World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:3, No:10, 2009

Bioleaching of Heavy Metals from Sewage Sludge Using Indigenous Iron-Oxidizing Microorganisms: Effect of Substrate Concentration and Total Solids

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Abstract**—**In the present study, the effect of ferrous sulfate concentration and total solids on bioleaching of heavy metals from sewage sludge has been examined using indigenous iron-oxidizing microorganisms. The experiments on effects of ferrous sulfate concentrations on bioleaching were carried out using ferrous sulfate of different concentrations (5-20 g L^{-1}) to optimize the concentration of ferrous sulfate for maximum bioleaching. A rapid change in the pH and ORP took place in first 2 days followed by a slow change till 16^{th} day in all the sludge samples. A 10 g L^{-1} ferrous sulfate concentration was found to be sufficient in metal bioleaching in the following order: Zn: 69%>Cu: 52%>Cr: 46%>Ni: 45. Further, bioleaching using 10 g/L ferrous sulfate was found to be efficient up to 20 g L^{-1} sludge solids concentration. The results of the present study strongly indicate that using 10 g L^{-1} ferrous sulfate indigenous iron-oxidizing microorganisms can bring down pH to a value needed for significant metal solubilization.

Keywords**—**Bioleaching, heavy metals, sewage sludge, iron-oxidizing microorganisms

I. INTRODUCTION

THE disposal of sewage sludge on land as a fertilizer is an old practice due to the presence of nitrogen, phosphorus and other nutrients in the sludge [1]. However, the presence of heavy metals in sludge restricts its use on land. The application of sewage sludge contaminated with heavy metals poses serious threat to the environment due to the potential risk of metal leaching to ground water and surface water and is also because of their entry in the food chain [2]. Therefore, removal of heavy metals from contaminated sewage sludge assumes great importance to ensure safe disposal of the sludge on land.

Over the years, bioleaching technique involving iron and sulfur-oxidizing microorganisms has been gaining importance as an efficient and economical method for decontamination of sewage sludge [3]. Bioleaching process using iron-oxidizing microorganisms and ferrous sulfate as an energy source is considered superior as there is less risk of soil re-acidification. When ferrous sulfate is used as a substrate, the oxidation of ferrous iron leads to the production of ferric iron, acting as an oxidant causing solubilization of metals. The amount of ferrous sulfate used in metal bioleaching affects the ferrous-ferric ratio and hence pH of the system. Using lower concentrations of ferrous sulfate, the change in pH may not be adequate to solubilize the metals. On the other hand, too much of ferrous sulfate will not enhance the solubilization of metals and therefore, will increase the process economy. Further, excess iron will cause generation of huge amount of sludge, the disposal of which will be an added problem. Therefore, ferrous sulfate concentration is an important parameter which has to be optimized for efficient bioleaching.

Besides substrate concentration, the solids content of the sludge also plays an important role in determining the efficiency of bioleaching process. Bioleaching with higher sludge solids provide an attractive opportunity since higher amount of the sludge can be treated in given time. However, at higher sludge solids content, the reduction in pH decreased due to higher buffering capacity of the sludge, ultimately requiring more time for attaining the pH values necessary for solubilization of metals. Therefore, it is worth examining the optimum sludge solids concentration at which efficient bioleaching can take place.

In the present study, an attempt has been made for optimization of the ferrous sulfate concentration as well as sludge solids concentration for efficient bioleaching. The experiments were performed with anaerobically digested sewage sludge employing indigenous iron-oxidizing microorganisms of the sludge using varying amount of ferrous sulfate (5-20 g L^{-1}) and sludge solids (5-40 g L^{-1}).

II. MATERIALS AND METHODS

2.1 *Collection of the sludge:* The anaerobically digested sewage sludge was procured from one of the largest wastewater treatment plants in Delhi, the capital city of India, having treatment capacity of more than 100 MGD.

