International Journal of Recent Technology and Engineering (IJRTE)
ISSN: 2277-3878 (Online), Volume-8 Issue-4, November 2019

Biosolubilization of Cr (VI) from Tannery Sludge: Process Modeling, Optimization, Rate Kinetics and Thermodynamics Aspects

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Abstract*: Leather is one among the significant commodities carry extensive fare profit to the Federal Democratic Republic of Ethiopia. In leather industries, chrome tanning is one of the main process for producing less susceptible to decomposition and more durable leather. Chrome tanning results in a huge amount of Cr content toxic sludge waste which poses a risk to the earth. In the present work, the optimization process parameters, initial pH, temperature, and elemental sulfur (S^0) concentration were examined by Response Surface Methodology (RSM) for the bacterial evacuation (bioleaching) of Cr from the tannery sludge. From the RSM analysis, an equation of polynomial model was produced for the Cr removal effectiveness. Further, the optimized parameters have been recognized by solving the polynomial model through RSM. So as to get the worldwide optimized conditions, the model was settled using a technique dependent on a MATLAB tool, Genetic Algorithm (GA). Moreover, an investigation was led at various temperatures with fixed optimized initial pH and S^0 concentration to assess the impact of temperature on the Cr removal by bioleaching. Using these exploratory outcomes, the kinetics for the activation energy, reaction rate-constant, rate-controlling step, and thermodynamic parameters were resolved. Such a study will be useful for designing and building up the ideal bioleaching system for sludge detoxification in leather processing industries.

Keywords: Bioleaching, Chromium, pH, Reaction rate, Thermodynamics, Temperature.

I. INTRODUCTION

Tanning is one of the significant processes in leather industries for producing less susceptible to decomposition and more durable leather [1]. Tanning procedure comprises in reinforcing the protein structure of the putrescible skin by making a bond among tannins and peptide chains. It rises the dispersing between protein chains in collagen from 10 to 17 Å [2]. At the time of tanning process, alkalis, acids, enzymes, salts, and tanning agents are used to break down the non-fibrous and fats proteins, just as chemically bond the collagen fibers with the tanning agents [3]. The basic strategies of the tanning process are Free of Chrome (FOC) tanning and chrome tanning. These days, 80−90% of leathers on the planet are tanned by chrome tanning since this method has a few advantages, for example, fast and simple to create, water can roll off the surface effectively with proper retaining, and conceivable to acquire a leather with a stable color and high degree of thermal resistance [4]. Chrome tanning utilizes a solution of salts like chromium (III) sulfate to tan the hide [5,6]. Consequent to use of the chromium agent, the bath is treated with sodium bicarbonate for expanding the pH about 4.0–4.5 to instigate cross-linking between the collagen and the chromium [7]. Chromium can frame such stable bridged bonds that makes it one of the most productive tanning agents [8].

In the chrome tanning process, only 60% of the chromium (III) is used and the rest is dropped in sludge [9,10]. The disposal of sludge on land is an old, economical practice [11]. Various investigations found that sun-drying and boiling can oxidize and change over the different chromium (III) compounds stay in the sludge into Hexavalent Chromium [Cr(VI)] which is toxic heavy metal and carcinogenic [12,13]. In order to get rid of various health hazards caused due to this tannery sludge disposal, it is necessary to give immense importance for Cr(VI) removal from the sludge. Various physical and chemical methods are available to remove the hazardous toxins like Cr(VI) from the sludge [14,15]. Though they have been widely applied in practice, they also possess several limitations such as high process cost and low detoxification efficiency [16]. On the other hand, a biological method that employs microorganisms as the leaching agent for evacuating overwhelming metal toxic which is known as bioleaching. This method is proven to be economical and more environmentally friendly.

Bioleaching process depends on the solubilization of overwhelming heavy metals by bacterially created sulfuric acid using sulfur-oxidizing chemolithotrophic [17-19]. The intensively used microorganism in this process is seemed to be *Acidithiobacillus ferrooxidans* [20,21]. They obtain energy by oxidizing elemental sulfur (S^0) to sulfuric acid (Eq. 1) [22]. Then the sulfuric acid aids the dissolution of metals from the sludge (Eq. 2) [23].

Manuscript published on November 30, 2019.
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$$S^{\circ} + H_2O + 1.5O_2 \xrightarrow{A.\ ferrooxidans} H_2SO_4 \quad (1)$$

