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Solubility of heavy metals added to MSW

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ABSTRACT

This paper aims to investigate the six heavy metal levels (Cd, Cr, Cu, Pb, Ni and Zn) in municipal solid waste (MSW) at different pHs. It intends to provide the baseline information of metals solubility in MSW co-disposed or co-digested with MSW incinerator ashes in landfill or anaerobic bioreactors or heavy metals contaminated in anaerobic digesters. One milliliter (equal to 1 mg) of each metal was added to the 100 ml MSW and the batch reactor test was carried out. The results showed that higher HNO_3 and NaOH were consumed at extreme pH of 1 and 13 compared to those from pH 2 to 11 due to the comparably higher buffer capacity. Pb was found to have the least soluble level, highest metal adsorption (%) and highest partitioning K_d ($l\,g^{-1}$) between pH 3 and 12. In contrast, Ni showed the highest soluble level, lowest metal adsorption (%) and lowest K_d ($l\,g^{-1}$) between pH 4 and 12. Except Ni and Cr, other four metals seemed to show the amphibious properties as comparative higher solubility was found in the acidic and basic conditions.

1. Introduction

Municipal solid waste (MSW) has been mostly treated with incineration accompanying with partly landfill disposal in Taiwan. MSW incinerator (MSWI) has the advantage of reducing MSW weight and volume while gaining the steam and energy recovery. However, residues such as bottom and fly ash generated in the incineration process still remain an environmental problem and need further treatment to prevent secondary pollution. Residues have been reused in several purposes such as aggregate, backfill, soil amendment and geotechnical application [1–6]. However, using residues as landfill cover have been a potential and particularly an aggressive option for fly ash. Specifically, the released heavy metals in the co-disposal or co-digestion process may affect the landfill and anaerobic bioreactors performance [7–15]. Further, released heavy metals and other hazardous materials have the potential to cause risk to human health and the ecological environment [16–20]. Therefore, heavy metal release and distribution in MSW is the key concern in landfill or anaerobic digester co-disposing or co-digesting MSW with MSWI ash or MSW anaerobic bioreactor containing possibly influential levels of heavy metals.

Metal levels and uptake in different media such as soil, sludge, forest, river, MSW, leachate, groundwater and landfill, etc. were reported by several researchers [21–34]. Partitioning of metals in different media, pH and organic matter was also investigated and its potential effects on the environment were presented. However, research regarding heavy metals distribution in MSW at different pHs was few [27,28]. Lo and Liao [7] and Lo [8] have presented the likely metal release in MSW co-disposed or co-digested with MSWI ash. In these reports, more than 30 metals ions were found in the released leachate. Thus, the effect of individual metal on the MSW digestion needs to be understood because of the possible synergistic or antagonistic effect by mixed metals. Therefore, this study aims to investigate the individual metal addition and its adsorption and solubility in MSW particularly focusing on the six heavy metals that may provide baseline information for MSW digestion in landfill or anaerobic bioreactor.

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2. Materials and methods

2.1. MSW and metal stock solution

This study aims to investigate the heavy metals adsorption and solubility in MSW. Thus, synthetic MSW typical of organic fraction was made with office paper (30%), newspaper (35%), hay (30%) and food waste (5%). Chemical constituents of C, H, O, N, etc. was analyzed by elemental analyzer (elementar vario EL III) and was found to be approximately ∼46, ∼6, ∼41, ∼1.4 and ∼5.6%, respectively. In order to obtain the results quickly and without interference, MSW of dry basis was cut into pieces of ∼5 mm and was blended with distilled water to get a high water content of total solid (TS) 6% of MSW. This TS content is typical of MSW treatment of anaerobic bioreactor [35,36] or similar to landfill sites with saturated water content that is easily for metal ions diffusion and microbial attack.

The added six heavy metals stock solution of 1000 mg l^{-1} were purchased from Merck Com. In these levels, 1 ml solution is equal to 1 mg metal content.

2.2. Experimental

This study aims to investigate the pH effect on the solubility of added heavy metals in MSW. The total content of added heavy metals of Cd, Cr, Cu, Ni, Pb and Zn was 1 ml (1 ml equal to 1 mg). One milliliter metal solution was added into 100 ml MSW substrate in 200 ml beaker leading to a total level of 10 mg l^{-1}. Thereafter, NaOH or HNO_3 with different normality was added and stirred completely with MSW to adjust the pH from 1 to 13. The pHs in MSW suspension were occasionally measured with a pH meter (pH330i) to ensure the desired exact pH values. The blank pH of MSW suspension without metal addition was measured to be 6.77 ± 0.21. The added quantity in mequiv. H^+ or mequiv. OH^- was recorded and plotted as a function of pH. Further, MSW substrate in each beaker with adjusted different pH was filtered by 0.45 μm filter membrane with vacuum pump and the filtrate was analyzed with ICP-OES (Thermal Electron Corp.). Soluble and calculated adsorbed metals in MSW substrate versus pH were plotted. Similarly, control batch reactor test without metal addition was carried out for comparison.

