

Full Length Research Paper

Dissolution of heavy metals from electrostatic precipitator (ESP) dust of a coal based sponge iron plant by fungal leaching

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Accepted 19 March, 2012

Coal based sponge iron industries in India generate considerable quantity of solid waste, 40% of which is flue dust produced from the electrostatic precipitator (ESP) connected to rotary kiln. This paper reports the dissolution of Zn, Cu, Pb, Mn and Fe from the ESP dust using three fungal species, *Aspergillus niger*, *Aspergillus fumigatus* and *Aspergillus flavus* at 5 and 10% pulp densities over a period of 28 days. Highest metal leaching was achieved with *A. niger* followed by *A. flavus*. The least metal leaching was achieved with *A. fumigatus*. The pH of the medium declined consistently over the incubation period. Maximum leaching for Zn, Cu, Pb, Mn and Fe were 81, 76, 74, 72 and 52% respectively.

Key words: Fungal leaching, sponge iron, electrostatic precipitator (ESP) dust, metal dissolution.

INTRODUCTION

Sponge iron (Direct reduced iron) has a major role in the global steel industry. Over the past few years India has been the largest producer of sponge iron, majority of which are coal based. The manufacturing processes involve reduction of iron ore by using non-coking coal with small quantity of dolomite in a rotary kiln. During the manufacturing process, approximately 45 to 50 tonnes of solid wastes are generated per 100 tonnes of sponge iron. Dust from electrostatic precipitator (ESP) connected to a rotary kiln constitutes nearly 40% of the solid waste (Jena et al., 2008). It is generally used for land filling and to a smaller extent for manufacturing bricks. We have reported earlier the heavy metal content of ESP dust of a sponge iron plant (Jena et al., 2008).

The application of bio hydrometallurgy in the field of environmental management has found critical attention in scientific community at large. Biohydrometallurgical approaches generally involve low cost and low energy requirement. Microbial leaching is based on the natural

ability of micro organisms to transform solid compounds into a soluble and extractable form. Microbial leaching for the extraction of metals from low grade ores (Sukla et al., 1993; Sukla et al., 1995a; Valeix et al., 2001), municipality solid wastes (Hung and Ting, 2006) and secondary raw materials (Brandl et al., 2001; Alvarez, 2007; Mishra et al., 2008) have been reported earlier. The application of fungus for the biobenefication of low grade iron ore bearing a high content of alumina and silica has also been reported (Mishra et al., 2010). Fungi produce various organic acids as a result of carbohydrate metabolism like oxalic, citric, lactic and gluconic acid etc., (Ducam et al., 1967; Turma and Sing, 1993; Bosshard et al., 1996).

Fungal bioleaching is advantageous in comparison to acid bioleaching because of the following reasons: (a) ability to grow in higher pH, and (b) ability of excreted metabolites (e.g organic acids) to form complexes with metal ion, thus reducing its toxicity to the biomass (Burgstaller and Schinner, 1993; Castro et al., 2000).

In the present paper we report the results of our study on dissolution of metals (Zn, Cu, Pb, Mn and Fe) from the sponge iron plant ESP dust using three different fungal strains namely *Aspergillus niger*, *Aspergillus fumigatus* and *Aspergillus flavus*.

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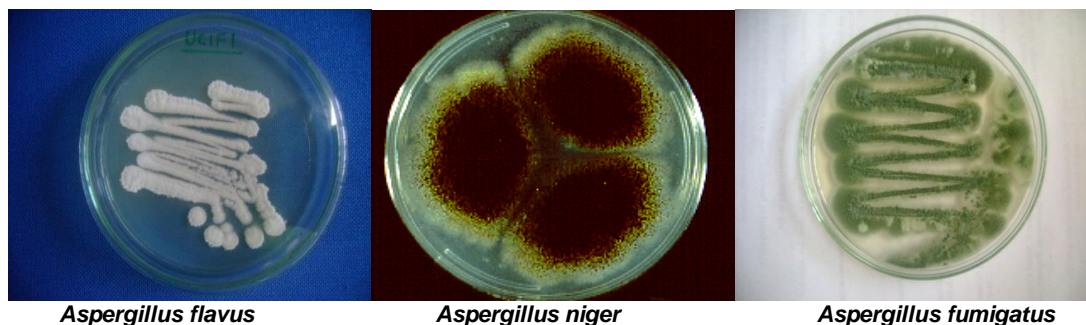


Figure 1. Fungal strains used in the bioleaching of ESP.

Table 1. Analysis result of ESP dust.

