



Research Article

Degree of Pb stabilization in MSWI fly ash using size-fractionated natural fishbone hydroxyapatite

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ABSTRACT

Incineration is a common technique worldwide for treating Municipal Solid Waste (MSW). However, incineration residues (e.g., bottom and fly ash) require special treatment to prevent environmental risks due to the high content of heavy metals. The present study evaluated the stabilization degree of Pb, a toxic heavy metal in MSW incineration fly ash (IFA) treating by size-fractionated natural fishbone (FB) hydroxyapatite (HA). Bones from various fish species were used at different size fractions (<600 µm, 600 µm–2 mm, and 0–2 mm). The effect of different fishbone hydroxyapatite (FB-HA) sizes was studied by batch tests under the FB/IFA ratios of 0.0 and 1:10 (wt.), the contact or settling time of 6, 12, 24, and 672 hours, and the fixed W/S ratio of 1.5 mL/g. Using only 10% FB, Pb stabilization efficiency after 672 hours obtained 95.55% and 94.24% for FB sizes <600 µm and 600 µm–2 mm, respectively, and about 86.1% for non-fractionated FB (0–2 mm). The results indicated that contact time was the most critical factor for enhanced Pb stabilization. The FB particle size of 0–2 mm was deemed appropriate for Pb immobilization in short and long time settling periods. The adsorption isotherms were fitted well with the Langmuir and Freundlich models. The R_L values of the Langmuir model were less than one and the n values of the Freundlich isotherm lie between 3 and 5, conferring the favorable adsorption of Pb to FB-HA for all size fractions.

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INTRODUCTION

Incineration is a common technique worldwide for treating municipal solid waste (MSW), because it shrinks the volume and weight of waste by about 90% and 70%, respectively [1]. In Japan, the solid waste incineration percentage was almost 75% in 2013 [2]. However, producing markedly huge amounts of solid remnants (e.g., bottom ash and fly ash) is one of the limitations of incineration technology.

Furthermore, because of the high content of heavy metals (Zn, Pb, Cd, Cu, Cr, Sb, etc.), chlorine, soluble salts, organic compounds, and particles fineness, the incineration fly ash (IFA) is classified as a hazardous waste [3]. Therefore, IFA requires appropriate treatment to prevent environmental risks before utilization or landfilling [4]. MSWI fly ash is treated through various methods, such as chemical stabilization by reagents (i.e., chelate compounds), cement or geopolymer solidification, advanced separation, thermal

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treatment via melting, treatment by synthetic phosphate (phosphoric acid), and hydrothermal techniques [5, 6].

Soluble phosphate has been widely used as a chemical treatment to convert heavy metals into insoluble compounds. Usually, phosphoric acid, potassium phosphates, sodium, and ammonium react with multivalent cations to comprise insoluble orthophosphates [7]. An insoluble metal phosphate produced through the reaction between soluble phosphate and the metal ions resembles a naturally growing mineral, which is geologically stable. In addition, various hydrogen and dihydrogen phosphates have also been explored for removing soluble heavy metals from toxic environments [7].

One of the typical examples of lead phosphate with a very low solubility ($K_{sp}=5\times 10^{-119}$) in a wide pH range, is pyromorphite, $Pb_5(PO_4)_3Cl$ [8]. Another frequently used phosphate is the apatite family, with hydroxyapatite (HA), which forms the principal member $[Ca_{10}(PO_4)_6(OH)_2]$ of a large category of substituted compounds with resembling compositions. Solid compounds may be formed with an extensive range of divalent or trivalent metals substituting fluorine, calcium or chlorine for hydroxyl ions, carbonates, vanadates, or arsenates found in place of phosphate [7].

Fishbones and mammal's skeletons contain calcium phosphate that highly resembles to HA. HA, such as synthetic HA, bones, and bone char have been explored for their high absorption capacity for removing heavy metals from aqueous solutions [9]. Therefore, HA can also be effectively used for the stabilization of heavy metals in contaminated waste materials. Compared to other phosphate sources, biogenic apatite (e.g., fishbones) has less initial contamination with heavy metals than processed or mined phosphate rocks and fertilizers. In addition, its high solubility allows it to trap metals easily and release phosphate slowly, thus allowing for long-term stabilization [10]. Many studies have been performed on the efficiency of phosphates and particularly apatites $[M_{10}(PO_4)_6(OH)_2, M: \text{Metal}]$, and the mechanisms involved in immobilizing heavy metals in contaminated soil, wastewater, groundwater, and dredged sludge [7, 11, 12].

