DEPHOSPHORIZATION OF LD SLAG BY PENICILLIUM CITRINUM

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INTRODUCTION

In different metallurgical operations, huge quantities of waste materials are generated from different industries such as Iron, Steel etc. LD slag is one of the waste products generated in large quantities and poses a substantial disposal problem in these industries. LD slag is produced in large quantities poses a substantial disposal problem in the iron and steel making industry. LD slag contains lime which varies from 40-49%. Due to presence of Ca in high amount, it can be used as flux in blast furnace provided it’s phosphorous is reduced to <0.5% (Pradhan and Shukla, 2007).

Removals of phosphorus from LD slag through microbial treatment need to be tried. Phosphorus is one of the major nutrients, and microbial solubilisation of insoluble mineral phosphate in soil is an important process in natural ecosystem and in agricultural soil. Many phosphorus solubilising microorganisms (PSM) of soil display the ability to solubilize insoluble phosphates when provided as the sole ‘P’ source in laboratory media (Leagon et al., 2010, Pradhan and Shukla, 2007 and Nautiyal, 2000). In this study an attempt was made to look into the phosphorus solubilisation efficiency of commonly available soil fungi and its possible application in bio-beneficiation of metallurgical waste like LD Slag.

MATERIALS AND METHODS

LD Slag sample was obtained from Steel Plant of Vishakhapatnam

Microorganism

The fungus *Penicillium citrinum* (BPSF1) was isolated from Conveyer belt of Paradip Port area. The fungus was cultivated in a medium containing glucose (1%) as carbon source with crushed slag sample as a sole source of phosphorous. Phosphorus solubilisation efficiency was studied at different pulp density, incubation period, NaCl concentration and at different initial pH of the medium. About 46.87 % of ‘P’ could be solubilized as P2O5 from LD slag at 5% pulp density after 24 days of incubation. This is a novel method for dephosphorization of LD slag and subsequent waste utilization. The dephosphorized slag can thus have application as a fluxing material in iron and steel production.

Analytical determination

The phosphorous content in LD Slag sample was acid digested and determined by molybdenum blue method (Jackson, 1987). The calcium and magnesium content was determined by complexometric titration with EDTA (Vogel, 1969). The quantitative evaluation of elements like Al, Ti, and Si were done by ICP (PERKIN ELMER, PLASMA-400) Spectrophotometer. A high temperature (10,000k) Argon Plasma source is used for the excitation of the element and the
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concentrations are measured as a function of the emission intensity of the emission spectra generated by the particular element (Vogel, 1969).

Biobenification experiments
In Pikovskaya broth tri-calcium phosphate (TCP) was replaced by LD Slag. The result on chemical composition of the sample has been presented in Table 1. Experiments of biobenification were carried out in sterile 250mL glass flasks. Each flask received the sterile sample, 100mL of sterile liquid medium and 0.25mL of inoculum, under sterile conditions provided by a laminar flow chamber. Uninoculated flasks were left as blank/controls. The flasks were incubated in a shaker at 150 rpm and at 30°C.

The effect of NaCl, initial pH and sugar concentration was tested in PVK medium with fungi P.citrinum as inoculum under above mentioned conditions in 100mL medium. The NaCl concentration varied from 1g/L to 9g/L. The flasks were incubated for 30 days at 30°C and 150rpm. After incubation for specified period of time the contents of the flasks were carefully filtered through filter paper followed by washing with distilled water. The LD slag residues were air dried and used for analysis of phosphorus.

At regular interval an aliquot of sample was withdrawn for analysis. The concentration of ‘P’ released in the medium as phosphate was analyzed by molybdenum blue method (Jackson, 1987).

RESULTS AND DISCUSSION

Chemical analysis of LD Slag
The results indicate that the major components of LD Slag were CaO (48.82 wt %), Fe₂O₃ (19.61 wt %), SiO₂ (10.26 wt %), Al₂O₃ (5.87 wt %) and MgO (4.84 wt %) (Table 1) Other oxides such as TiO₂, MnO, P₂O₅, and K₂O were in low concentrations i.e. 1.11, 1.34, 1.84 and 0.12 wt%. In general, steel slag mainly consists of CaO, Fe₂O₃, SiO₂, MgO, Al₂O₃ and MnO (Shen and Forssberg, 2009; Tsakiridis et al., 2010, Cha et al., 2006; Tossavainen et al., 2007). Other studies reported that the chemical composition of steel slag mainly contains CaO (45-60wt%), Fe₂O₃ (3-9wt%), FeO (7-20wt%), SiO₂ (10-15wt%), MgO (3-13wt%) and Al₂O₃ (1-5wt%) (Shi and Qian, 2000).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>P₂O₅</th>
<th>CaO</th>
<th>MgO</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>TiO₂</th>
<th>MnO</th>
<th>K₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%)</td>
<td>1.84</td>
<td>48.82</td>
<td>4.84</td>
<td>19.61</td>
<td>5.87</td>
<td>10.26</td>
<td>1.11</td>
<td>1.34</td>
<td>0.12</td>
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</tbody>
</table>

