THE REMEDIAL TREATMENT OF SOIL POLLUTED WITH HEAVY METALS USING FLY ASH

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The goal of this research was to investigate the effect of fly ash as amendment in the remediation of soil polluted with heavy metals, due to the industrial activity.

The ratio fly ash: polluted soil was determined as a function of pH. The mobility of copper and lead was investigated before and after treatment of soil with fly ash, using as extractants distilled water or an aqueous diluted solution (0.1N) of HNO3.

The impact of the presence of fly ash in soil (at ratio 0...10% weight) upon some characteristics of the soil was evaluated.

The results obtained in this research showed that fly ash is an appropriate amendment for the remediation of soil polluted with copper and lead.

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1. Introduction

Soil is a very complex medium which consists of solid and fluid phases which interact each other and is one of the key elements for all terrestrial ecosystems [1].

The ability of soils to adsorb metal ions has consequences for agricultural purposes and for environment, the adsorption being a major process responsible for accumulation of heavy metals in soil.

Reducing the presence of trace metals in plants is critical for the optimization of agricultural production on the lands contaminated due to urban or industrial activities.

There are several remediation technologies applied to contaminated soil: chemical treatment, soil flushing and washing, phytoremediation etc.

Stabilization is one of the most widely used technologies for the remediation of soil contaminated with heavy metals [2 – 5].

Particularly, “in – situ” chemical immobilization is a remediation technique that decreases the concentration of dissolved contaminants by sorption or precipitation [6]. Chemical immobilization limits the transport of pollutants into deeper soil layers and into groundwater [7].

There are many possible ways for the immobilization of heavy metals in polluted soils by example using organic manure [8], zeolites [5,9], clay minerals [10,11], calcium and magnesium carbonates and calcium oxide [12], waste products rich in iron, manganese and aluminum oxides [4,13] etc.

Coal – burning plants produce large amounts of fly ash as a residue. For many years, fly ash has been considered a waste material, the production of which has continued to increase; it is widely available and a cheap material.

Fly ash is an appropriate material for residual water treatment, several studies have pointed out their efficiency in the removal of heavy metal ions from aqueous phase [14 – 17].

The goal of this research was to investigate the effect of fly ash as amendment in the remediation of soil polluted with heavy metals due to the mining activity developed in a copper mine, situated in south - west county in Romania. After mining stopped, because of lack of the remediation measures, a large surface of soil was contaminated with mine tailings and flotation sludge containing critical quantities of heavy metals, especially copper and lead. A recent evaluation shows that over 1800 ha are contaminated with copper and over 400 ha are contaminated with lead.
3. Materials and methods

Polluted soil was collected from over 20 points situated in the old mine area, at a depth of 0 – 20 cm, air dried for 6 days and sieved to remove non-soil impurities and analyzed in agreement with Romanian legislation. Fractions smaller than 2 mm from each sample were mixed, homogenized and the resulted average sample was analyzed for physical and chemical characteristics determination.

The characteristics of the average sample polluted soil are presented in Tables 1 and 2.

The pH was measured in the clean aliquot above the soil, in agreement with Romanian Standard ISO 10390 – 1999.

The water content was analyzed using Romanian Standard ISO 11405 – 1997.

The heavy metal content of soil sample was determined in the clean aliquot above soil, in agreement with the recommendation of Romanian Standard ISO 11047 – 1999, by atomic absorption spectrometry.

In Table 3 are presented the characteristics of fly ash produced in a Romanian power plant. The mineralogical composition was determined by X-ray diffraction measurements and the specific surface using BET N₂ adsorption method.

Soil treatment with fly ash

Soil samples were mixed with different quantities of fly ash, to obtain mixtures containing 1…10% fly ash, after homogenization 2 hours in a vertical rotary shaker. The particle size of fly ash was less than 0.2mm.

The mixtures of polluted soil – fly ash were subjected to the Static Leaching Test [13], which predicts the following leaching conditions:
- leaching agent – distilled water and aqueous nitric acid solutions 0.1N to obtain the desired pH values;
- contact time: 2 hours;
- solid : liquid ratio 1:100;
- room temperature;
- continuous mixing

After the solid – liquid separation, in the solution was determined the concentration of metals by mass absorption spectrometry.