Elements	g/kg	Elements	g/kg
Al	109	Mg	12
C	62	Mn	28
Ca	14	Na	14
Cd	NT	Ni	11
CO	22	Pb	12
Cr	NT	Si	54
Cu	21	Ti	38
Fe	431	Zn	78
K	19	NT: Not tested	

MATERIALS AND METHODS

Sampling and analysis of ESP dust

ESP dust was collected from the 1500 tonnes per day (TPD) sponge iron plant located at Keonjhar, Orissa, India. The particle size distribution of the dust was measured by using low particle size analyzer (Hydro 2000 MU, MALVERN). The chemical composition of the dust was determined through total digestion as per Indian Standard procedure (IS: 3500). The heavy metal analysis of the dust was done by an atomic absorption spectrophotometer (S-series, TEC) and X-Ray Florescence Spectrophotometer (XRF), (Axios, PAN Analytical).

Microorganisms

Laboratory stock cultures of *A. niger* (MTCC2613), *A. fumigatus* (MTCC8877) and *A. flavus* (MTCC7355) were used in the present study. The organisms were grown in MSM medium with the following composition (g/L), sucrose (100), KH_2PO_4 (0.36), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (0.5) and KNO_3 (0.1) shown in Figure 1. Preparation of inoculum of microorganisms was carried out in 250 ml Erlenmeyer flasks with 90 ml MGY medium. Broth inoculated with 10 ml of stock culture was incubated at 37°C for 5 to 6 days, which resulted in the formation of a thick fungal mat. The spore suspension was obtained under aseptic conditions by mechanical disruption of fungal mats using a sterile glass homogeniser and was used as inoculum for the bioleaching experiments.

Bioleaching experiments

Bioleaching was carried out under sterile condition with 5 and 10% (w/v) ESP dust in 100 ml of MSM medium in shake flasks. A control

set of experiments (without inoculums) was given to evaluate the leaching of metals only due to environmental factors. All the other flasks were incubated at 30°C for 28 days. The leachate was analyzed for heavy metals with the help of an atomic absorption spectrophotometer (S-series, TEC). The changes in pH of the medium were measured using a digital pH meter (Elico, M – 1010). The initial pH of the medium was 6.8.

RESULTS AND DISCUSSION

Characterization of ESP dust

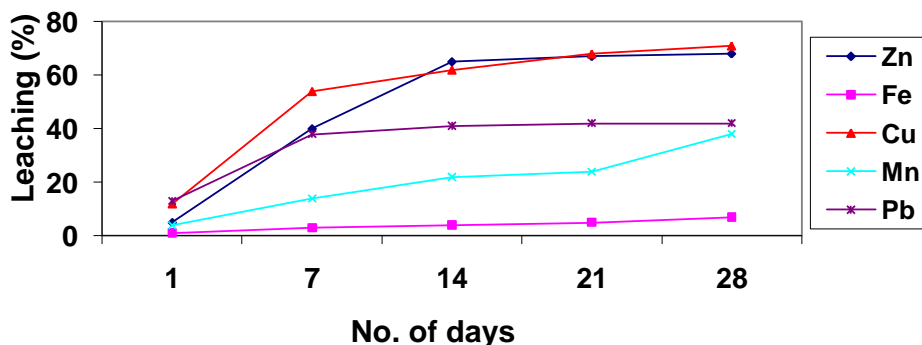
The particle size distribution of the ESP dust ranged from 0.01 to 2000 μm with a mean and mode of 172 and 27 μm respectively. The specific surface area was found to be 0.221 m^2/g . Table 1 shows the elemental composition of ESP dust. The most abundant elements present in ESP dust were Al, C, Fe, Si, Mg and Ca. Appreciable amount of heavy metals like Mn, Cu, Ni, Pb, Ti and Zn were also found in ESP dust are shown in Table 1. The likely sources of these elements are the raw materials namely iron ore, coal and dolomite.

pH change with respect to pulp densities

The change in pH during leaching period of 28 days by all the three fungal species at 5 and 10% pulp densities is shown in Table 2. *A. fumigatus* brought down the pH from 6.8 to 3.0 at 5% pulp density and from 6.8 to 4.4 at 10%

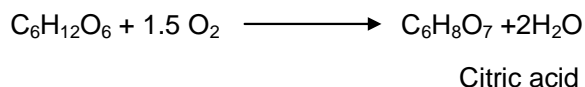
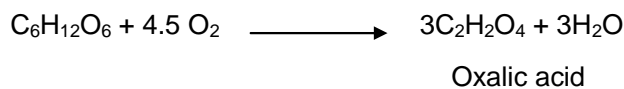
Table 2. Change of pH at 5 and 10% pulp density with different fungal strains during incubation period.