2.2 Microorganism and inoculum preparation: Iron-oxidizing microorganisms present originally in the sludge were used for inoculum preparation, for which the activated sludge from the

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secondary treatment stage of the sewage treatment plant was fortified with 30 g L^{-1} of ferrous sulfate. The flask was incubated in an orbital shaker at 28°C and 180 rpm and pH of the culture was monitored. When the pH from an initial value of 7 reduced to 3, the culture was transferred to the fresh sludge. This procedure was repeated three times so as to get an active inoculum (acclimatized sludge) for using it in the subsequent bioleaching experiments.

2.3 Characterization of sludge: The pH of the sludge was determined using Cyberscan 510 pH meter, whereas the ORP of the sludge was measured with standard ORP probe meter. The total solids content, ash content, the total nitrogen content and total phosphorous content was determined according to the standard methods [5]. For determination of total heavy metals content, the sludge samples were subjected to di-acid digestion (HNO_3 + $HClO_4$) and the heavy metals in the digested liquid were determined using atomic absorption spectrophotometer (Perkin Elmer AAnalyst 200). The physicochemical properties of the sludge are provided in Table 1

2.4 Bioleaching of metals: The bioleaching experiments on effect of substrate concentration were carried out in 500 ml Erlenmeyer flasks with 250 ml of the sludge (20 g L^{-1} solids concentration) containing 10% of the active inoculum. The experiments were performed for 16 days at 28°C and 180 rpm using different concentrations (5, 10, 15 and 20 g L^{-1}) of ferrous sulfate. A control run without addition of both ferrous sulfate and inoculum was also carried out to compare the results. The samples were withdrawn at every two days from each flask and analyzed for pH, ORP and metals content. The experiments were performed in duplicate. The metals in the mixture (sludge + inoculum) were recorded as a zero day reading.

Similar procedure was performed for carrying out experiments on effect of sludge solids using different concentrations (5-40 g L^{-1}) of sludge solids.

TABLE 1
PHYSICOCHEMICAL PROPERTIES OF ANAEROBICALLY DIGESTED SLUDGE

Parameters	Value
pH	7.22
Total solids (g L^{-1})	20
Cu (mg kg-1 dry sludge)	472
Ni (mg kg-1 dry sludge)	294
Zn (mg kg-1 dry sludge)	1310
Cr (mg kg-1 dry sludge)	332

III. RESULT AND DISCUSSION

3.1 Effect of substrate concentration

3.1.1. Change in pH and ORP: The change in pH with time during bioleaching at different concentrations of ferrous sulfate along with the control is shown in Figure 1. In the control, without the addition of ferrous sulfate and inoculum, only a slight decrease in pH was observed from an initial value of 7.0 to 6.9 on the 16th day. This was expected as no inoculum of active microbes and also no energy source were supplied externally to support the in-situ iron-oxidizing microorganisms of the sludge.

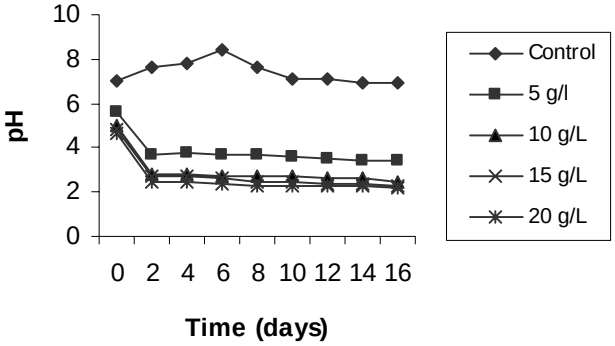


Fig. 1 Change in pH with time during bioleaching at different concentrations of ferrous sulfate