The ratios of fly ash: polluted soil at pH values 4…7 to ensure the remediation of polluted soil with copper and lead were determined and are presented in Figs. 1 and 2.
3. Results and discussion

Table 1 presents some chemical characteristics of soil sample used in this experiment.

<table>
<thead>
<tr>
<th>pH (H₂O)</th>
<th>Humus %</th>
<th>C_total %</th>
<th>N_total %</th>
<th>P_al %</th>
<th>K_al mg/kg</th>
<th>Pb mg/kg</th>
<th>Cu mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.95</td>
<td>2.14</td>
<td>1.21</td>
<td>0.166</td>
<td>5.44</td>
<td>187.0</td>
<td>50.8</td>
<td>865.0</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Coarse sand (2-0.2mm)</th>
<th>Fine sand (0.2-0.02mm)</th>
<th>Dust 0.02mm</th>
<th>Clay 0.002mm</th>
<th>Texture</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.0</td>
<td>24.7</td>
<td>23.0</td>
<td>16.2</td>
<td>SG</td>
</tr>
</tbody>
</table>

Some characteristics of fly ash are presented in Table 3

<table>
<thead>
<tr>
<th>Crt.no.</th>
<th>Parameter</th>
<th>%/g/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SiO₂</td>
<td>48.27</td>
</tr>
<tr>
<td>2</td>
<td>Al₂O₃</td>
<td>25.93</td>
</tr>
<tr>
<td>3</td>
<td>Fe₂O₃</td>
<td>10.54</td>
</tr>
<tr>
<td>4</td>
<td>CaO</td>
<td>5.30</td>
</tr>
<tr>
<td>5</td>
<td>K₂O</td>
<td>2.35</td>
</tr>
<tr>
<td>6</td>
<td>MgO</td>
<td>1.25</td>
</tr>
<tr>
<td>7</td>
<td>TiO₂</td>
<td>0.88</td>
</tr>
<tr>
<td>8</td>
<td>Na₂O</td>
<td>0.55</td>
</tr>
<tr>
<td>9</td>
<td>P₂O₅</td>
<td>0.47</td>
</tr>
<tr>
<td>10</td>
<td>BET surface,g/cm²</td>
<td>9350</td>
</tr>
</tbody>
</table>

The pH influence upon the solubility of copper and lead from untreated soil and treated soil with different amounts of fly ash (1…10%) is illustrated in Figs. 1 and 2, respectively.

From Figs. 1 and 2 it is evident that with pH decreasing an increase in solubility of copper and lead takes place.

Fly ash is efficient in decreasing the concentration of the metal in solution. The ration fly ash: polluted soil increases with pH decreasing.

Because of the lack in legislation concerning the limit of the concentration of heavy metals in soil solution, the authors have considered the limit of metal concentration imposed for purified polluted water (0.1 mg Cu/l and 0.2 mg Pb/l) imposed by Romanian legislation.

In these conditions, the ratios fly ash: polluted soil depend on heavy metal concentration in soil and on the pH in soil solution, between pH 4…7 and the
amount of fly ash necessary for heavy metal immobilization is 10–5%, respectively.

Fig 1. Influence of pH on copper solubilization (mg Cu/l) from treated and untreated soil

Fig 2. Influence of pH on lead solubilization (mg Pb/l) from treated and untreated soil

The next question was how high is the impact of the presence of fly ash in polluted soil upon soil characteristics? For the evaluation of this impact mixtures of polluted soil containing 1–10% fly ash were prepared. These mixtures were analyzed to observe the variation of total nitrogen, total carbon and potassium contents. The results are presented graphically in Figs. 3 and 4.
From the Figs. 3 and 4 it is evident that the presence of fly ash in soil has not produced important changes in total nitrogen, total carbon and potassium contents. From this point of view fly ash is an appropriate material for soil polluted with heavy metals remediation.
4. Conclusions

The soil from the vicinity of the industrial area (the old copper mine) is polluted with copper and lead. For the immobilization of these metals we have used fly ash - a waste produced in a Romanian power plant.

The results of this research have demonstrated the capability of fly ash to stabilize the polluted soil with copper and lead, for soil remediation. For the polluted soil used in this study the suggested dose of fly ash is 1…5 %weight, depending on soil pH value.

REFERENCES

Acknowledgment

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