$$H_2SO_4 + \text{Sludge-A} \longrightarrow \text{Sludge-2H} + ASO_4 \quad (2)$$

Where A is the bivalent metal. A brief review of several studies with respect to *A. ferrooxidans* shows that the bacterial growth and metal solubilization efficiency are predominantly affected by several factors, for example, initial pH, temperature, redox oxidation potential, sludge loading, particle size, S° concentration, availability of nutrients, oxygen and carbon dioxide, presence of toxic elements, and organic matter in the sludge [24]. Thus, more attention to be paid for finding the optimum conditions of the above-mentioned factors to enhance bioleaching efficiency. The optimization for these factors has been investigated previously by one-variable-at-a-time approach (OVAT). In the OVAT approach, the level of anyone independent parameter is changed at a time, while keeping the other parameters remain fixed. This traditional optimization approach is time and work demanding. This method also seems to omit any effects of interaction between different factors. So as to conquer these issues, a statistical technique, Response Surface Methodology (RSM) is broadly applied for optimizing the process. It is an exceptionally proficient experimental tool in which the optimal parameters are resolved and besides gives clear data about the communication between the controllable input parameters in the process. This robust statistical optimization results in the saving of time, chemicals, glassware, and work. In the present work, the ideal degree of three significant factors specifically, initial pH, temperature, and S° concentration were studied using RSM for bioleaching of Cr by *A. ferrooxidans* from the tannery sludge. An equation of polynomial model was created by RSM for the Cr bioleaching system as the capacity of these three parameters. In order to get the global optimized conditions, the model was resolved using a technique based on genetic algorithm (GA). Further, a test was directed at various temperatures to evaluate the influence of temperature in the bioleaching of chromium. Using these experimental results, the kinetics for the activation energy, rate-constant, and rate-controlling step were studied using the Arrhenius equation, pseudo-first-order equation, and shirking core model (SCM), respectively. In addition, thermodynamic parameters for Cr solubilization reaction such as a change in Gibbs free energy (ΔG°), change in enthalpy (ΔH°), and change in entropy (ΔS°) were also calculated.

II. EXPERIMENTAL

A. Characterization of Tannery Sludge

Tannery sludge sample was gathered from the effluent treatment plant of Leather Industry Development Institute (LIDI) located at Kaliti, Addis Ababa. It was air-dried at room temperature overnight. The absolute content of Cr(VI) in the sludge was controlled by atomic absorption spectrometry (AA200 model; PerkinElmer) subsequent to dissolving sludge sample with HNO_3, $HClO_4$, and HF [25]. The available phosphorus present in the sludge was estimated using the micro-vanadate-molybdate method after extracting with 0.5 M sodium bicarbonate using spectrophotometry. The nearness of sodium, potassium, and calcium in the sludge was broke down by the flame photometry (CL378 model; Elico; India) [26]. The all out solvent sulfate content was evaluated after the precipitation as barium sulfate using UV-visible spectrophotometer (U2900 model; Hitachi; Japan). Total Kjeldahl nitrogen and organic carbon present in the sludge were dictated by micro-Kjeldahl apparatus and the Walkley–Black technique, individually. The procedures for sludge characterization were pursued as delineated in the American Public Health Association (APHA) standard.

B. Microorganism and Sludge Adaptation

The sulfur-oxidizing bioleaching strain, A. ferrooxidans (KSRBTAF001) was procured from Microorganism Collection Centre, Department of Biotechnology, K.S. Rangasamy College of Technology, India. The culture was cultivated in 9K synthetic medium with S^0 as a key nutrient. The medium contained the following chemical 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 value of media pH was adjusted to 3 using 1N H_2SO_4 to stimulate bacterial growth. It was subcultured two additional occasions using the same medium in an orbital shaker at 150 rpm in room temperature (30 °C) for about fourteen days for further activation. To enhance the bacterial resistance against sludge toxicity, the *A. ferrooxidans* culture was made to adapt to sludge. For sludge adaptation, the culture was cultivated in 90 mL sterilized 9K media supplemented with 0.05% (w/v) of sludge along with 10% (v/v) of inoculum. In the late logarithmic stage, 10 mL culture medium was moved to the new media enhanced with 0.25% (w/v) sludge. Comparable advance insightful exchanges were made to the fresh media containing sludge levels of 0.5%, 0.75%, and 1.0% (w/v). The improved culture with 1% (w/v) of sludge was used as the inoculum for trials.

C. Response Surface Methodology

RSM is a measurable statistical tool which uses to build up a regression model equation and decide the enhanced operating conditions utilizing quantitative information from the fitting investigations [27]. RSM can develop the functional connection among the response (Y) and the chosen independent variables. It is used to predict the best value for the response. A polynomial model developed by RSM is as follows:

$$Y = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii} X_i^2 + \sum_{i=1}^{n-1}\sum_{j=2}^{n} b_{ij} X_i X_j + \varepsilon \quad (3)$$

where X_1, X_2,…, X_n are the input factors that can influence the response Y; n is the number of variables, b_0 is the constant, b_{ii} (I = 1, 2,…n) is the quadratic coefficient, b_{ij} (I = 1, 2,…., n; j = 1, 2,…, n) is the interaction of the coefficient, and ε represents the random error. Expecting that the factors are independent, continuous, and experimentally controllable with negligible errors, an appropriate estimation for a response (Y) is dictated by solving the polynomial model which gives the ideal estimations of the chosen parameters. In this study, the response, Y, was solubilization efficiency of Cr and the chosen independent parameters were initial pH, temperature, and S^0 concentration.

The Central Composite Rotatable Design (CCRD) is the most widely used experimental design for the RSM approach. This is seen as a powerful plan for successive experimentation as it gives a sensible measure of data to test the absence of fit with the necessary number of trial esteems. The scopes of estimations of the picked factors are coded to lie at ±1 for the factorial levels, ±α for the axial levels, and 0 for the centre levels.

The codes are determined from the elements of the scope of enthusiasm of each factor as given in Table 1.