X-ray diffraction analysis of LD Slag
The mineral phases constituting LD slag are dependent upon slag composition and the cooling rate during solidification. As shown in Fig. 1, the composition of LD slag was Dicalcium ferrite, Calcium Aluminate, Wustite, and Dicalcium Silicate. It is apparent that phosphorus exists in the dicalcium silicate phase. The existence of phosphorus in this phase has already been reported by Narita et al. (2010).

Biobenification Experiments

Effect of Incubation Period and Pulp density
The maximum P solubilisation from LD Slag by P.citrinum was 46.87% on 24th day of incubation (Fig. 2). The highest P solubilisation was found in lowest pulp density i.e. at 5% and lowest P solubilisation was observed in highest pulp density i.e. at 25% (Fig. 3). The P solubilisation gradually increased with increasing in incubation period up to 24th day and after that the leaching activity was stopped and further P solubilisation was not observed. After 24th day The P solubilisation decreased due to the deficiency of nutrients in the culture media. From (Fig. 2) it was observed that the P solubilisation was accompanied with reduction in pH of the media. The minimum reduction of pH varied from 4.18 to 4.86, the highest reduction was observed in 5% pulp density and lowest was found in 25% pulp density on 24th day of incubation (Fig. 3). An increase in Pulp density adversely affects P solubilisation. This can be...
although it was less. This finding suggests that sea water may not inhibit solubilisation of phosphorus from LD Slag concentration (Fig. 5). The concentration of NaCl up to 9 g/L solubilisation of phosphorus was obtained at 6 g/L of NaCl concentration. High pH and high salinity do not inhibit the bacteria and P'solubilization. Dephosphorisation yields were somewhat low and long term treatments (24 days) were needed to attain a dephosphorisation degree of 46.78%. The dephosphorised LD slag can be reused as fluxing material by blending with limestone in iron and steel making process.

**Effect of Salt and pH**

The phosphate solubilisation by microorganisms is reported to be influenced by the source of carbon, type of nitrogen source, period of exposure, concentration of sucrose or glucose and yeast extract, change in pH and temperature etc (Kucey et al., 2005 and Pradhan et al., 2003). Tolerance to high salt, high pH may be important growth parameter for survival, multiplication and spread of the fungal strain. Phosphate solubilisation activity of *Penicillium citrinum* was evaluated with respect to effect of initial pH, sugar concentration in medium and concentration of NaCl (salinity).

*P.citrinum* was grown at varying pH (4, 5, 6, 7, 8, 9, 10 and 11). Maximum phosphorus solubilisation was observed in the medium of initial pH 7 (Fig. 4). The final pH of the medium as observed was 4.5. The pH of the medium in all the experiment decreased from their initial pH. Organic acids were produced which decreased the pH of the medium almost to 4.5. Direct relationship between phosphorus solubilization and decrease in pH of medium was observed due to organic acid production.

To study the effect of salt concentration on phosphate solubilisation *P.citrinum* was grown in the presence of varying concentration of NaCl up to 8 g/L. This experiment was performed with objective to see if sea water could be used in place of normal tap water in the process. Maximum solubilisation of phosphorus was obtained at 6 g/L of NaCl concentration (Fig. 5). The concentration of NaCl up to 9 g/L did not inhibit solubilisation of phosphorus from LD Slag although it was less. This finding suggests that sea water may be used in place of tap water for this process.

**CONCLUSION**

The biological route to remove phosphorous from LD Slag was found to be feasible using the fungus *Penicillium citrinum*. Optimum solubilization was observed at 5% pulp density, initial pH of 7 and 6 g/L of NaCl concentration. High pH and high salinity do not inhibit the bacteria and P'solubilization. Dephosphorisation yields were somewhat low and long term treatments (24 days) were needed to attain a dephosphorisation degree of 46.78%. The dephosphorised LD slag can be reused as fluxing material by blending with limestone in iron and steel making process.

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