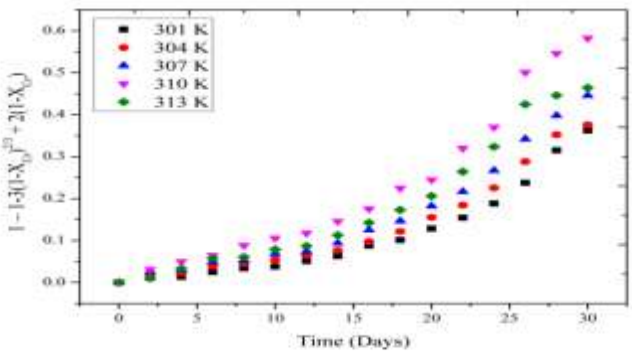

Figure 4. Fitting of bioleaching data to ash layer diffusion model at various temperatures.

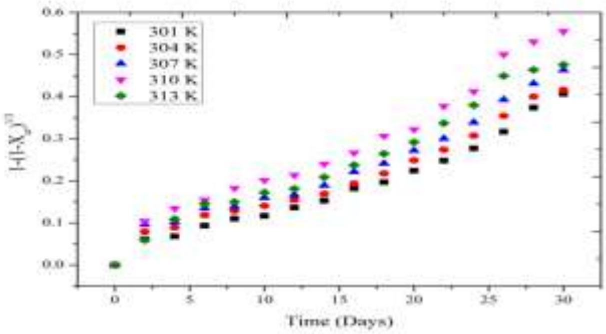

Figure 5. Fitting of bioleaching data to chemical reaction control model at various temperatures.

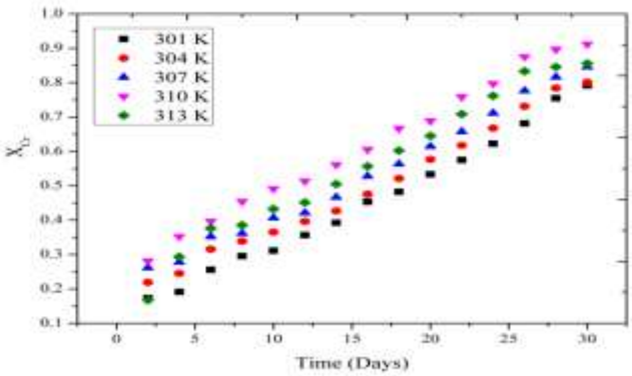

Figure 6. Fitting of bioleaching data to liquid film control model at various temperatures.