On the other hand, in the presence of inoculum and ferrous sulfate (5, 10, 15 and 20 g L^{-1}) a drastic drop in pH to <4 was observed in first 2 days in all the sludge samples having ferrous sulfate as an energy source. The decrease in pH was faster with increase in ferrous sulfate concentration. However, after 16 days there was not much difference in the final pH achieved for all the sludges (except 5 g L^{-1}) having ferrous sulfate. The sharp decrease in pH in first 2 days indicates better acclimatization and rapid growth of iron-oxidizing microorganisms using ferrous sulfate as an energy source. In the sludges having ferrous sulfate beyond 5 g L^{-1}, the pH decreased faster to <3 in first 2 days and then remained almost constant at the end of 16th day. At the end of 16th day bioleaching period, the final pH was 3.4, 2.5, 2.3 and 2.2 for the sludges having 5, 10, 15 and 20 g L^{-1} of ferrous sulfate, respectively. Therefore, it is apparent that 10 g L^{-1} ferrous sulfate is sufficient for bringing down pH to a value less than 3 needed for effective metals solubilization. The bio-oxidation of ferrous sulfate by indigenous iron-oxidizing microorganisms also caused an increase in ORP of the system. Figure 2 shows the change in ORP of the sludge with time at different concentrations of ferrous sulfate along with control. The decrease in pH associated with an increase in ORP is an indicator of the substantial growth of the microorganisms [6]. In the control, the ORP reached only up to 102 mV from an initial value of -98 mV after 16 days. On the other hand, in the sludges having ferrous sulfate and inoculum, the ORP increased rapidly in first 2 days and then remained constant till the 16th days. After 16 days, the ORP values were 446, 472 and 492 mV respectively for the sludges receiving 10, 15 and 20 g L^{-1} of ferrous sulfate.

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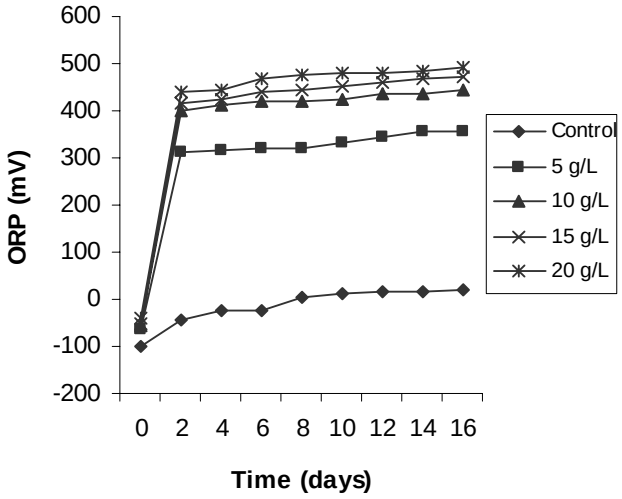


Fig. 2 Change in ORP with time during bioleaching at different concentrations of ferrous sulfate

3.1.2 Heavy metals solubilization: The change in % solubilization of Cu is presented in Figure 3. In the control, only 10% Cu was solubilized on the 16th day of bioleaching. In the presence of ferrous sulfate, a significant quantity of Cu was solubilized. At ferrous sulfate concentration of 10 g L^{-1}, a maximum of 52% Cu was solubilized on the 16th day compared to 28% using 5 g L^{-1} ferrous sulfate. Further, increase in ferrous sulfate concentration did not yield significant solubilization of Cu which was 55% and 58% for the sludges receiving 15 and 20 g L^{-1} ferrous sulfate, respectively. It has been reported that the solubilization of Cu is strongly dependent on ORP and to solubilize Cu, ORP of the medium should be more than 250 mV [7]. In the present study, high ORP of more than 400 mV was achieved on the 16th day using 10-20 g L^{-1} of ferrous sulfate which favours the Cu solubilization.

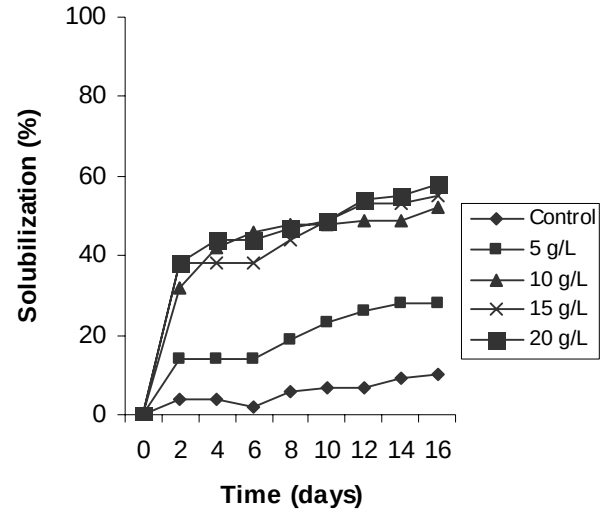


Fig. 3. % solubilization of Cu with time during bioleaching at different concentrations of ferrous sulfate