Table I. The codes and calculated functions

Code	Actual value
$+\alpha$	X_{max}
+1	$[(X_{max}+X_{min})/2]+[(X_{max}-X_{min})/(2\beta)]$
0	$(X_{max}+X_{min})/2$
−1	$[(X_{max}+X_{min})/2]-[(X_{max}-X_{min})/(2\beta)]$
$-\alpha$	X_{min}

D. Determination of Central Levels

Prior to following CCRD in biosolubilization experiments, the central-levels of chosen parameters (initial pH, temperature, and S° concentration) were determined through the OVAT approach. That is, the level of any one parameter is varied at a time keeping fixed other parameters. Based on this, the independent sequence of bioleaching experiments was carried out using basal salts of 9K synthetic medium, 10% (v/v) adapted inoculums and adjusted to initial pH 3 by varying S° concentration while keeping fixed levels of S° concentration and temperature. The similar OVAT procedure was applied to determine the central-levels of other parameters such as S° concentration. The parameters were set in a range of 0.1 to 0.9% (w/v) for S° concentration, 1.5 to 3.5 for initial pH value, 31 to 39°C for temperature. It was selected based on a brief literature survey. Bioleaching analyses were done in 250 mL flasks with a working solution of 100 mL volume. Bioleaching efficiency was calculated for the samples collected after 10 days incubation. Experiments producing maximized leaching efficiency were taken as central levels.

E. Bioleaching experiments based on Experimental Design

Bioleaching experiments were completed in 250mL capacity Erlenmeyer flasks with 100 mL working volume and enhanced with 5g of sludge. The flasks were vaccinated with 10% (v/v) bacterial culture and conditions in the flasks were kept up as referenced in the central level determination. The three powerful parameters that influence the bioleaching process have been taken for the study which includes initial pH, temperature, and S° concentration. 5g/L sludge was loaded equally in all the flasks. The experiments were designed using CCRD. The range of values for each chosen variable is given in Table II.

Table II. The experimental values range designed using CCRD

Parameters	Units	-2	-1	0	+1	+2
pH		1.6591	2	2.5	3	3.3409
Temperature	K	297.909	306	308	310	318.091
S°	g/L	0.16364	0.3	0.5	0.7	0.83635

The combinations of variables based on the design matrix are shown in Table III. In these states of bioleaching tests, 8 tests as full factorial by four factors in high and low levels and six tests in axial points were executed. Experimental results were fitted to a model equation for bioleaching of Cr. The confidence level of the empirical statistical model was examined using ANOVA. The statistical software package, Design-Expert 8.0.0 (Stat-Ease, Inc., Minneapolis, USA), was utilized to create response contour and surface plots and for the regression investigation of the experimental information.

F. Genetic Algorithm Based Optimization of Polynomial Model

GA is a technique for unraveling both constrained and unconstrained optimization issues that depend on natural selection. This mimics the process of natural selection by artificial intelligence. This metaheuristic is routinely used to create helpful answers for optimization enhancement and search issues. The model created by RSM was utilized the fitness function for GA in this study. GA was implemented for further identification of optimal parameters including initial pH, temperature and S° concentration, as a non-linear optimization for Cr bioleaching. For GA optimization studies, the GA-toolbox at MATLAB 7.0 was used with the following parameters, population size: 30, crossover fraction: 0.8, mutation probability: 0.2, the number of generations: 50, elite count: 2, migration fraction: 0.2, and migration interval: 20. The objective function that can be sensed as follows:

$$\text{Maximize } y = f(x);\ x_i^L \le x_i \le x_i^U,\ i=1, 2, \ldots, n \qquad (4)$$

where f(x) is the objective function that acquired from RSM model to be optimized, x is the input vector, y is the yield of Cr bioleaching, n refers to the number of independent factors, and x_i^L and x_i^U are lower and the upper limits of x_i.

G. Validation Experiment, Analytical Procedure and Kinetic Approaches

So as to affirm the outcomes acquired from the model, the validation of the model was broke down by performing two copy experiments. Validation experiments were done for 20 days of incubation period applying the optimal parameters obtained by RSM-GA approach with the same remaining conditions as mentioned earlier in central-level determinations. Optimal parameters obtained by RSM-GA approach with the same retaining conditions, validation experiments were done for 20 days of incubation. The pH and ORP of the medium were regularly monitored using a calibrated pH meter and an ORP meter (Eutech Instruments, Singapore) daily. The samples (5 mL) were withdrawn at 2 d intervals from each of the flasks centrifuged at 8,000 r/min for 20 min. The supernatants were filtrated using a 0.45 µm membrane and were analysed for solubilized Cr content. The volume losses due to sample collection and evaporation were repaid by including a new nutrient solution (medium without S°). The percentage of Cr bioleaching (E_{Cr}) was determined by the accompanying Eq.5,

$$E_{Cr}\,(\%) = \frac{\text{Cr content in leachate} - \text{Cr content at zero time}}{\text{Total Cr content in the raw sludge}} \times 100\ \% \qquad (5)$$

