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BIOREMEDIATION OF LOW GRADE ORES

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ABSTRACT

The research work presented in this paper is on a Bioremediation for the recovery of zinc from mining waste i.e. Low grade ore of Hindustan Zinc Limited. They are waste product for the mines, as the recovery process is expensive compared to the recovery product moreover it causes lots of pollution

Bioleaching Studies were carried out at different pH using mixed culture grown from mine water. Recovery of zinc in control set (without culture) was 8% in 37 days and at the same pH (1.6) with the culture of Bioleaching bacteria, the recovery of zinc was 89%, whereas at pH 1.8 and 2.0 zinc recovery was 47% and 46% respectively. The best Bioleaching of low grade ore was obtained at pH 1.6.

From the results obtained during experimentation it is found that the recovery of zinc is not dependent only on the iron content in the solution because with the same content of iron there is a difference of recovery of zinc. It shows that both types of reaction mechanisms, direct & indirect are involved during Bioleaching process.

KEYWORDS: Bioremediation; Microbes; Mining waste.

INTRODUCTION

Zinc is one of the most important non-ferrous metals known to mankind since the beginning of civilization and is the most extensively used non ferrous metal after Aluminium and copper. About 45% of world production of zinc is used in galvanising, 21% in brass, 15% in casting and 19% in other use like dry batteries, photoengraving, paints and paper making.

The country was dependent almost entirely on imports of lead and zinc metals until indigenous production of these metals was started by Hindustan Zinc Ltd.

Lead and Zinc ores in India occurs in a variety of geological environments. Total economical zinc resources in India 164 million tons, more than 95% happen to occurs in Rajpura Dariba and Zawar groups of mines in Udaipur and Rampura Agucha deposit in Bhillwara District of Rajasthan.

In India lead- zinc ores with 4-14 % zinc metal mined from underground and open pit mechanized mines are crushed, ground and beneficiated using differential froth flotation technique to separate lead concentrates (50-65% lead as PbS) and zinc concentrates (50-52% as ZnS).

At present, most zinc metal around the world is extracted by hydrometallurgical process. The traditional zinc hydrometallurgical technology has many disadvantages with long flow sheet, high cost and serious pollution contrary to bio-hydrometallurgical process. Therefore, more attention has been paid to the bio-hydrometallurgical technology and a more extensive investigation has been done [1].

MATERIAL AND METHODS

Ore: The mining waste used in the present investigation was procured from Hindustan Zinc Limited Udaipur that contained 9.556% of zinc. The ore was ground and -8 ISS size was taken for the Bioleaching experiments.

Micro-organisms: Microbes present in mine sludge of Surda mines, Jharkhand (India) were enriched in 9K media. These bacteria grow in the pH range of 1.0-2.8. The best growth was found at pH 1.6, 1.8 and 2.0. Hence, Bioleaching experiments were set up at pH 16, 18 and 2.0.

Experimental: The Bioleaching experiments (triplicate of each) were setup at pH 1.6, 1.8, 2.0 in 500ml conical flasks. In each set up10g of ore and 100ml of 9K media without iron and sulphur were taken. Three sets were inoculated with 5ml of active culture grown at pH 1.6, 1.8 and 2.0 respectively. Control (without bacteria) experiment was conducted at pH 1.6; all sets were incubated at 35ºC.

Analyses: Periodic analysis of pH, Eh, iron and zinc were done by standard methods. Eh and pH were measured by pH/Eh meter **JENWAY**, model 3505, using redox platinum electrode (924003) and combined pH electrode (924001). Iron was analysed by $KMnO_4$ titration method after reducing with stannous chloride [2]. Zinc was analysed by colorimetric method [3] using Spectrophotometer Model DREL/2010, HACH, USA. The pH of each set was measured twice a day and adjusted to its initial value to keep constant during experimentation.

RESULT AND DISCUSSION

Mean values of results (of triplicate experiments) are shown in tables 1 - 4 and comparative recovery of zinc is shown in figure 1.

In control set at pH 1.6 maximum iron leached out was 0.3351g in 23 days and got declined to 0.14g after 37 days and zinc leached out was 0.0775g after 37 days giving a recovery of 8%. Results are depicted in the **Table 1**, pH was kept constant at 1.6 by adding dilute sulphuric acid, though there was a tendency of increase of pH due to the leached out gangue material. Initially Eh of the control set was 399, after 7 days it got declined to 316. This declination in Eh may be due to the presence of reduced form of iron in the solution. Again the value of Eh rose showing the presence of oxidised form of iron in the solution. Eh value finally rose to 494 after 37 days.