Figure 4 shows % solubilization of Ni with time. A similar trend was observed in Ni solubilization as was observed in case of Cu. However, in all the metals lowest solubilization of Ni was achieved. About 45% Ni was solubilized on the 16th day using 10 g L^{-1} ferrous sulfate as compared to 12% solubilization in the control. A further increase in ferrous sulfate concentration beyond 10 g L^{-1} didn't yield much enhancement in solubilization of Ni and after 16 days of bioleaching only 48% and 52% Ni were solubilized using 15 and 20 g L^{-1} of ferrous sulfate, respectively.

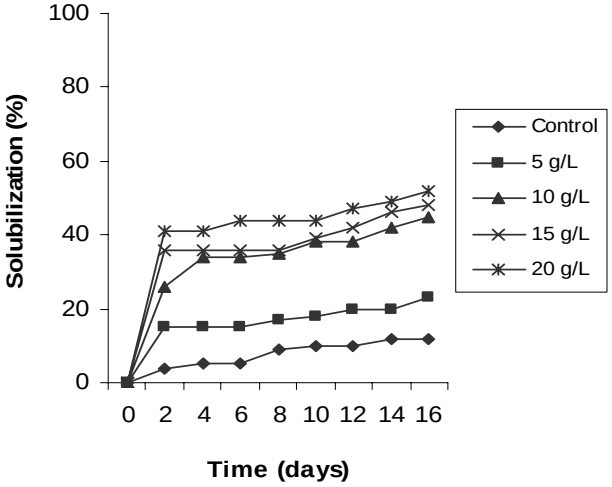


Fig. 4 % solubilization of Ni with time during bioleaching at different concentrations of ferrous sulfate

Figure 5 shows % solubilization of Zn with time. In all the metals, maximum solubilization was achieved for Zn. In the control, a maximum of 16% Zn was solubilized in 16 days compared to 69% solubilization for the sludge receiving 10 g/L ferrous sulfate. Further increase in ferrous sulfate yields only a marginal enhancement in Zn solubilization which was 74 and 75% for the sludges having 15 and 20 g L^{-1} ferrous sulfate.

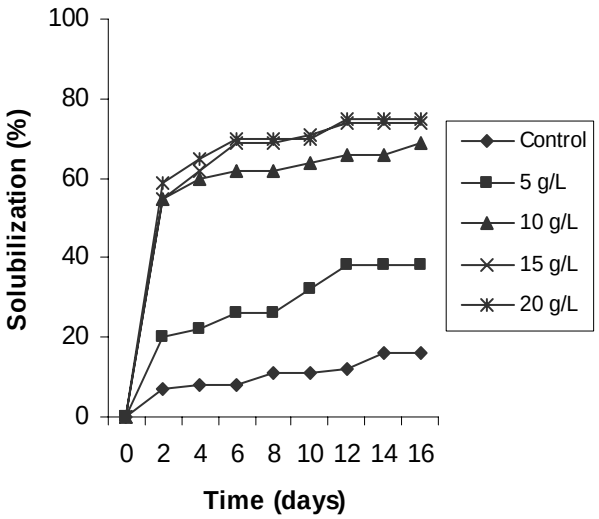


Fig 5. % solubilization of Zn with time during bioleaching at different concentrations of ferrous sulfate

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The % solubilization of Cr with time is shown in Figure 6. In the control only 12% Cr was solubilized compared to 46% in the sludge having 10 g L^{-1} ferrous sulfate. Further increase in Cr concentration beyond 10 g L^{-1} caused only a slight increase in Cr solubilization and final Cr solubilization achieved for Cr was 51 and 55% for the sludge having 15 and 20 g L^{-1} respectively. The low solubility of Cr in bioleaching could be explained on the basis of it's predominate presence as trivalent hydroxide in anaerobic sludge. Due to the reducing conditions prevailing in the anaerobic sludge, Cr exists as Cr (III). Therefore, Cr requires a prolonged time and low pH value to be solubilized during bioleaching. From the above results it can be seen that a ferrous sulfate concentration of 10 g L^{-1} is sufficient to bring the pH to the level desired for significant metal solubilization.