Table III. Combinations of variables based on the design matrix

Run	Combinations of variables		
	pH	Temp	S°
1	3.0	310	0.30
2	2.0	306	0.70
3	2.0	310	0.70
4	2.5	308	0.50
5	3.0	310	0.70
6	2.0	310	0.30
7	2.5	308	0.50
8	2.5	308	0.50
9	3.0	306	0.30
0	1.66	308	0.50
11	2.5	308	0.50
12	2.5	308	0.16
13	3.34	308	0.50
14	2.5	311.36	0.50
15	2.5	308	0.50
16	2.5	308	0.50
17	2.0	306	0.30
18	2.5	308	0.84
19	2.5	306	0.70
20	2.5	304.64	0.50

A pseudo first order kinetic model (Eq. 6) was used to assess the rate of the Cr bioleaching by evaluating rate constant. Where (dC_{Cr}/dt) is the rate of increment of Cr solubilization by bioleaching with respect to time, k is the bioleaching rate constant, and C_{Cr} and $C_{Cr,t}$ is the overall Cr content in the raw sludge and solubilized Cr content in the aqueous extract at time t, respectively. By integrating Eq. (5) between the initial moment (t = 0 d, $C_{Cr,t}$ = 0) and the conditions corresponding to a time t (t = t d, $C_{Cr,t} = C_{Cr,t}$), the linear Eq. (7) can be derived. Using Eq.(7), the value of rate constant (k) was deduced from the slope of plot $\ln[C_{Cr}/(C_{Cr}–C_{Cr,t})]$ vs time.

$$\frac{dC_{Cr}}{dt} = k(C_{Cr} - C_{Cr,t}) \qquad (6)$$

$$\ln\left(\frac{C_{Cr}}{C_{Cr}-C_{Cr,t}}\right) = kt \qquad (7)$$

The activation energy, the min. amount of energy to realize about the reaction, was resolved using the Arrhenius equation, which is given as pursues:

$$\ln k = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \qquad (8)$$

Where, E = Activation Energy (cal/mol), A = Frequency Factor, k = Rate constant of Bioleaching, R = Gas Constant (J/mol K), and T = Absolute Temperature (K). Following Eq. (8), an Arrhenius plot [ln k vs (1/T)] was set up to decide the activation energy from the slope. The ΔG° was determined using the correlation, $\Delta G^{\circ} = -RT\ln K_c$, where R = Gas constant (8.314 J/mol/K), T = Absolute temperature (K), and K_c = Equilibrium constant. K_c was determined as the ratio of leached Cr concentration in the aqueous solution to Cr concentration in leach residue after attaining the saturation leaching. ΔG° can be correlated with thermodynamic parameters, ΔS°, and ΔH by the van't-Hoff equation as given below.

K_c was determined as the proportion of drained Cr focus in the fluid answer for Cr fixation in filter buildup in the wake of accomplishing the immersion filtering. ΔG° can be corresponded with thermodynamic parameters, ΔS°, and ΔH by the van't-Hoff condition as given underneath.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad (9)$$

Replacing ΔG° by $–RT \ln K_c$ in Eq. 9 and arranging, the accompanying equation can be acquired:

$$\frac{\Delta S}{R} - \frac{\Delta H}{RT} = \ln K_c \qquad (10)$$

Using the relationship in Eq. 10, ΔH° and ΔS° were resolved by the slope and intercept of the linear plot ($\ln K_c$) vs (1/T).

IV. RESULTS AND DISCUSSION

A. Characteristics of Tannery Sludge

The characterization study of the sludge showed it to be alkaline (pH 8.7). It was found that the sludge was containing high levels of nitrogen (3134 mg/kg) and phosphorus (2317 mg/kg), and also moderate levels of potassium (381 mg/kg). 22350 and 9120 mg/kg of Calcium and magnesium concentrations in the sludge. The presence of organic matter in the sludge was comparatively low (3.1 mg/kg). The analysis showed that the sludge was enriched with Chromium heavy metal and considerable content of Iron (15230, and 2180 mg/kg for Cr, and Fe, respectively). These overwhelming heavy metal contents are incredibly high, representing a genuine risk to the earth in this way much significance ought to be given for Cr expulsion.

B. Central Levels for Bioleaching Experiments

OVAT approach was utilized to decide the central levels of chosen parameters which is very significant for implementing DOE. The table shows the central levels of initial pH, temperature and S° concentration that were acquired from the OVAT method for the bioleaching of Cr. The primary set of experiments were done by varying the temperature in the media from 31 to 39° C with constant initial pH (3.0), S° concentration (0.6 w/v) and the maximum Cr bioleaching efficiency was found to be 56.14% for the experiment conducted at a temperature of 35° C. It indicated that 35°C is appropriate for Cr removal through bioleaching. Second OVAT method was carried out by keeping the initial pH as a variable (range 1.5 - 3.5) and constant 0.6% (w/v) S° concentration and at temperature 35°C which showed that the max. Cr removal occurred for the experiment with initial pH 2.5 with the efficiency of 52.15%. It is exceptionally evident that the Cr removal system is very much upheld by the conditions with a temperature of 35° C and initial pH of 2.5 is maintained. With these two parameters fixed as constant, S° concentration is varied (0.1 to 0.9 w/v) for the third OVAT approach and 0.6 was found to be showing more efficiency of 49.67%.

Retrieval Number: D7771118419/2019©BEIESP
DOI:10.35940/ijrte.D7771.118419
Journal Website: www.ijrte.org

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Thus based on this, central levels for the design of experiment studies can be chosen. Using this central level of independent parameter variables, further studies for design-matrix interaction and optimization were carried out.

