Recovery of heavy metals from Indian LD slag using acidophilic and heterotrophic bacteria: A comparative study

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Indian steel slag (LD slag) is one of the most important by-product of the steel making process in Iron and steel industries (Chand et al 2016). LD slag is normally disposed off, and causes economic and environmental losses. This slag can be used for various industrial applications, such as agricultural soil conditioner, in cement industry and as raw material in steel industry. However, due to the presence of various metals it is not commonly used (Das et al 2007; Chand et al 2016). In India, only 20% of the total slag is used for industrial applications (URL 1). Leaching of both toxic and valuable metals are important for re-use of the slag for different purposes and for resource recovery. The commonly used leaching methods include pyrometallurgy and hydrometallurgy. However, these methods are both cost and energy intensive. These chemical intensive methods generate huge amount of sludge and also release harmful gases, such as, sulphur-dioxide and hydrogen sulphide (Mirazimi et al 2015). Use of microorganism for the leaching purposes may lead to an environmental friendly technology. Bioleaching uses various acidophilic and heterotrophic microorganism to convert insoluble metals from solid waste into soluble form. Mostly this technology is used for extracting metals from electronic waste, however, limited work has been done towards using it for slag (Hocheng et al 2014; Mirazimi et al 2015).

In this study, LD slag containing various toxic and valuable metals was collected from an Indian steel industry. The slag was found to be phytotoxic even at a low concentration of 5%, which thus prevented its use as a soil conditioner. Bioleaching experiments were done using the acidophilic bacteria, *Acidithiobacillus ferrooxidans*, and the heterotrophic bacteria, *Pseudomonas aeruginosa* RS1. LD slag was found to be highly alkaline in nature and had pH of 13. Hence, initially pretreatment with distilled water was performed to lower its pH. After five cycles of water washing pre-treatment, the pH was lowered to 9 and the slag could be used for bioleaching studies. Toxic metals, such as aluminium, chromium, copper, manganese and zinc, and valuable metals, such as, strontium and vanadium were analysed in the leachate. Both the cultures were pre-acclimatized on the slag solution initially to increase the resistance of the strains towards the toxic metals present in the slag. Media composition used for acidophilic bacteria was: $(NH_4)_2SO_4$ (0.5 g/L); K_2HPO_4 (0.5 g/L); $MgSO_4.7H_2O$ (0.5 g/L); $FeSO_4·7H_2O$ (167.0 g/L) and 1N H_2SO_4 (55 mL). The media for heterotrophic bacteria contained (g/L): peptone (20); yeast extract (2); glucose (20); KH_2PO_4 (0.75) and $MgSO_4.7H_2O$ (0.3) (Mirazimi et al 2015). Bioleaching experiments were done using three processes: one-step (in which slag and bacteria were inoculated together), two-step (after growth of bacteria for 48 h, slag was inoculated) and culture supernatant (after growth of bacteria, supernatant was filter sterilized and was mixed with the slag) to evaluate the mechanism of leaching. Experiments were performed using 100 mL media, 10% inoculum and 1 g/L of slag, incubated at 120 rpm in a rotary shaker at 37°C for 21 days. At every alternate day, pH and leached metal concentration were evaluated using a pH meter and ICP-AES, respectively. All the experiments were done in duplicate.

As can be seen from Figure 1, maximum leaching efficiency was found in case of the two-step process and culture supernatant process. The toxic effect of metals on bacteria growth, was thus reduced when slag was added after some time. In case of acidophilic bacteria, sulfate ions may play a major role in leaching, hence sulfate ion concentration was measured. Bacteria can act upon sulphides present in the slag matrix and releases sulfate ions into the solution during leaching (Rawlings et al 2003). The maximum concentration of sulfate ions was released in the two-step process, followed by the one-step process. In the culture supernatant process, there was no contact between slag and bacteria, hence, sulfate ions were least in this case. Thus, the sulfate ions could be correlated to the leaching efficiency. Two-step process showed maximum amount of leaching in case of acidophilic bacteria. Direct bioleaching may also occur in the two-step process, where bacteria can act on the slag matrix, get attached on to the slag by forming EPS layer which thereby helps in the release of metals into the solution. It can be seen from Figure 1 (a), 94% Al, 78% Cr, 92% Mn, 94% Sr, 95% Zn and 84% V were released in the two-step process, however, almost similar amount of Al (92%), Cr (69%), Mn (98%) and Zn (97%) were leached out in the culture supernatant process. However, low leaching of Sr (67%) and V (53%) was observed. It is thereby concluded that the growth of acidophilic bacteria helps in the leaching process of metals through an indirect mechanism, however, direct mechanism may have played some role in increasing the efficiency. Also, it was found that copper was not leached out from the slag, which may have been caused due to inhibition from ferrous ions in solution. Maximum leaching was observed within 14-16 days, after which the leaching stabilized.