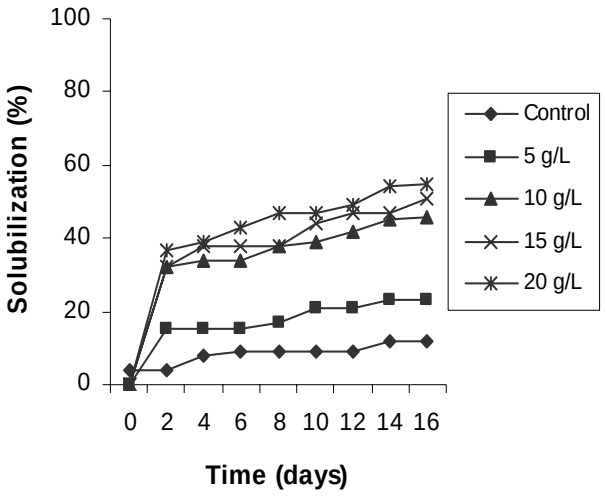


Fig. 6 % solubilization of Cr with time during bioleaching at different concentrations of ferrous sulfate

Further increase in ferrous sulfate didn't yield significant solubilization of the metals and hence 10 g L^{-1} ferrous sulfate concentration seems to be the viable option for efficient bioleaching.

3.2 Effect of Total Solids

3.2.1 Change in pH and ORP: The change in pH with time at different concentrations of sludge solids is shown in Figure 7. It can be seen that at higher concentrations of sludge solids, the decrease in pH was marginal. This is due to the higher buffering capacity of the sludge at the higher solids concentration which required more time and acid for same decrease in pH.

The change in pH was rapid at lower sludge solids concentration up to 20 g L^{-1}. It took only 2 days to reach the pH less then 3 for the sludge having solids concentrations of 5-20 g L^{-1}, whereas it took 4 days for the sludge having sludge solids of 30 g L^{-1}. At higher sludge solids of 40 g L^{-1}, the decrease in pH was marginal and even after 16 days of bioleaching, pH reached only to 3.7. After 16 days of bioleaching, pH values were 1.9, 2.1, 2.5 and 2.9 for the sludges having 5, 10, 20 and 30 g L^{-1} solids, respectively. Therefore, It appears that the amount of ferrous sulfate (10 g L^{-1}) used was not adequate for sufficient acid production for the sludges having solids content beyond 20 g/L.

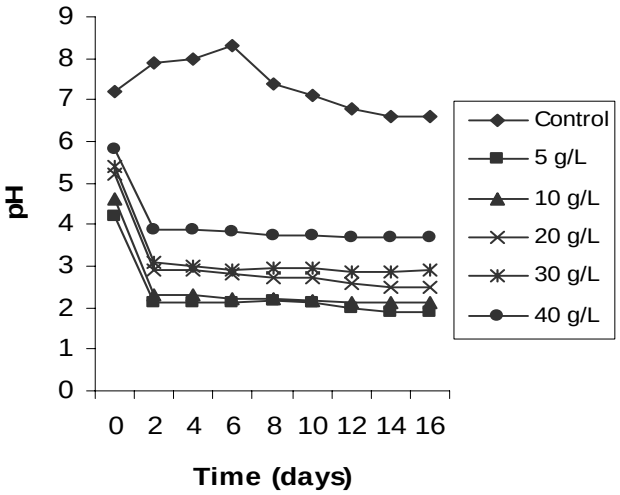


Fig. 7 Change in pH with time at different concentrations of sludge solids

The change in ORP with time during 16 days of bioleaching period is shown in Figure 8. The ORP of all the sludges increased gradually and after 2 days the ORP of all the sludges was more than 300 mV. However, at the higher solids concentration, the increase in ORP was less. The higher sludge solids caused a drop in the rate of ORP increase. The sludge having the lowest solids content showed maximum ORP with maximum value of 465 mV after 16 days of bioleaching.

