Stabilization of Heavy Metals Present in Municipal Solid Waste using Hydrothermally Synthesized Iron Oxide

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Abstract---This study is an attempt to stabilize the heavy metals present in the municipal solid waste. A hydrothermal processing system setup with a mixture of ferric sulphate. Experimental results showed the reduction in the heavy metals concentration in the municipal solid waste ash after the treatment with iron oxides. Initial values of Cr, Cu, Pb, Cr, Hg was 0.001 mg/L, 4.322 mg/L, 0.578 mg/L, 0.769 mg/L and 0.001 mg/L respectively. After the treatment with iron oxides the concentration of all heavy metals were reduced to less than 0.0001 mg/L.

Keywords: MSW ash, XRD, AAS, Hydrothermal Treatment, Heavy metals.

I. INTRODUCTION

Municipal solid waste (MSW) is the waste most commonly used in composting. It is an extremely heterogeneous material in its geometry, particle size and chemical composition. (Flyhammar P. (1997)). It may, moreover, contain high concentrations of Pb, Cu, Cd, and Zn, as has been shown by several studies (Flyhammar P. (1998)). Consequently, subsequent application of MSW composts in rich heavy metals to agricultural soils may cause heavy metals accumulation to toxic levels (King L.D et al., (1990) : Veeken A et al.,(2002)). When the compost from MSW is used as manure some heavy metals are being subject to bioaccumulation and may cause risk to human health when transferred to the food chain. Exposure of heavy metals may cause blood and bone disorders, kidney damage and decreased mental capacity and neurological damage. Therefore, heavy metal needs serious attention before the application of compost made from MSW. In certain cases the metal contents exceed the specified limits (Merian,1991). The occurrence of cadmium, cobalt, manganese, nickel, lead and zinc in MSW compost was reported by Ciba et al., (1999).

The characterization of heavy metals in landfill sites has given rise to number of studies in recent years by several researchers (Abu Rukah & Al-Kofahi 2001). Although numerous studies in literature ( Foose et al., 2002, kalbe et. al., 2002, Lu et al., 2011) have been conducted to investigate the heavy metals in landfill leachate. However, this work studies the contribution of selected municipal refuse dumps to heavy metals concentration in Mysore city, Karnataka, India. The iron oxides were prepared by hydrothermal method. The collected M.S.W samples were dried and then burnt off to ash. The heavy metals concentration was determined using AAS.

II. MATERIALS AND METHODS

A. Experimental materials:

Mysore is the second largest city in Karnataka after Bangalore. Mysore was the capital of Mysore state until 1956, when the capital was shifted from Mysore to Bangalore. Mysore is spread over an area of about 128 sq. km with the growing population at faster rate due to influx of many service industry activities, the generation of municipal waste both garbage and sewage has been on the rise. Anthropogenic activities in society generate large quantities of wastes posing a problem for their disposal. Improper disposal leads to spreading of diseases and unhygienic condition besides spoiling the aesthetics. The city has several major and small industries present in Nanjangud 20 Km away from the Mysore city together with many educational and commercial establishments. In India, every year 30.3 million tons of Municipal solid waste is generated. This equate to about 350 gms of waste per person on average.

M.S.W samples were collected from Municipal solid waste composting site, Vidyaranyapuram, Mysore. The sampling points were divided into 4 points. Two points were selected at windrow platform and two points were selected from compost yard. The samples were properly labeled and brought to the lab for further analysis. Two samples from windrow platform were mixed together thoroughly and two samples of compost were mixed thoroughly and one representative samples each from windrow and compost yard was prepared. Samples were first dried at 105° C in hot air oven, crushed well and sieved through 0.2 mm mesh. The powdered samples were then used for further analysis and spectral characterization.

1) Acid digestion:

For the determination of total metal contents, Aqua regia extract of Municipal solid waste fine fraction was prepared by digesting 3g of sample with 25ml of aqua regia (HCl + Hno₃, 3+1(v/v)), after cooling and filtration the sample was made up to know volume.

2) Heavy metal analysis:

For estimation of Heavy metals Triacid (Nitric acid: Sulphuric acid: Perchloric acid in 9:2:1 ratio) extract of the compost sample was used for AAS.

3) Preparation of Iron oxide:

In a typical hydrothermal run, the starting precursors are taken in the Teflon liner in a definite molar proportion. The liner is tightly closed on the upper portion of the liner and then the cap of the autoclave provided with a spring system inside (to hold the liner tightly) is used to close the autoclave tightly. Finally the autoclave assembly is placed inside the oven at a desired temperature for a desired duration.

After the treatment the products are removed and rinsed with mild acid when alkaline solvents are used in the hydrothermal experiment and mild base when acidic solvents are used to remove any residual alkalinity/acidity in the product and then thoroughly washed with double
distilled water to remove any persisting acid or alkali till the pH of the wash becomes neutral.

B. Experimental method:
An autoclave was used for the study. For each experiment batch 500 gms of raw MSW was washed with deionised water and it was autoclaved to preset temperature of 100°C. The samples were then burnt and it was converted into fine ash. Later the ash was treated with 2M Fe₂O₃ 50 gms of MSW ash was mixed with 1gms of iron oxide (Fe₂O₃) in 100 ml distilled water. Later the mixture was placed in a continuous stirrer for a period of 60 minutes. The solution was then filtered using whatmans filter paper No.1. The filtrate was taken for Heavy metals analysis using AAS and the filtered residue was dried in a Hot air oven and then taken for XRD and SEM analysis.

