Removal of alkyllead using blast furnace granulated slag

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The blast furnace granulated slag when treated with a solution of silver nitrate indicates a shiny deposition of metallic silver showing its capacity to cause electrochemical reduction. The major and minor components of the slag have been determined. The capacity of the slag to cause chemical reduction has been attributed to the presence of certain reactive metals in their elemental states. Alkyllead, in gasoline or aqueous system, when treated with the blast furnace granulated slag is found to be substantially or completely removed depending on the conditions of the treatment. The method has been found simple, economical and useful for the treatment of alkyllead-contaminated aqueous systems.

The principal sources of tetraethyllead (TEL) as pollutant have been identified as waste sludges from petroleum refineries and waste sludges as well as wastewater from manufacturing plants of alkyl lead compounds. The organic lead in wastewater from TEL manufacture has been reported to be in the range 126.7-144.8 mg/L. On account of its solubility in lipids, TEL is readily absorbed by the skin as well as the respiratory and gastrointestinal tracts. Its major portion accumulates in the brain due to a special affinity between organic lead and the lipid of nerve tissues. According to Schroeder, TEL is more than hundred times as toxic as inorganic lead. The maximum allowable concentration of lead in effluents being discharged to a storm sewer or a stream is 0.1 ppm.

TEL contaminated wastewater has been treated by various methods which include the use of lime and ferrous sulphate, use of cation exchange resin for the removal of organic lead followed by caustic soda and conversion into inorganic lead by chlorine gas, and also the use of ozone containing gas. According to a process developed by Taylor, TEL is being removed by contacting the effluent in an alkaline medium with iron filings. A procedure developed by Zimmerman involves the use of amorphous activated carbon impregnated with CuCl₂ while the method adopted by Buckholder involves the use of FeSO₄, NaBH₄ and anionic polyelectrolyte. Lill has used a suspension of zinc particles for lowering the lead content of the wastewater. The method presented in this paper has been found to eliminate the entire presence of inorganic and organic lead from contaminated water by the simple contacting operation using blast furnace granulated slag.

Blast furnace granulated slag: Its characterization—The use of blast furnace granulated slag has been made. The availability of this slag in India is about 615 kg/tonne of steel manufactured. The major components of the slag on analysis by standard methods have been found as follows: SiO₂-30.7%, Fe₂O₃-3.20%, Al₂O₃-20.80%, CaO-33.90%, MgO-8.43%, SO₄⁻-1.50%, S⁻-0.66%, Na₂O-0.60%, K₂O-0.50% and MnO-1.83%. The minor components have been determined by atomic absorption spectrophotometry and found as follows: Cu-18 mg/L, Co-40 mg/L, Ni-41 mg/L, Pb-44 mg/L, Zn-28 mg/L, Cr-100 mg/L, Li-20 mg/L, Cd-6 mg/L, Bi-20 mg/L and V-10 mg/L. The slag matter on treatment with silver nitrate solution exhibited a deposition of metallic silver, suggesting that the slag is capable of causing electrochemical reduction on account of the presence of a number of reactive metals in their elemental states. This capacity of electrochemical reduction of the slag has already been successfully used in the removal of Cr(VI), Hg(II), Cu(II), Pb(II) and Zn(II) from aqueous solutions.

Study of removal of inorganic lead—Glass columns (ht 50 cm, dia 2.5 cm) were packed separately with weighed quantities (25 g) of iron filings, aluminium filings and granulated slag. Lead solutions containing 100-1000 mg/L of lead were prepared in HCl-water medium using Pb(NO₃)₂ of Analar grade.

The solutions were flowed through the column at a rate of 5.2 mL/min and the lead levels were determined in eluate titrimetrically using EDTA (0.01 M), hexammine powder and xylene orange as indicator. The highest concentration of lead solutions which showed 100% removal of Pb(II) ions with different treatment materials are found to be as follows: iron filings-800 mg/L, aluminium filings-450 mg/L, slag-200 mg/L. These observations show similarity of mechanism of lead removal in cases of the three treatment materials.