Phosphation or phosphate treatment is also a promising remediation technique applied to IFA, BA and scrubber residues for heavy metal stabilization [13]. Assessing the effects of the fishbone (a natural phosphate) on heavy metal stabilization in MSW IFA is one of the principal objectives of the present study. Previous researches [14–16] have shown that the fishbone hydroxyapatite (FB-HA) is an effective stabilizer of heavy metals in IFA by considering various parameters such as modified fishbone, varied fishbone species, reaction time, fishbone dosage, and W/S ratio. In this study, size-fractionated natural FB-HA was used to enhance the degree of Pb stabilization in IFA. Therefore, three different sizes of FB-HA were used, and the effect of each size on Pb stabilization was investigated. The mechanism of Pb adsorption by FB-

HA and relevant adsorption isotherms were also studied. FB-HA can help reduce the need for disposal of fishbone waste, increase its recycling, reduce secondary contamination, and provide a low-cost and environmentally friendly technology for stabilizing heavy metals in MSWI fly ash.

MATERIALS AND METHODS

Collection and Preparation of Fishbone and Fly Ash

Waste fishbone from miscellaneous species of fishes (salmon, fly fish sea bream, horse mackerel, mackerel, yellowtail, lizardfish, and Japanese amberjack) was collected from local fish markets in Japan. Fishbones except heads and tails were boiled for about 40 minutes. Upon completion of boiling, the flesh, spinal cords, and soft tissues were cautiously dispelled from bones and rinsed. Afterward, the bones were dipped in a detergent solution and boiled for 1 hour on low heat. The water to detergent ratio was 5:1. Again the bones were rinsed and dipped for 24 h in a hydrogen peroxide (30% H_2O_2) solution. The water to H_2O_2 ratio was maintained at 5:1. Next, the bones were thoroughly rinsed and dried for 24 hours at room temperature (under the dry mode of the air-conditioning system). Finally the dried bones were ground by a kitchen blender. The sieving method was used to separate the ground fishbone into three particle size fractions ($<600\ \mu\text{m}$, $600\ \mu\text{m}-2\ \text{mm}$, and $0-2\ \text{mm}$). The details of the fishbone processing have been explained elsewhere [17].

Untreated IFA sample was collected from a WtE facility (S) in Fukuoka, Japan, and stored in hermetically sealed containers. Here "untreated" IFA means that the IFA was not stabilized with any stabilizing agents (such as chelate) in the facility before collection. The IFA sample was directly used for conducting metal stabilization and leaching experiments in the laboratory without any pretreatment. For bulk mineralogical and compositional analyses, IFA was manually ground in an agate mortar.

Characterization of Fishbone and Fly Ash

The chemical composition of the bulk IFA sample was measured with the technique of X-ray fluorescence (XRF). Elemental concentration in the leachate from batch leaching tests was analyzed with the inductively coupled plasma optical emission spectroscopy (ICP-OES). The mineral phases of IFA ash and FB-HA were analyzed with X-ray diffractometry (XRD). Before and after the experiments, the compositions of both IFA and fishbone were measured by the scanning electron microscope coupled with an energy dispersive X-ray (SEM-EDX) detector in the mode of backscattered electron (BSE). Fourier Transform Infrared (FT-IR) Spectroscopy tests were performed on IFA samples (with and without FB-HA treatment) with an instrument of Infrared Spectrophotometer JASCO FT/IR-4200. Details of QA/QC for instrumental analysis has been provided in Supplementary Materials (Appendix 1, 2).

Table 1. Chemical composition of MSWI fly ash

Components (%)	CaO	Cl	Na ₂ O	SiO ₂	K ₂ O	Al ₂ O ₃	MgO	Zn	S	P ₂ O ₅
	35.70	21.07	9.31	9.39	4.06	3.52	2.93	0.06	2.73	2.08
Components (%)	Fe ₂ O ₃	TiO ₂	Pb	Sb	Cu	Ba	Cr	Cd	Others	LOI
	1.40	0.14	0.06	0.07	0.04	0.096	0.02	0.01	7.03	6.50

Pb Stabilization Experimental Method

Two different size ranges of FB (<600 μm and 600 μm–2 mm) and bulk (0–2 mm) were selected to stabilize Pb in IFA. Tests were conducted by batch experiments with 250 ml polypropylene bottles at room temperature. In each bottle, 20.0 g of IFA, 2.0 g of FB (10% of IFA weight), and de-ionized water were added to maintain the initial W/S ratio at 1.5 mL/g. Bottles were settled for 6, 12, 24, and 672 h (28 days) in the ambient condition. Deionized water was added to each bottle to increase the total leachant to 200 mL after each settlement period and the admixtures were subjected to a standard Japanese leaching test (JLT-46). Bottles were centrifuged for 20 min at 3000 rpm to obtain the leachate. The liquid and solid parts were separated by vacuum filtration through the 0.45 μm pore-size membrane. Every test was done in duplicate, and the results were conferred as mean values with standard errors.