Biomass	Pulp density (%)	Day-1	Day-7	Day-14	Day-21	Day-28
<i>Aspergillus fumigatus</i>	5	6.8	7.0	6.8	5.0	3.0
	10	6.8	7.1	6.1	6.3	4.4
<i>Aspergillus niger</i>	5	6.8	3.7	1.4	0.5	0.5
	10	6.8	4.6	2.2	0.5	0.3
<i>Aspergillus flavus</i>	5	6.8	7.3	5.8	2.0	0.77
	10	6.8	6.3	6.0	3.6	1.7

**Figure 2(a).** Leaching of heavy metals at 5% pd using *A. fumigatus*.

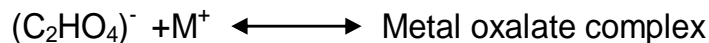
pulp density after 28 days. The pH at 5% pulp density declined sharply from 6.8 to 0.5 and at 10% pulp density from 6.8 to 0.3 with *A. niger* strain. The pH decreased from 6.8 to 0.77 (at 5% pulp density) and 6.8 to 1.7 (at 10% pulp density) over a period of 28 days on *A. flavus* inoculation. Irrespective of fungal species, treatments with 5% pulp density showed significantly lower pH compared to treatments with 10% pulp density.

Formation of strongly acidic complexing agents (polycarboxylic organic acid) such as oxalic acid, citric acid and gluconic acid etc., during the course of bioleaching of fly ash, low grade ore and silicates etc., have been reported (Sukla et al., 1993, 1995b; Hung and Ting, 2006; Rezza et al., 2001; Alvarez, 2007). In the present study the decline in pH in both the pulp densities, irrespective of fungal species used is due to formation of the organic acids by the utilization of carbohydrate by the fungal biomass.



The acidic environment during the leaching favors dissolution of heavy metals (Mishra et al., 2010). It has

also been reported that the acidic metabolites favor formation of soluble metal complexes (Turma and Sing, 1993).



Metal dissolution

At 5% pulp density the dissolution of Zn steadily increased with all the three species of *Aspergillus* over the period of 28 days. The highest percentage leaching (81%) was observed with *A. niger* on 28th day followed by *A. flavus* (76%) and *A. fumigatus* (68%) (Figures 2a to 4a). At 10% pulp density the percentage dissolution of Zn indicated an identical trend. *A. flavus* showed the highest percent leaching (66%) followed by *A. fumigatus* (61%) and *A. niger* (60%) (Figures 2b to 4b).

At 5% pulp density the highest percent dissolution of Fe (52%) was achieved with *A. niger* followed by *A. flavus* (41%) and lowest in *A. fumigatus* (7%) over a period of 28

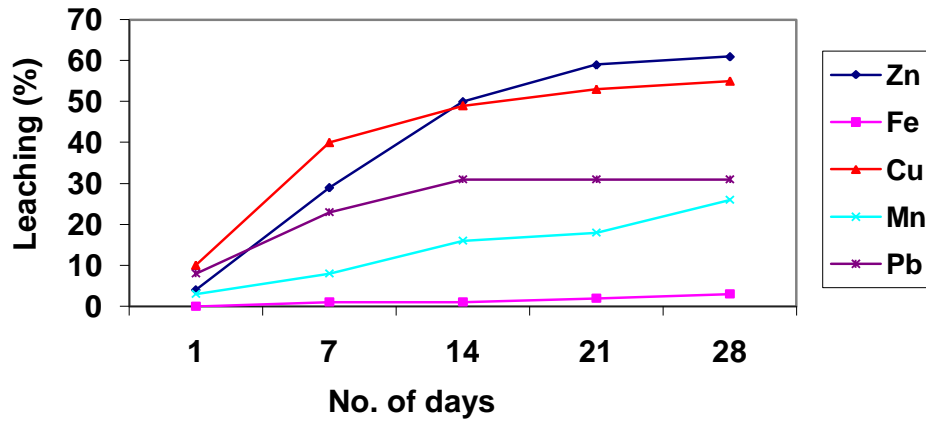


Figure 2(b). Leaching of heavy metals at 10% pd using *A. fumigatus*.