In case of heterotrophic culture, maximum leaching was observed for the culture supernatant process as shown in Figure 1(b) (24% Cr, 46% Cu, 24% Mn). Zn and V showed similar leaching (8% and 75%, respectively) in both culture supernatant as well as the two-step process. Only strontium showed higher leaching in the two-step process as compared to the culture supernatant process. The possible reason may be toxic effect of metals on bacteria. The heterotrophic bacteria produced organic acids as well as surfactants during their growth. Also, it was observed that acidophilic bacteria leached out higher amount of metals as compared to heterotrophic bacteria. This was possibly due to the lower pH employed for the acidophilic bacteria (in the range of 1.5-2) as compared to the heterotrophic bacteria (in the range of 8-9). The leaching efficiency was also dependent on the stability/solubility of the complexes formed under both the conditions.

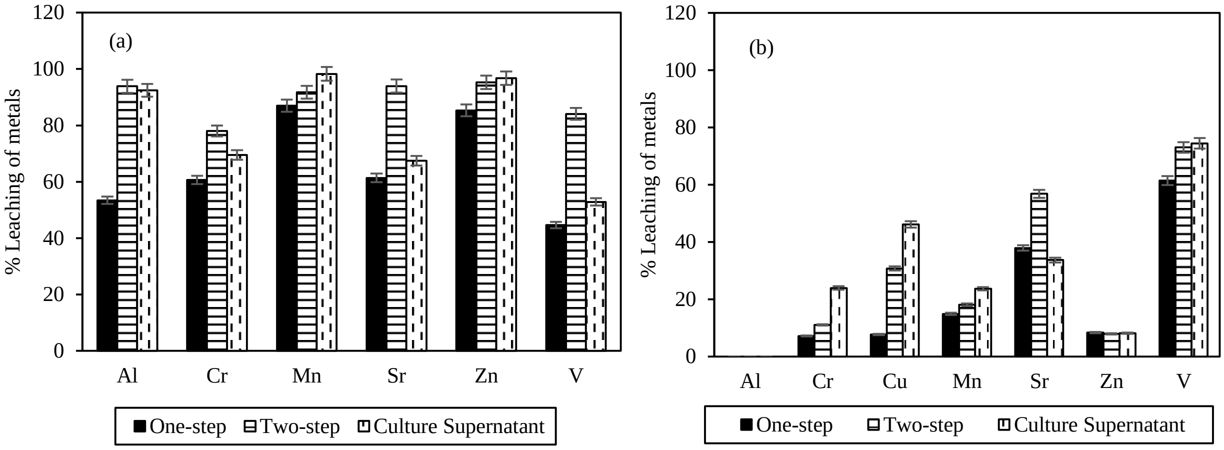

Figure 1. % Leaching of metals using (a) acidophilic bacteria and (b) heterotrophic bacteria after 21 days incubated in various bioleaching protocols

The results were also compared with those reported by Amiri *et al* (2011) employing *Penicillium simplicissimum* for extraction of W, Fe, Mo, Ni and Al from spent hydrocracking catalyst waste. Spent catalyst at 3% (w/v) promoted the maximum extraction in the two-step bioleaching process, i.e., 100% W, 100% Fe, 92.7% Mo, 66.43% Ni, and 25% Al. A study by Mirazimi *et al* (2015) using roasted LD slag showed leaching of 86% V when acidophilic bacteria was used and 75% leaching of V when heterotrophic bacteria was used in the two-step process. However, in case of one-step process, efficiency was found to be reduced, i.e., 45% and 36% for acidophilic and heterotrophic culture, respectively. Comparison with the literature also showed that with differences in the solid matrix as well as inoculum type, leaching efficiency may vary greatly. It may be concluded that acidophilic bacteria have better potential to leach out various metals from the slag matrix. For both the cultures, two-step process and culture supernatant process yielded better bioleaching compared to the one-step process.

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