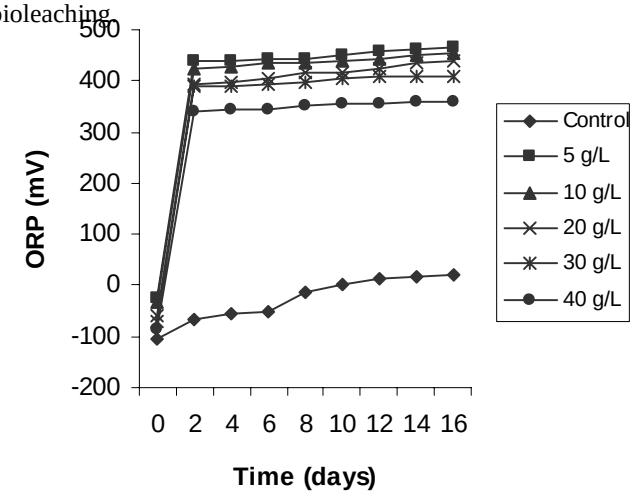


Fig. 8 Changes in ORP with time at different concentrations of sludge solid

3.2.2 Heavy metals solubilization: The change in Cu solubilization at different concentration of sludge solids during bioleaching is shown in Figure 9.

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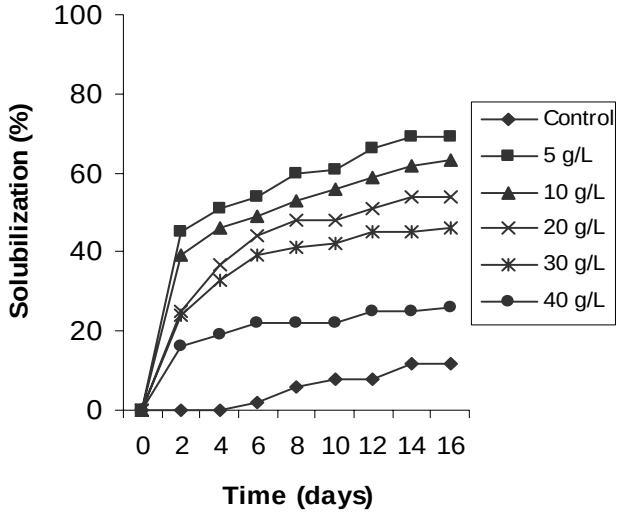


Fig. 9 Change in Cu solubilization at different concentrations of sludge solids

As can been seen, at higher sludge solids concentration, lower solubilization of Cu was achieved. At lower sludge solids concentration of 5 g L^{-1}, maximum Cu removal of 69% was achieved. At 20 g/L sludge solids concentration about 54% Cu was solubilized, whereas at 30 and 40 g L^{-1} sludge solids concentration, only 46 and 26% Cu were solubilized. A similar trend in solubilization was achieved with Ni (Fig. 10), Zn (Fig. 11) and Cr (Fig 12).