C. Model Construction

Table IV demonstrates the design matrix and corresponding Cr bioleaching results of CCRD tests which are used for the determination of the effects of the three independent variables. They were assessed at the coded levels . The results were shaped to a second-order polynomial equation by applying multiple regression analysis for Cr bioleaching. The model equation representing the Cr bioleaching (Y) was expressed as functions of temperature (B), initial pH (A), and S ° concentration (C) can be written in terms of actual factors as follows:

$$Y=-51689.84644-10.06468A+336.80189B-729.9085C+0.145AB+3.95AC+2.4685C-7.35021A^2-0.54866B^2-35.59738\times10^{-3}C^2 \quad (11)$$

The significant and insignificant effects of the Eq.3 were tested by carrying out the analysis of Variance. Regression was found to be significant from the relatively high coefficient of determination value (R^2=0.9913) and the developed model for Cr bioleaching is statistically accurate for the system under the given experimental conditions. The high value of the adjusted determination coefficient (R_{adj}^2=0.9834) indicates the significance of the model. It can be observed that the coefficients of linear terms (pH), interaction terms (except pH-temperature), and the square terms are quite significant. Coefficient of Variation (CV) = 0.82% (< 10%), which represents the results from experiments were reliable and accurate. The insignificant value of "lack of fit" (>0.05) indicated that the model was statistically appropriate for further applicability.

D. Response Surface and Contour Plots

RSM uses quantitative data to determine regression model equations and operating conditions. The connection between the effective parameters in Cr bioleaching from tannery sludge was optimized utilizing RSM. Examinations were made using three-dimensional (3D) surface and two-dimensional (2D) contour plots. 3D Plots represent the graphical diagram which interprets the individual and aggregate impacts of the factors and the mutual interaction between variable. This is assessed by making the plot for bioleaching efficiency of one parameter as 3D surface curves against the two parameters as the free independent variables and the parameters, by keeping the other two parameters at its central level. The response surface geometry may maximized or minimized to decide the optimum level. The contour plot is the projection of the response surface as a 2D plane by plotting constant z-slices called contours.

The intuitive impact of the variables, initial pH (A) and temperature (B) in the range of 1.5 - 3.5 and 31-39 ºC respectively, on the Cr bioleaching efficiency in the 3D surface plot is as appeared in Fig 1(a) and contour plot in Fig. 1(b). It is exceptionally evident that there is a combined effect of initial pH (A) of the media and temperature (B) at constant Sº Concentration. The maximum of 49.33% Cr leaching occurred at initial pH 2.49 and 308.41 K. The significant interaction was confirmed because of the elliptical idea of the corresponding contour plot. The highest yield of Cr bioleaching at optimum initial pH indicates the sensitiveness of *A. ferrooxidans* to pH. It is well quoted that the optimum pH of media speeds up the development of culture and achieves efficient bioleaching.

Table IV. Cr bioleaching results from CCRD matrix

Run No	Experimental Results	Predicted Value
1	42.50	42.20
2	42.49	42.91
3	46.66	46.29
4	49.11	49.25
5	47.11	47.19
6	42.76	42.88
7	49.12	49.25
8	49.15	49.25
9	41.70	42.19
10	44.27	44.20
11	49.05	49.25
12	43.50	43.35
13	44.00	43.90
14	44.13	44.67
15	49.75	49.25
16	49.28	49.25
17	43.41	43.45
18	47.11	47.09
19	42.23	43.27
20	42.12	41.61

The effect of two variables initial pH (A) and Sº concentration (C) in the range of 1.5-3.5 and 0.1-0.9% on Cr bioleaching is shown in Fig. 2(a) as a 3D surface and Fig. 2(b) as a 2D contour plot. As per these figures, Cr leaching increased when the sulfur concentration is increased. The maximum Cr leaching (49.4659%) occurred at the optimum levels at the initial pH of 2.51 and Sº of 0.58g/L. Reduced Cr removal efficiency was observed beyond the optimum levels. Circular idea of the contour plot points that mutual interaction between the two independent variables (Sº concentration and initial pH) was highly significant in bioleaching. It is also apparent that the bioleaching was highly influenced by these parameters