The removal efficiency of Pb was calculated using Equation 1:

$$Pb_{ref.}(\%) = \left(1 - \frac{C_t}{C_c}\right) \times 100 \tag{1}$$

where $Pb_{ref.}$ =Pb removal efficiency; C_t =Pb concentration in the test group; and C_c =Pb concentration in the control group.

The competency of using FB-HA for stabilizing a target heavy metal (here Pb) was calculated using Equation 2 as the amount of metal stabilized by the unit mass of FB-HA.

$$Stabilization\ capacity\ of\ Pb\ \left(\frac{mg}{g}\right) = (C_c - C_t) \times v / mass\ (FB-HA) \tag{2}$$

where C_c and C_t are the concentrations of Pb in the control and test groups, respectively, and v is the volume of leachant (i.e., 100 mL).

Calculation of Adsorption Isotherm Constants

The sorption data were applied in two widely used sorption isotherm models such as the Langmuir and the Freundlich isotherms. The equilibrium data for Pb cation over the concentration of 48.5 mg/L at room temperature has been correlated with the Langmuir isotherm, following Equation 3.

$$1/q_e = 1/Q_{max} + 1/b \cdot Q \cdot 1/C_e \tag{3}$$

where C_e =equilibrium concentration, q_e =number of metal ions sorbed onto FB-HA, Q and b are Langmuir constants related to the sorption capacity and energy, respectively. The linear plot is obtained when $1/C_e$ is plotted against $1/q_e$. The Freundlich adsorption isotherms were also applied to

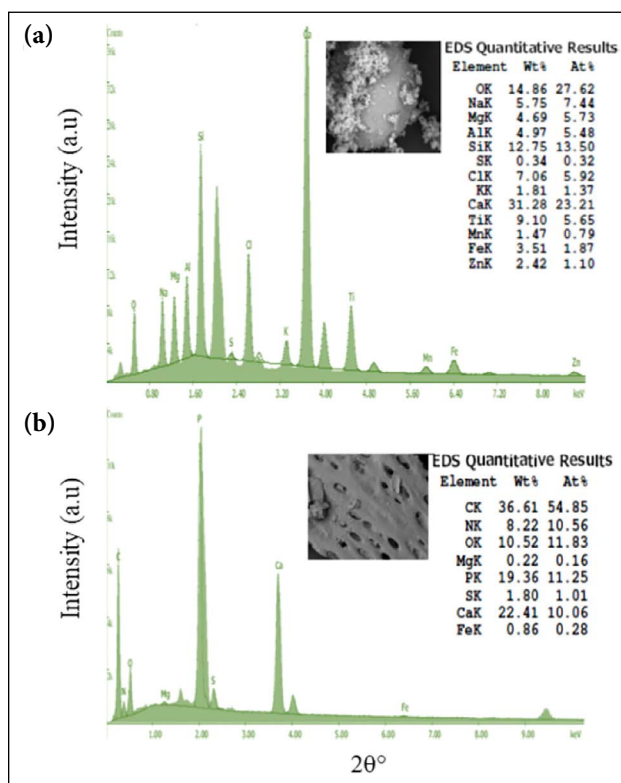


Figure 1. The BSE images and detailed composition of (a) fly ash S and (b) yellowtail fishbone.

investigate the removal of Pb by the size-fractionated natural fishbone, FB-HA using Equation 4.

$$\log q_e = \log K_f + 1/n \log C_e \tag{4}$$

K_f and n are the Freundlich adsorption equation constants, where K_f is the adsorption capacity. The constants K_f and n were determined by plotting $\log q_e$ vs $\log C_e$.

RESULTS AND DISCUSSIONS

Chemical Composition of Fly Ash and Fishbone

The major elements of the IFA sample analyzed by XRF were Ca, Cl, Al, Zn, K, Mg, Na, Si, Ti, P, and S. Among all heavy metals, Pb and Zn were found remarkably higher than other elements as shown in Table 1. Detailed phase analysis was done by SEM-EDX technique. Figure 1a and 1b exhibit the BSE images and detailed composition of an IFA particle (from source S) and the FB-HA, respectively. As shown in Figure 1b, FB-HA presents a coarse and porous texture.