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Table 1—Removal of alkyllead by blast furnace slag

<table>
<thead>
<tr>
<th>Treatment material and conditions</th>
<th>Initial Conc. of alkyllead* Conc.: mg/L</th>
<th>Concentration of alkyllead* found after (mg/L)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 day</td>
<td>2 days</td>
<td>3 days</td>
</tr>
<tr>
<td>Gasoline (100 mL) + slag (10 g)</td>
<td>540.00</td>
<td>210.60</td>
<td>114.00</td>
</tr>
<tr>
<td>Gasoline (100 mL) + slag (10 g) soaked in HCl</td>
<td>540.00</td>
<td>354.24</td>
<td>294.03</td>
</tr>
<tr>
<td>Gasoline (100 mL) + slag (10 g) + glacial acetic acid (10 mL)</td>
<td>540.00</td>
<td>205.00</td>
<td>147.80</td>
</tr>
<tr>
<td>Alkyllead extract in NaOH solution (100 mL) + Slag (10 g)</td>
<td>540.00</td>
<td>63.90</td>
<td>43.20</td>
</tr>
</tbody>
</table>

* Calculated as tetraethyllead (TEL)

Study of removal of alkyllead—The commercial leaded gasoline was taken as a source of alkyllead, isolated by refluxing an aliquot (10 mL) of gasoline with conc. HCl (5 mL) in a round bottom flask (250 mL) for 30 min. The gasoline and aqueous layers were separated. The gasoline was further refluxed with two 25 mL portions of water. All the aqueous layers were then combined together and evaporated to a dry residue. 5 mL conc. nitric acid was then added and the mixture evaporated to dryness to oxidize any organic material. The lead nitrate formed was dissolved in 10 mL of 1:10 nitric acid and diluted to 50 mL. An aliquot (10 mL) was taken, and its pH was adjusted to 9.7 using NH₄OH. This was then treated with 10 mL solution of dithizone (2.5 mg/100 mL CCl₄). The CCl₄ layer was separated and its absorbance was measured at 520 nm. A blank using all reagents except the sample was also run. The concentration of lead in the sample was determined by a calibration graph prepared by using standard solutions of lead nitrate. The concentration of alkyllead in terms of TEL was found to be 540 mg/L gasoline. The blast furnace slag (size 2-4 mm) was collected from a steel plant.

Four sets of treatment mixtures in separate glass vessels were prepared as:
(1) Gasoline 100 mL + 10 g slag
(2) Gasoline 100 mL + 10 g slag soaked in conc. HCl
(3) Gasoline 100 mL + 10 g slag + 10 mL glacial acetic acid
(4) Alkyllead extract in NaOH solution (100 mL) (pH 11.0) + 10 g slag.

The extract was obtained by shaking 100 mL of gasoline repeatedly with portions of NaOH solution till traces of alkyllead were found undetectable in gasoline.

Aliquots (10 mL each) of clear supernatant liquid were drawn at intervals of one day from each reaction mixture. The lead was determined spectrophotometrically using dithizone reagent, till conclusive results were obtained. The results have been shown in Table 1.

Results and discussion—It has been found that blast furnace granulated slag is capable of acting as electrochemical reductant. The capacity of the slag is, however, smaller compared to that of iron filings or aluminium filings on account of lesser amount of reactive metals in it. When applied to the removal of Pb(II) ions in aqueous solution, it is found that 25 g slag when packed in a glass column is able to remove entire lead from 150 mL of a solution containing 200 mg/L of Pb(II), at a flow rate of 5.2 mL/min. In case of alkyllead, it is found that a 100 mL aliquot containing 540 mg/L of alkyllead (as TEL) is completely removed by 10 g of the slag in a period of three days. Thus, 1 g of slag is found capable of removing 5.4 mg of alkyllead (as TEL) in three days. The aqueous medium has been found to be more favourable compared to the gasoline medium in the removal process. Further, the presence of acidity has been found to inhibit the removal process, and a strongly alkaline aqueous medium has been found to promote the process. The effectiveness of blast furnace granulated slag for the removal of lead ions as well as alkyllead has thus been confirmed and the method is found to be simple in operation and inexpensive.

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References