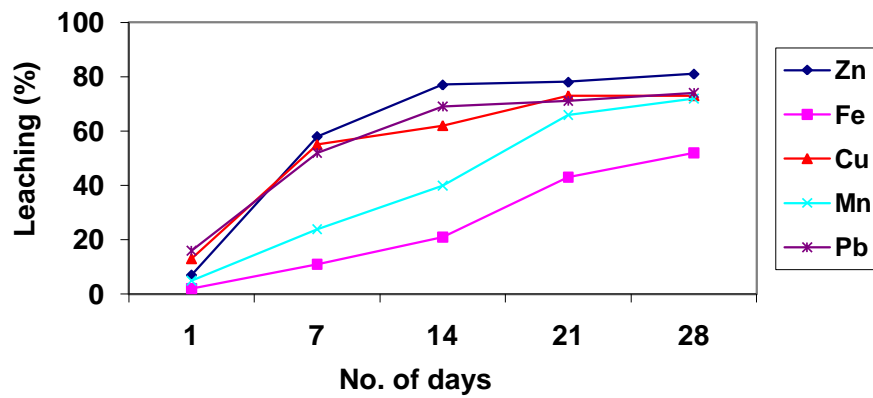


Figure 3(a). Leaching of heavy metals at 10% pd using *A. niger*.

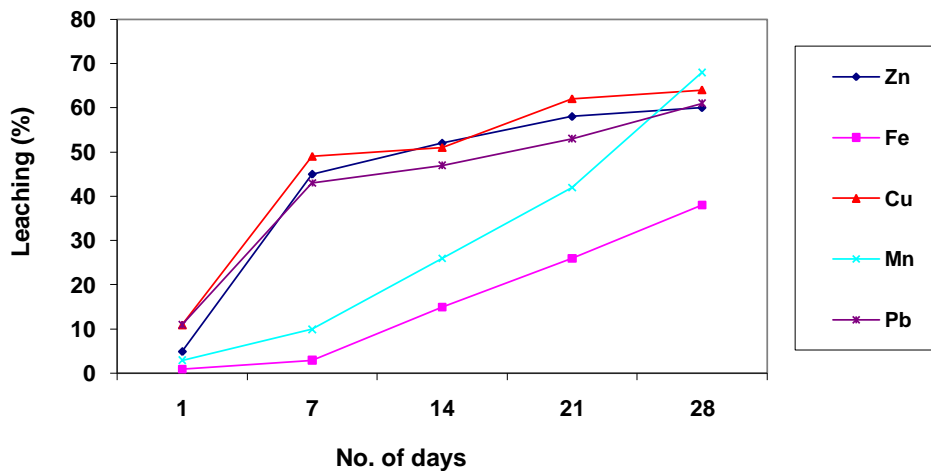


Figure 3(b). Leaching of heavy metals at 10% pd using *A. niger*.

days. Percentage of Fe dissolution at 10% pulp density was highest (38%) by *A. niger* followed by *A. flavus* (18%) and lowest with *A. fumigatus* (3%).

All the three *Aspergillus* species were found to be

potential enough to leach Cu on the day 21. The percentage dissolution at 5% pulp density was found to be 70 to 75%. At 10% pulp density the percentage leachability of Cu was (55 to 64%) that is, 5 to 10% less in comparison

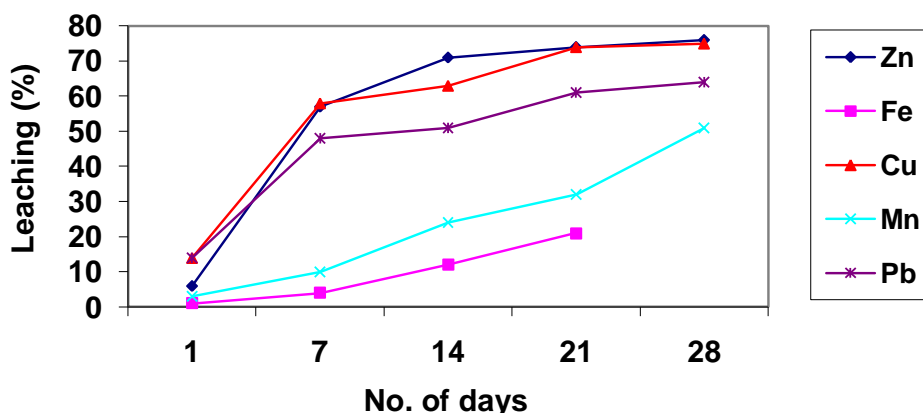


Figure 4(a). Leaching of heavy metals at 5% pd using *A. flavus*.