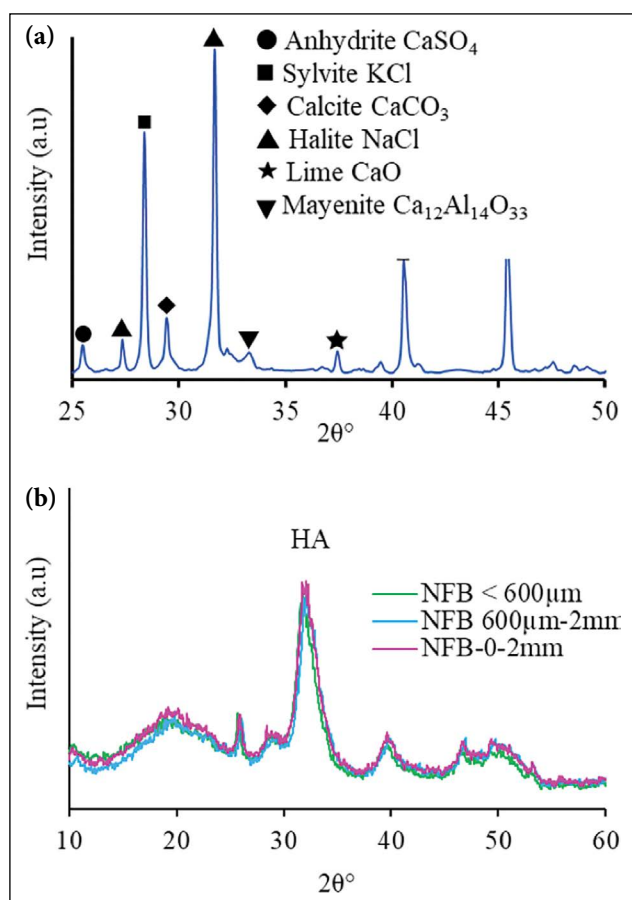


Figure 2. The XRD patterns of (a) fly ash (S) and (b) size-fractionated fishbones.

Mineralogy of Fly Ash and Fishbone

The existing mineral phases in the IFA sample (S) are shown in Figure 2a. Sylvite (KCl) and Halite (NaCl) have found the major mineral phases, since the main sources of Cl is notably high in the IFA (Table 1). A series of Ca-rich minerals such as calcite (CaCO_3), lime (CaO), anhydrite (calcium sulfate: CaSO_4), and mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) were identified, which can elucidate the high concentration of Ca in IFA. It should be noted that IFA is not a completely crystalline material, but contains amorphous phases that cannot be detected directly using XRD technique.

The mixed fishbone meal consisting of various fish species was divided into three different size fractions ($<600\ \mu\text{m}$, $600\ \mu\text{m}-2\ \text{mm}$, and $0-2\ \text{mm}$) and analyzed by XRD pattern, which showed similar patterns. As shown in Figure 2b, hydroxyapatite (HA) with the chemical formula of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is the only typical crystalline phase detected in all fishbone fractions.

Effects of Fishbone Hydroxyapatite on Pb Stabilization

Pb stabilization in MSWI fly ash was primarily pursued at few selected settling periods and a fixed W/S ratio. The tests

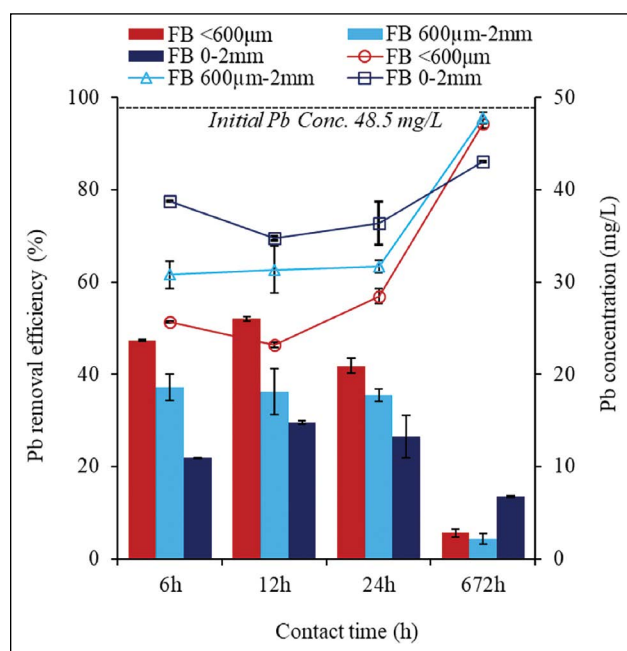


Figure 3. The removal efficiency and the concentration of Pb with different FB-HA sizes.