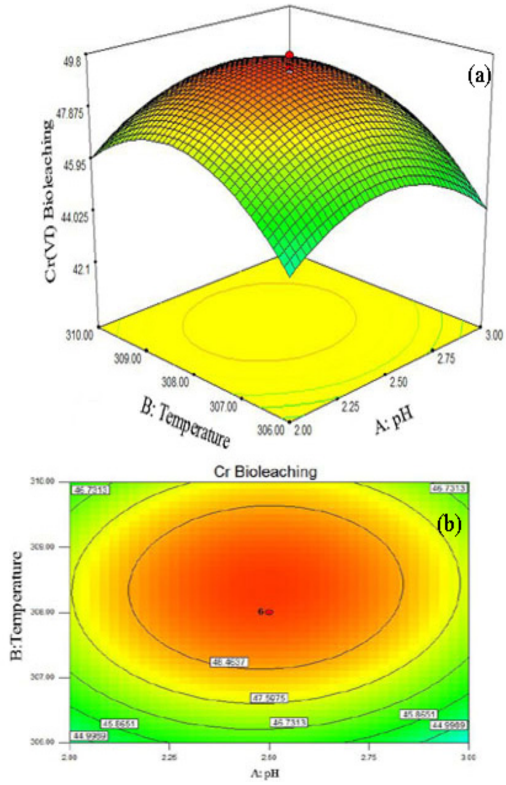

Fig. 1 Response surface (a) and contour graph (b) for temperature vs. initial pH

The 3D surface plot of the interactive impact of S° (C) and temperature (B) on Cr bioleaching at a fixed initial pH (3.0) is as appeared in Fig. 3 (a) and the contour plot as in Fig. 3 (b). As per RSM, maximized yield with 49.6534% Cr leaching occurred at an optimum level of temperature of 308.62 K and S° concentration of 0.6g/L. The elliptical nature of the contour plot cleared that mutual interaction between these two independent variables was significant.

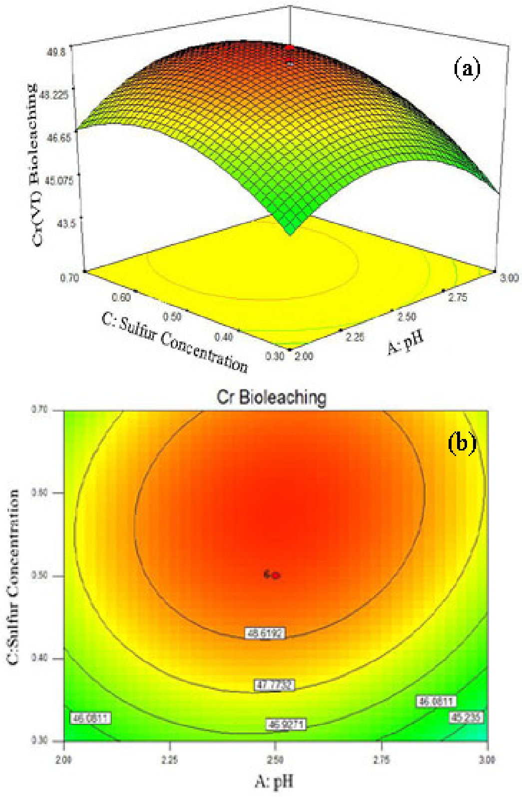

Fig. 2 Response surface (a) and contour (b) graph for Sulfur concentration vs. initial pH

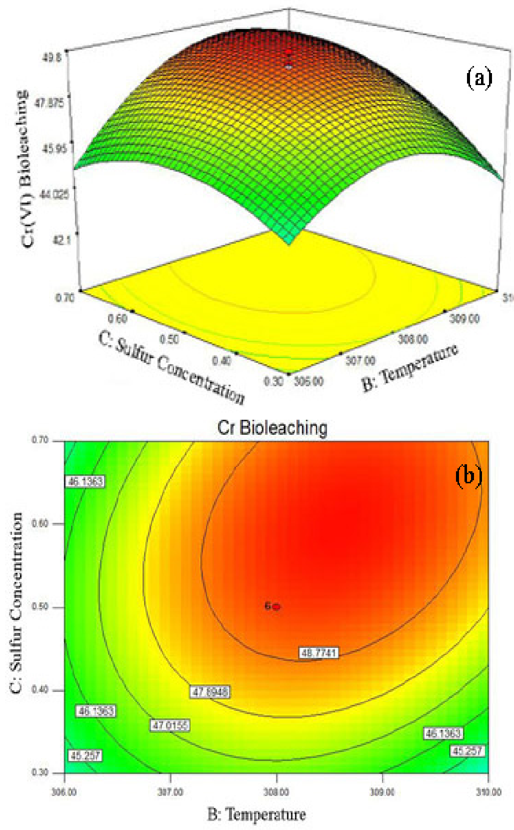

Fig. 3 Response surface (a) and contour (b) graph for Sulfur concentration vs. temperature

E. Optimization of Parameters Based on Genetic Algorithm

The maximum Cr leaching predicted by RSM was 49.75% with parameters of initial pH, temperature and S° concentration were 2.5, 308 K, and 0.5g/L. It ought to be noticed that the goal of this optimization is to determine a good combination of parameters that will meet the highest Cr removal by bioleaching. The model of Cr bioleaching predicted by RSM was verified with R^2, CV, PRESS, and "lack of fit," which showed good fit. However, the optimal condition identified by RSM was not guaranteed to be optimal because RSM provides only a local solution for nonlinear problems. But, GA-associated similar solution was observed at various initial conditions, suggesting it to be a global solution. Many researchers have reported that the GA-based optimization of the model was much better than that determined by RSM alone. Thus, GA was further implemented to optimize the model obtained by RSM with the aim of maximizing Cr bioleaching efficiency. Executing GA-based optimization, the optimal parameters were discovered to be 2.52 initial pH, 308.62 K temperature, and 0.60g/L S°. The Cr bioleaching predicted (RSM-GA approach) at optimal condition was 55.56%.

F. Confirmatory Bioleaching Experiment and Kinetic Studies

The validity of the optimal bioleaching conditions optimized by GA-based technique was tested by carrying out with the parameters suggested by RSM-GA approach. The results of Cr removal efficiency during the 10 d of bioleaching period at optimal conditions are presented Fig. 4.