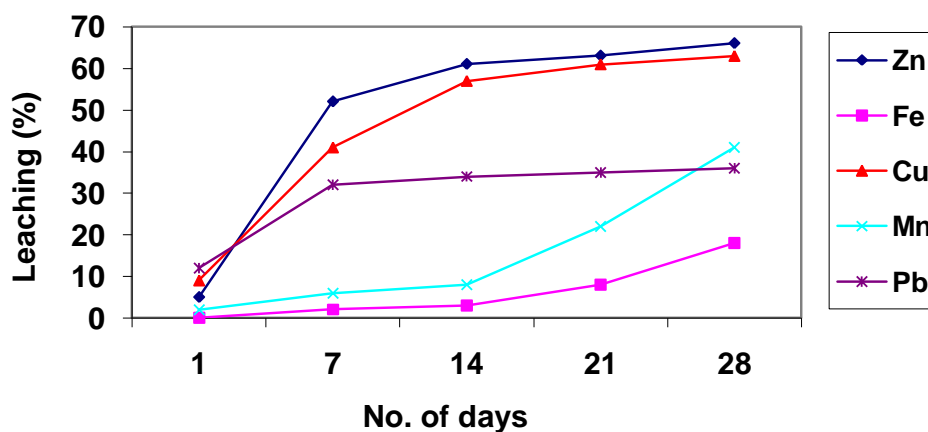


Figure 4(b). Leaching of heavy metals at 10% pd using *A. flavus*.

to 5% pulp density over the period of incubation. The highest percentage of leaching achieved with *A. flavus* was 75% followed by *A. niger* - 73% and *A. fumigatus* - 71%. At 5% pulp density the maximum percentage of leaching of Mn was 72% with *A. niger* on day 28 followed by *A. flavus* - 51% and *A. fumigatus* - 38%. At 10% pulp density the maximum percent leaching of Mn with *A. niger* achieved was 68% on day 28 followed by *A. flavus* - 41% and *A. fumigatus* - 26% over the same period of time.

Pb dissolution was highest (74%) with *A. niger*, followed by *A. flavus* (64%) and *A. fumigatus* (42%) at 5% pulp density but at 10% pulp density highest percent dissolution was achieved with *A. niger* (61%), followed by *A. flavus* (36%) and *A. fumigatus* (31%) over the same period. In the control sets the metal dissolution was negligible.

A consistent increase in the leaching of metals (w/v) with decrease in pH has been observed in both the pulp densities irrespective of fungal species. In an earlier study (Hung and Ting, 2006), the inhibition of growth of *A. niger* and leaching at higher pulp densities was linked to higher concentration of toxic metals. In the present study consistently higher metal leaching at 5% pulp density in comparison to 10% pulp density irrespective of fungal

biomass corroborate these earlier findings. The results also showed that a treatment with 5% pulp density is more suitable to achieve higher metal yield in comparison to treatments with 10% pulp density.

From Figures 2 to 4, it is seen that solubilization of Cu, Zn and Pb reached maximum on day 14 whereas, Fe and Mn reached maximum on day 21.

In the present study the metal extraction yield is in the following order: by *A. niger* Zn > Cu, Mn, Pb > Fe; by *A. flavus* Zn, Cu > Pb > Mn > Fe; by *A. fumigatus* Zn ≈, Cu > Pb > Mn > Fe.

It has been reported that the fungi solubilised Zn most easily amongst a series of heavy metals (Hung and Ting, 2006). The lower extraction of iron in the fungal bioleaching may be due to its precipitation and surface adsorption into the ESP dust (Hung and Ting, 2006). Our results are generally in good agreement with the earlier studies by Zhou et al. (2008).

Conclusion

Fungal bioleaching of ESP dust from sponge iron plant is strongly influenced by pulp density. The inhibition of

leaching of heavy metals at higher pulp density might be due to higher concentration of toxic metals present in ESP dust. Although fungal leaching requires a longer period of operation than chemical/acid leaching, it achieves a higher extraction of heavy metals at lower cost. The results of our study suggest that *A. niger* may be used for dissolution of Cu, Fe, Zn, Mn and Pb, *A. fumigatus* for dissolution of Zn and Cu and *A. flavus* may be used for dissolution of Zn Cu and Pb from ESP dust generated by sponge iron plants.

ACKNOWLEDGEMENTS

The authors are thankful to TATA Sponge and Iron Ltd, Keonjhar, Orissa, India for supplying the ESP dust. The authors are also thankful to Prof. B. K. Mishra, Director, IMMT, Bhubaneswar, Orissa, India for the laboratory facilities.

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