Table 1: Leaching of low grade ore at pH 1.6 without microbes (control)

Days	Eh	Iron in total volume (g)	Zinc in total volume (g)	Recovery %
0	399	$0.02513\pm 3.299\times10^{-5}$	0	0
7	316	$0.02793\pm 4.83\times10^{-5}$	0	0
14	448	$0.02793\pm5.66\times10^{-5}$	$0.0339\pm2.36\times10^{-4}$	3.7
23	459	$0.3351\pm2.36\times10^{-4}$	$0.0572\pm3.299\times10^{-4}$	6.3
37	494	$0.14\pm2.35\times10^{-2}$	$0.0775\pm2.83\times10^{-4}$	8.0

All results are represented by ± SEM

In experiments at pH1.6 with leaching bacteria, maximum iron leached out was 0.9385g in 23 days that is three times more than that in control set. Soluble iron got declined to 0.5585g after 37days. Zinc leached out at this pH was 0.8704 after 37 days giving a recovery of 89%. The results are depicted in **Table 2**. Tendency of increase in pH of experiments with active culture was less than that of control experiments showing active bacteria had produce some acid. The pH was maintained at 1.6 by adding diluted sulphuric acid. Initial value of Eh of the experimental set was 416 at pH 1.6, after 7 days it has got declined to 317 due to release of some ferrous iron in solution and as soon as the iron got oxidised the Eh value started rising.

Table 2: Leaching of low grade ore at pH 1.6 with microbes

Days	Eh	Iron in Total Vol. (gm.)	Zinc in Total Vol. (gm.)	Recovery %
0	416	$0.014\pm1.89\times10^{-3}$	0	0
7	317	$0.3910\pm3..78\times10^{-4}$	$0.243\pm4.6\times10^{-3}$	25.4
14	485	$0.5585\pm5.66\times10^{-4}$	$0.2571\pm7.07\times10^{-4}$	27
23	550	$0.93576\pm5.19\times10^{-4}$	$0.774\pm1.89\times10^{-3}$	81
37	546	$0.5585\pm4.24\times10^{-4}$	$0.87041\pm6.59\times10^{-4}$	89

All results are represented by ± SEM

At pH 1.8 the iron leached out was in the same range as with pH 1.6 but zinc leached out was only 0.4493g in 37 days giving a recovery of 47% of zinc. In this experiment pH value had gone up to 2.5 after 14 days, but it was readjusted to 1.8. Initial Eh value was 422 and got declined to 287 in 7 days and then rose to 535 on 37th day. This indicates that the bacterial activity was slightly less in compared to experiment at pH 1.6. When bacterial oxidising rate is slow this fluctuation of Eh value is there because as per the reaction, ferrous sulphate gets leached out from the ore. If bacteria are highly active then ferrous immediately gets converted to ferric form giving a high redox potential value.

Table 3 Leaching of low grade ore at pH 1.8 using microbes

Days	Eh	Iron in Total Vol. (g)	Zinc in Total Vol. (g)	Recovery%
0	422	$0.014\pm2.83\times10^{-3}$	0	0
7	287	$0.5585\pm2.36\times10^{-4}$	$0.1195\pm2.83\times10^{-4}$	13
14	599	$0.5585\pm2.45\times10^{-4}$	$0.1319\pm2.83\times10^{-4}$	14
23	458	$0.93576\pm5.19\times10^{-5}$	$0.388\pm7.07\times10^{-4}$	41
37	535	$0.5585\pm5.19\times10^{-5}$	$0.4493\pm5.72\times10^{-4}$	47

All results are represented by ± SEM

On further increasing the pH value to 2.0, the iron leached out remained the same as at pH 1.6 and 1.8 and zinc leached out at this pH was 0.440g in 37 days giving a recovery of 46 %.

In this case the rise of pH value was up to 2.8, readjusted as to initial pH 2.0 by adding dilute $H_2 SO_4$. Initial Eh was 432 which declined to 266 in 7 days and enhanced to 554 in 14 days, again declined to 451 in 23 days and then showing an increase to 522 in 37 days, exhibiting a slow activity of microbes.

Table 4 Leaching of low grade ore at pH 2.0 (Initial Zinc 9.556)

Days	Eh	Iron in Total Vol. (gm.)	Zinc in Total Vol. (gm.)	Recovery %
0	432	$0.014\pm1.89\times10^{-3}$	0	0
7	260	$0.5585\pm2.45\times10^{-4}$	$0.127\pm4.6\times10^{-3}$	11
14	554	$0.5585\pm2.45\times10^{-4}$	$0.1222\pm3.27\times10^{-3}$	13
23	451	$0.9356\pm5.19\times10^{-4}$	$0.353\pm4.89\times10^{-3}$	37
37	522	$0.05585\pm5.19\times10^{-5}$	$0.440\pm1.22\times10^{-3}$	46

All results are represented by ± SEM

As depicted in figure 1, recovery of zinc at 1.6 pH (in control) set was only 8% in 37 days while at the same pH with the microbes the recovery of zinc was 89%, whereas at pH 1.8 and 2.0 it was 47% and 46% respectively. This shows that the leaching of ore is best at pH 1.6. In seven days maximum recovery was found at pH 1.6 that is 25.4% and at pH 1.8 and 2.0 it was 13.5% and 11% respectively. Till 14th day there was a negligible rise in the recovery of zinc, which indicates that this is a lag phase of the microorganism due to gangue material leached out from the ore. Later on, after 23days the recoveries were 81%, 41% and 37% at pH values of 1.6, 1.8 and 2.0 respectively. This rise in recovery is due to the acclimatization of the bacterial culture, with the gangue material of ore. In 37 days maximum recovery was 89%, 47% and 46% at pH 1.6, 1.8 and 2.0 respectively; at the same time in control set at pH 1.6 the maximum recovery was found to be 8% after 37 days due to absence of active microbes. From the result it is inferred that best pH for the recovery of zinc from the ore is 1.6 as on increasing the pH to 1.8 or 2.0, the recovery was in the range of 46% - 47%. It is also inferred that the recovery of zinc is not dependent only on the iron content in the solution because with the same content of iron there is a difference of recovery of zinc; this shows that both direct and indirect types of reaction are involved in this set of experiments.