In the experiment, the bioleaching efficiency of Cr was found to be 49.78% at the finish of 10th day whereas, the efficiencies optimized by RSM was 49.75%. From the RSM-GA analysis, the best fitness and mean fitness values were discovered to be same and it corresponds to the Cr bioleaching efficiency of 49.25%. It is the maximum Cr bioleaching efficiency achieved by the model. The best fit plot is depicted in Fig. 5

This indicates that the experiment and predicted values from the optimization of the model were in close agreement with above 95% confidence level, and thus the polynomial equation is quite successful in predicting the response. Toward the finish of 30th day, 91.2% of Cr was removed in the confirmatory bioleaching experiment performed using optimal condition.

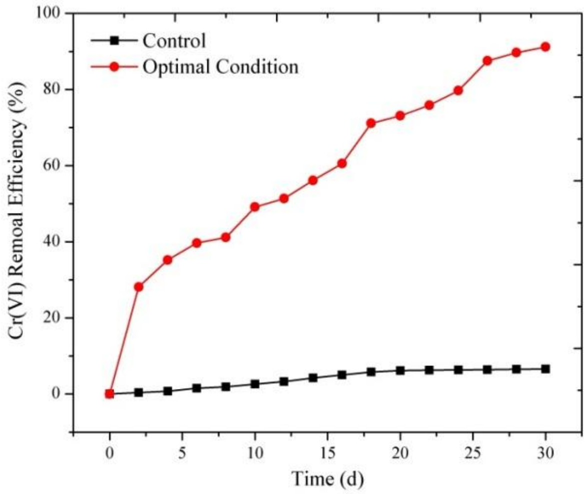

Fig. 4 Cr Leached (%) function of time at optimal condition.

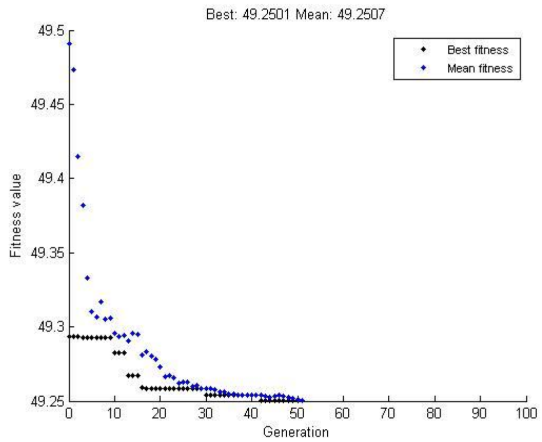

Fig. 5 Best fitness plot

The raw tannery sludge and bioleached residue obtained from the experiment with the optimized condition were subjected to energy-dispersive X-ray spectroscopic (EDX) analyses. The spectra obtained from the EDX analyses are given in Figs. 6. Results from the EDX analysis showed that elements O, Na, Mg, Al, Si, S, Cl, Ca, Cr, and Fe were at weight percent of 56.13, 4.96, 0.70, 4.44, 7.01, 3.06, 3.14, 4.59, 13.66, and 2.31, respectively for raw sludge and 47.47, 1.87, 0.63, 4.61, 7.93, 1.05, 1.41, 3.02, 6.84, and 3.74, respectively for bioleached residue. It confirmed the reduction in Cr content in treated sludge.

The rate constant is a statistical measure of the reaction at which all the reactants are brought at the unit concentration. So as to decide the rate constant of Cr bioleaching process, plotting of experimental data to Eq. (6) with the linear line of best fit were made and the equivalent is displayed in Fig.7. From the plot, equation of linear best fit line was determined as y = 0.0708x which indicated the rate constant of Cr bioleaching is to be 0.0708 d^{-1}.

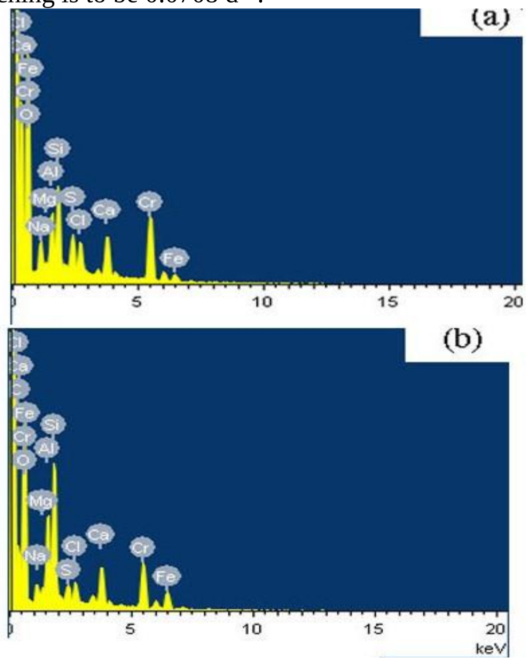

Fig. 6 The EDX spectra for raw tannery sludge (a) and bioleached residue (b).