1) Heavy metal analysis:
For estimation of Heavy metals Triacid (Nitric acid: Sulphuric acid: Perchloric acid in 9:2:1 ratio) extract of the compost sample was used for AAS.

2) X-Ray Diffraction method:
The overall structural changes during the decomposition can be studied using X-Ray Diffraction method. Samples were ground to fine powder and spectra were recorded on RIGAKU Miniflex-II XRD instrument.

III. RESULTS AND DISCUSSION

A. Heavy metals analysis:
Various heavy metal concentrations for the composting samples from pile A and B are listed in Table 1 and 2. Heavy metals concentration of samples after being treated with iron oxides is listed in Table 3.

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Heavy metals</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cadmium</td>
<td>0.001</td>
</tr>
<tr>
<td>2</td>
<td>Copper</td>
<td>4.322</td>
</tr>
<tr>
<td>3</td>
<td>Lead</td>
<td>0.578</td>
</tr>
<tr>
<td>4</td>
<td>Chromium</td>
<td>0.769</td>
</tr>
<tr>
<td>5</td>
<td>Mercury</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Table 1: The heavy metal concentrations for the samples from Pile A

Sample from pile A were rich in copper content compared to other heavy metals. Metals such as Chromium and lead were found at lower concentrations whereas cadmium and mercury concentration was found to be 0.001 mg/L.

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</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cadmium</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>2</td>
<td>Copper</td>
<td>1.158</td>
</tr>
<tr>
<td>3</td>
<td>Lead</td>
<td>0.257</td>
</tr>
<tr>
<td>4</td>
<td>Chromium</td>
<td>0.315</td>
</tr>
<tr>
<td>5</td>
<td>Mercury</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

Table 2: The heavy metal concentrations for the samples from Pile B

Heavy metal concentrations have been decreased in pile B due to of composting process which is undergone for 30 days. This was due to release of metal ions from larger solid wastes materials during the decomposition and further decrease was due to leaching of metal ions by water.

<table>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Cadmium</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>2</td>
<td>Copper</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>3</td>
<td>Lead</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>4</td>
<td>Chromium</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>5</td>
<td>Mercury</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

Table 3: The heavy metal concentrations of samples after treatment with Iron oxide.

Heavy metals concentration was decreased to a minimum values after being treated with the iron oxides. This may be due to the stabilization of heavy metals by iron oxides.

B. A X-Ray Diffraction analysis:
X-Ray diffraction spectra of composting samples from pile A and B had shown in fig 1.1 and 1.2. X-Ray diffraction spectra of composting samples from pile A and B after being treated with iron oxides have shown in fig 1.3 and 1.4 respectively. Each signal in XRD represents the plane of a crystal. The number of peaks got reduced in sample at pile B compared to that of pile A. From the overall data obtained from the X-Ray Diffraction spectra it is clear that particle size decreasing during the degradation of solid waste.

Fig. 1: XRD spectra of sample at pile A

Fig. 2: XRD spectra of sample at pile B
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Fig. 3: XRD spectra of sample at pile A after treatment

Xrd spectra have been analyzed using Match software of CRYSTAL IMPACT, Bonn, Germany. The results showed that the Mercury have been transformed into mercury chromium and calomel, lead into Moeloite, cadmium into monteponite, chromium into Mercury chromium and trimataphosphate, copper into Housleyite and cyanochroite.

C. Scanning Electron Microscopy (SEM):

Fig. 5: SEM image of sample at pile A

Fig. 6: SEM image of sample at pile B

Fig. 7: SEM image of sample at pile A after treatment

Fig. 8: SEM image of sample at pile B after treatment

The collected material was taken under the SEM without any treatment. The SEM images are shown as in above figure. Observing the SEM image of Fig.1.4, it can be seen that the material looks bit porous in nature. Also it is observed that the material looks more coiled and bit clustered on the surface may due to the presence of high amount of organic materials along with inorganic and heavy metals too that are found to be present. From fig 1.5, we can observe that the coiling of materials found to be cleared at the surface. This means due to decomposition of the material for certain period, observing the SEM images of fig 1.6 and 1.7, it can be stated that the material takes another form with the surface cleared with organic decomposition along with leaching of the heavy metals, which is important to be noted that the result is supported by AAS spectroscopy results.
IV. CONCLUSION

Concentration of the heavy metals at the earlier stage of sample and further decrease in concentration of heavy metals revealed that the decomposition of organic matter followed by the formation of stable products in addition to variation in the different parameters were observed during the degradation of municipal solid waste by aerobic composting. Degradation of complex molecules into smaller constituents and Transformation of heavy metals have been confirmed by X-ray Diffraction and SEM studies. Decreased concentration of heavy metals by the AAS analysis has been observed clearly. From the above study it is clearly indicating the structural changes have taken place during the treatment process.

ACKNOWLEDGEMENT

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REFERENCES

[18] Paola Castaldi, Laura Santona and Pietro Melis, evolution of heavy metals mobility during municipal solid waste composting, psp volume 15, fresenius Environmental Bulletin