2.3. Theoretical definition

In theory, metal hydroxides formation can be described as follows [24]:

$$M^{z+} + n(OH)^{-1} = M_z(OH)_n{}^{(z-n)} \quad (1)$$

$$[M_z(OH)_n{}^{(z-n)}] = \beta_{(OH)n}[OH^{-1}][M^{z+}], \qquad n = 1, 2, \ldots \quad (2)$$

where $M_z(OH)_n{}^{(z-n)}$ and M^{z+} are metal hydroxide and free metal ion, respectively; $\beta_{(OH)n}$ is overall formation constant for metal hydroxide and n is the number of hydroxide ions associated with each metal ion.

In addition, solubility of metal oxides and hydroxides can be described as follows [21]:

$$p[M^{z+}] = -\log[M^{z+}] = -\log {}^{c}K_{so} - zpK_W + zpH \quad (3)$$

$${}^{c}K_{so} = [M^{z+}][OH^-]^z \quad (4)$$

where M^{z+} is free metal ion and ${}^{c}K_{so}$ is conventional solubility product based on the levels of individual metal ion.

The above equations can be used to predict the free metal level and checked with experimental data analyzed by ICP-OES. However, metal adsorption (surface complex formation) onto MSW can be calculated by the following definition:

$$M_{adsorbed\,(\%)} = \frac{M_{total} - M_{solubility}}{M_{total}} \times 100 \quad (5)$$

where $M_{adsorbed\,(\%)}$ is the adsorbed metal (%), M_{total} is the total metal content within MSW volume (mg l^{-1}) and $M_{solubility}$ is the metal solubility (metal ion levels) in MSW (mg l^{-1}). This definition is general and similar to $R = \{SOM^+\}/M_T$ derived by Wang et al. [23,24], where R, SOM^+ and M_T are ratios of adsorbed metal, metal–sludge (metal–MSW in this study) complex and total metal concentrations, respectively. M_T is the summation of adsorbed metal and free metal ion (M^{z+}).

Other expression of metal binding in mg g^{-1} TS can be calculated as below:

$$M_{adsorbed(mg/g\,TS)} = \frac{(M_{total} - M_{solubility}) \times V}{TS_{MSW}} \quad (6)$$

where $M_{adsorbed\,(mg/g\,TS)}$ is the adsorbed metal in MSW (mg g^{-1} TS), M_{total} is the total metal content within MSW volume (mg l^{-1}), $M_{solubility}$ is the metal solubility (metal ions levels) in MSW (mg l^{-1}), V is the working volume of MSW (l) and TS_{MSW} is total solid (TS) of MSW (g).

Through metal adsorption and free metal ions, metal partitioning can be evaluated by K_d coefficient (l kg^{-1}) which is the ratio of metal adsorption in solid phase such as soil over the concentration in soil solution [25]. K_d coefficient can be used in the similar condition with the replacement of soil by sludge or MSW and can be expressed as follow:

$$K_d = \frac{M_{adsorbed(mg/g\,TS)}}{M_{solubility(mg/l)}} \quad (7)$$

where $M_{adsorbed\,(mg/g\,TS)}$ is the adsorbed metal in MSW (mg g^{-1} TS) and $M_{solubility\,(mg/l)}$ is the metal solubility in MSW (mg l^{-1}).

Using the above equations and definitions, metal solubility, metal adsorption and K_d values in MSW over different pHs can be obtained.

3. Results and discussion

3.1. Acids or base addition as a function of pH

In this study, MSW with high water content (94%) similar to sludge (TS 6%) was used for batch reactor test by adding different quantity of NaOH or HNO_3. The results showed that pH increased as NaOH addition increased and pH decreased as HNO_3 addition increased. HNO_3 addition as mequiv. H^+ l^{-1} from pH 7 to 2 was found to increase linearly from 0 to ∼30–60 for six heavy metals, respectively. In a similar way, NaOH added batch reactors from pH 7 to 12 increased from 0 to ∼40–90 mequiv. OH^- l^{-1} for six heavy metals, respectively. These trends are shown in Fig. 1. In addition, it is noted that HNO_3 or NaOH addition were found higher at extreme pH 1 and 13 than that at pH between 2 and 12 shown in Fig. 2. In particular, HNO_3 of ∼320 mequiv. H^+ l^{-1} and NaOH of ∼620 mequiv. OH^- l^{-1} were added to reach pH 1 and pH 13 for Pb and Zn and Cd, respectively. These phenomena were due to the higher buffer capacity ($\beta = dV/d\,pH$ or d mequiv./d pH) found in the extreme pHs similar to the investigation [37].

3.2. Heavy metals solubility

Six heavy metals concentrations in MSW with metal addition showed that Cu, Zn, Pb and Cd had amphibious properties while that of Cr and Ni was not significant (Fig. 3). Metal levels appeared to increase as pH decreased. Soluble levels of Ni ion were found the highest while those of Pb ions were found the least as compared to