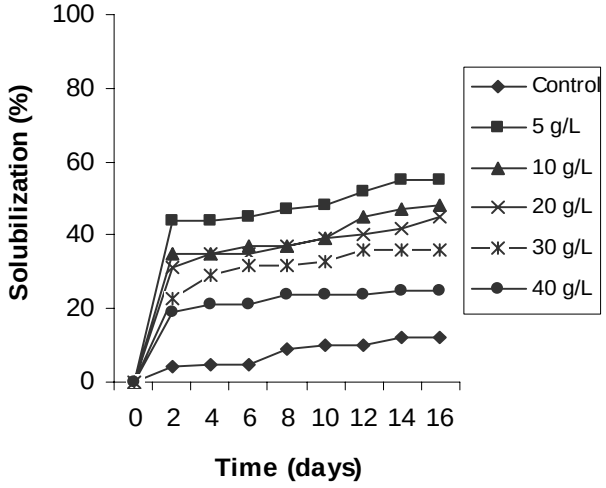


Fig. 10 Change in Ni solubilization at different concentrations of sludge solids

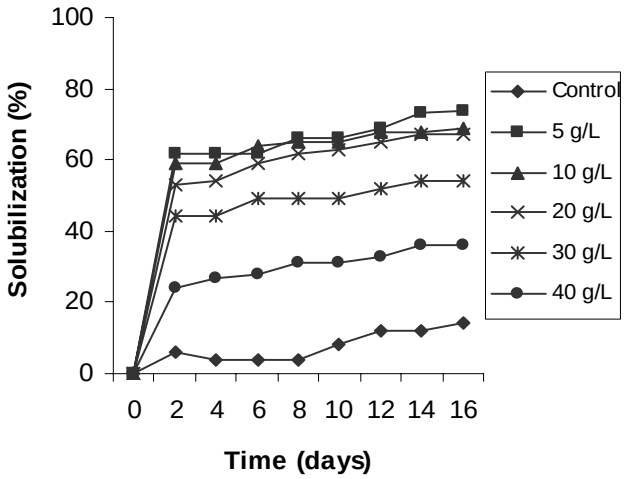


Fig. 11 Change in Zn solubilization at different concentrations of sludge solids

At 20 g L^{-1} sludge solids, about 45% Ni, 67% Zn and 48% Cr were solubilized. At increased sludge solids concentration of 40 g L^{-1}, reduced solubilization of metals was achieved which were 25%, 36% and 23% only for Ni, Zn and Cr, respectively. The above results clearly show that bioleaching using 10g L^{-1} ferrous sulfate is efficient up to 20 g L^{-1} sludge solids concentration. A further increase in sludge solids led to the lower solubilization of metals.

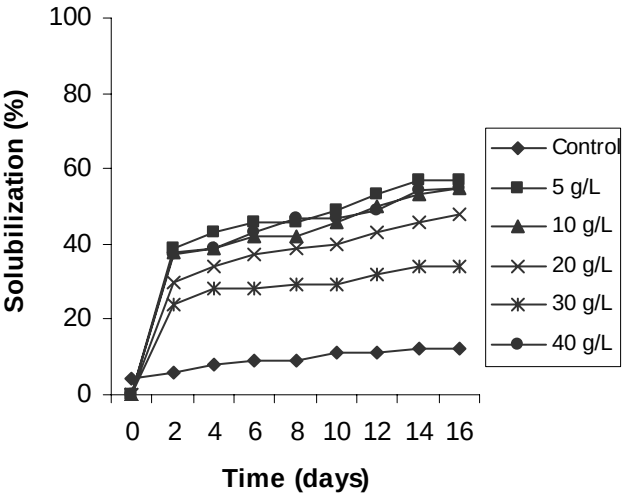


Fig. 12 Change in Cr solubilization at different concentrations of sludge solids

IV. CONCLUSION

The results of the present study show that 10 g/L is the optimum concentration of ferrous sulfate concentration which can bring the pH to the level desired for metal solubilization.

Using 10 g L^{-1} ferrous sulfate, on the 16^{th} day, the sludge pH dropped to 2.5 needed for efficient metals solubilization. After 16 days of bioleaching, about 52% Cu, 45% Ni, 69% Zn and 46% Cr were solubilized using 10 g L^{-1} ferrous sulfate as an energy source. However, bioleaching with 10 g L^{-1} ferrous sulfate is efficient only up to 20 g L^{-1} sludge solids concentration. At higher solids concentration, the percentage solubilization is inhibited due to the buffering capacity of the sludge. The results of the present study form the basis for suitable strategy to be developed for metal bioleaching operation to ensure safe disposal of the sludge.

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