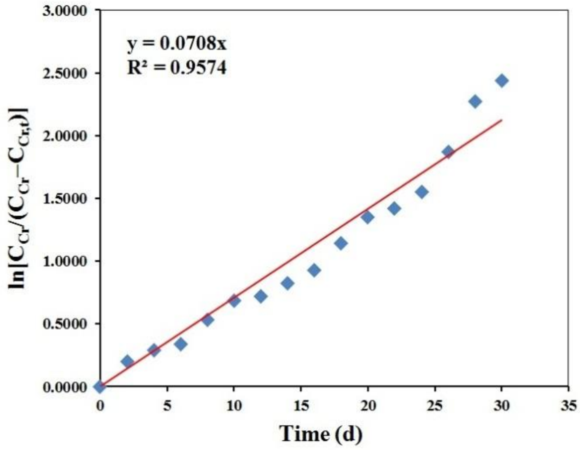

Fig. 7 First-order rate kinetic plot for Cr bioleaching

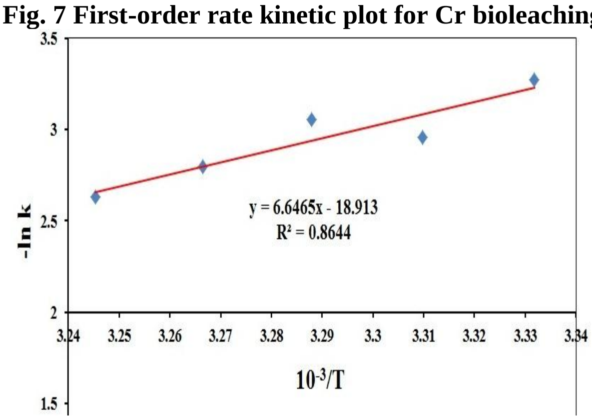

Fig. 8 Arrhenius plot for determination of activation energy

From the Arrhenius plot (Fig. 8), the activation energy for bioleaching was calculated to be 55.5 kJ/mol. The thermodynamic investigations have been performed to locate the regulation of the bioleaching experiment. The change in free energy of bioleaching at temperatures 300 K, 302 K, 304 K, 306 K, and 308 K was found to be −8160.26, −7426.73, −7731.53, −7118.76, and −6740.52 J/mol, respectively. The suddenness of the bioleaching procedure is shown by the negative values. The values of ΔH˚ and ΔS˚ were calculated to be 99.838×10^{-3} J/mol and 29.155 J/mol, respectively (from the Fig.9). The endothermic idea of the bioleaching process is spoken to by the positive value of ΔH˚.

This is continued by the observed increase in the bioleaching efficiency with the rise in temperature. The positive estimation of ΔS˚ demonstrates that randomness for sulfur ions which increases at the mineral/solution interface during their leaching.

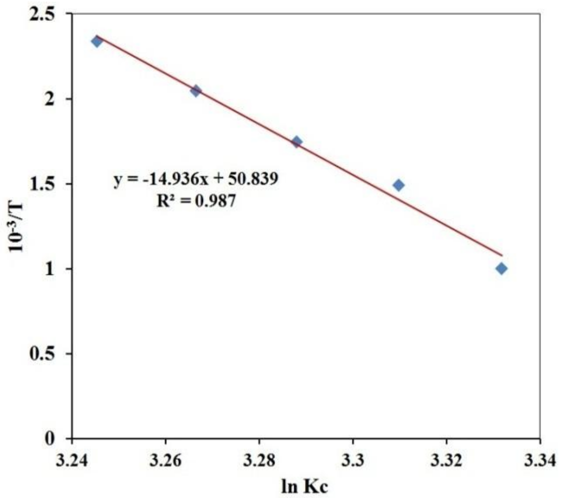

Fig. 9 Linear plot based on Van't-Hoff equation

V. CONCLUSION

The present study showed that the bioleaching using sulfur-oxidizing bacteria, A. ferrooxidans was successful in expelling chromium from the tannery sludge. Influencing parameters such as Initial pH, temperature and S^0 concentration were optimized to enhance the bioleaching of Cr using *A. ferrooxidans*. According to a satisfied nonlinear polynomial model developed by RSM, the optimal parameters were discovered to be 2.5 initial pH, 308 K temperature and 0.5% (w/v) S°. Under the optimal conditions, the predicted Cr leaching was 49.65%. In order to obtain a global solution, the model was further optimized using GA and this suggested 2.52 of initial pH, 308.62 of temperature and 0.6% (w/v) of S^0 as the optimum levels for maximized Cr removal of about 49.87%. The highest leaching of Cr was approved by carrying out a confirmatory experiment maintained with the conditions optimized using RSM-GA approach. The rate of Cr removal was determined using the pseudo-first-order kinetic model.

The confirmation experiment (with optimal condition obtained from RSM-GA approach) approved the highest leaching of Cr. Pseudo first-order kinetic model was used to decide the rate of Cr removal. It showed that the estimation value of the rate constant is to be 0.070 d^{-1}. From the present study, it was observed that the use of RSM coupled with GA-based optimization technique had distinguished the optimum levels of most effective factors.

ACKNOWLEDGMENT

This research was supported by Internal Research Grant (Ref No: AASTU/1006/3341/18) from Addis Ababa Science and Technology University, Ethiopia. Special thanks go to Leather Industry Development Institute, Kaliti, Addis Ababa, Ethiopia, and JCT College of Engineering and Technology, Coimbatore, India for valuable support.

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