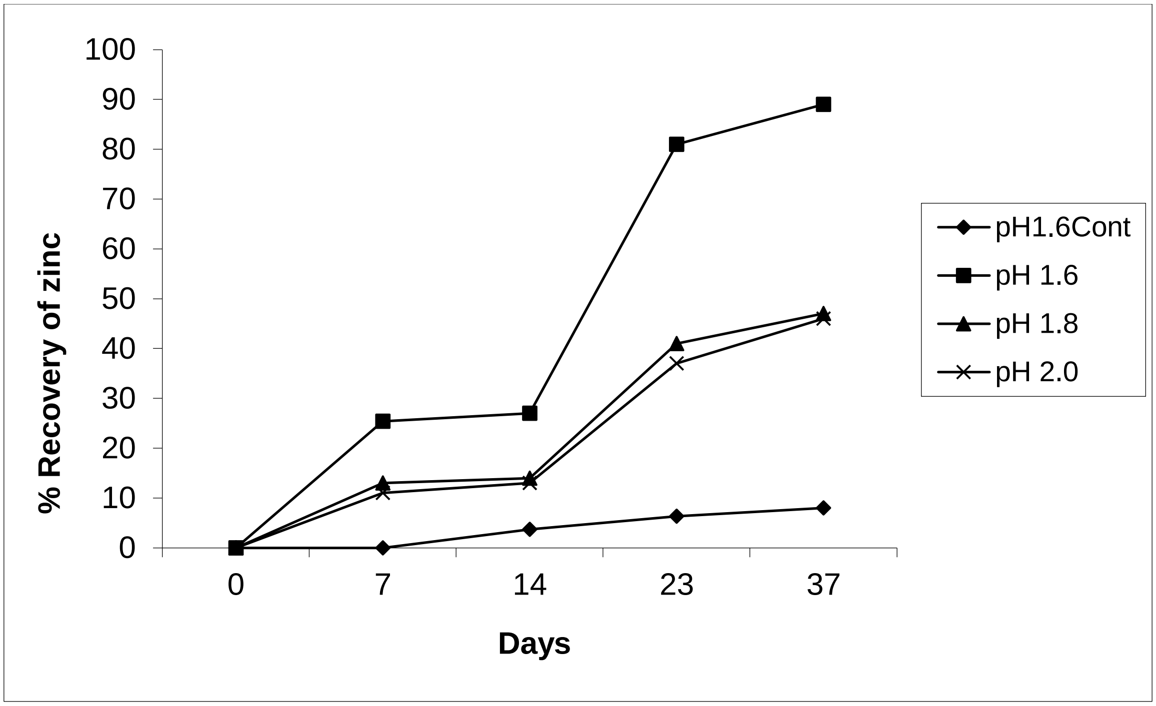

Figure 1: Leaching of low grade ore at different pH

Statistical analysis of the experimental data:
The experimental data were analyzed by One-way Analysis of Variance (ANOVA) technique. Variance is calculated as, the average of the squares of the deviations of each of the observed values from their mean value. In the One-way ANOVA, variance of the total population, variance between the groups (BSS-between sum of squares), and the variance within the groups (WSS-within sum of squares) are calculated. Then, so called **F-value** is calculated by taking the ratio of these two variances. Now the value of **F** is interrelated with reference to the standard ANOVA table, which gives the value of **F** for different degrees of freedom and at various levels of significance. If the calculated value of **F** is higher than the tabular value of F for the appropriate degrees of freedom at the selected level of significance, it is concluded that the difference between the variances within groups and between groups is significant. That is, the observed differences among these means do not arise from chance variation and the independent variable is effective.

ANOVA for leaching of Low-grade ore at different pH

Source of Variance	Sum of squares	DF	Mean of square
BSS	4.089972374	2	2.044986187
WSS	0.369328978	6	0.06155483
		F =	**33.222**

With the value of "DF" in the hand and ANOVA table, the Critical value of F at 0.01-level of Significance is 10.92. As the obtained value of F is greater than the Critical value (10.92), it is concluded that there is a significance difference among the three groups, thus the observed difference among these "means" do not arise from chance variation. In other words, the pH value has a significant effect on the recovery of Zinc.

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CONCLUSIONS

It is inferred from the results that recovery of zinc through bio-hydrometallurgical process with lesser environmental problem than conventional commercial application is feasible under controlled condition of pH. Maximum recovery can be obtained at the pH value of 1.6.

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