were conducted on the batch-scale with fishbone/fly ash ratios of 0 (control group) and 1:10 (test groups), settling times of 6, 12, 24, and 672 h (28 days), and a W/S ratio of 1.5 mL/g. The effects of FB-HA on Pb stabilization were characterized by the decrease of Pb concentration in the leachate with contact time and removal efficiency.

The results in Figure 3 show that the decreasing trend is similar for Pb with different size-fractions of FB from the initial Pb concentration (48.5 mg/L) in IFA. Up to 24 h of contact time, the concentration of Pb in the separated samples was higher than the mixed fishbone meal (0–2 mm). However, the Pb concentration in the size-fractionated samples ($<600\ \mu\text{m}$ and $600\ \mu\text{m}-2\ \text{mm}$) decreased significantly after 28 days, and the removal efficiency exceeded 95%. It was observed that even at the shortest contact time (6 h), the mixed FB (0–2 mm) achieved about 77.5% Pb stabilization, reaching a maximum value of about 86.08% after 28 days when only 10% (w/w) of FB was used.

The results show that FB immobilized a significant amount of Pb leached from fly ash within the first few hours. After adding FB to fly ash, hydroxyapatite can stabilize Pb and control its stability over time. Although Pb in IFA can be stabilized with a shorter settling time, the highest Pb stabilization was achieved at a longer period (28 days) in all cases. This implies that in addition to the dissolution–precipitation mechanism, reaction time is a crucial factor in reaching equilibrium during the settling stage.

A slight decrease in removal efficiency was observed between 6 to 12 hours of settling. Therefore, desorption mechanism may have occurred following the initial 6-h

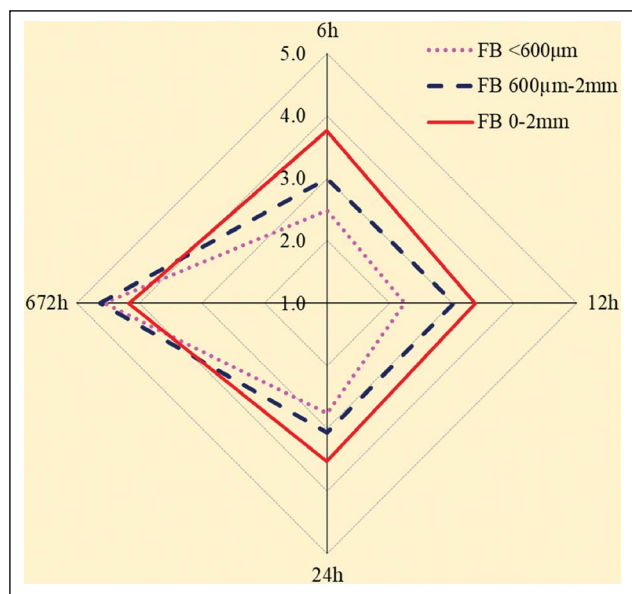


Figure 4. Pb stabilization competency with different sizes of FB-HA.

adsorption. High sorption of Pb onto FB-HA was achieved in the first 6 hours. However, shortly after that, the desorption process likely enhanced the amount of soluble Pb in the process.

It was presumed that sufficient time was needed to reach equilibrium. The results suggested that fishbone particle size in the range of 0–2 mm, there is no significant change in Pb stabilization, even with short or long settling periods. However, if the variation in fishbone particle size is relatively small, i.e., <math><600\mu\text{m}</math> or $600\mu\text{m}-2\text{mm}$, Pb can be stabilized significantly (>95%).

Competency of Fishbone Hydroxyapatite for Pb Stabilization in Fly Ash

As shown in Figure 4, the mixed particle size of FB (0–2 mm) was about 1.5 times more competent than fractionated FB-HA (<math><600\mu\text{m}</math> and $600\mu\text{m}-2\text{mm}$) for stabilizing Pb with a settling time of 6 hours. However, the size-fractionated FB (<math><600\mu\text{m}</math> and $600\mu\text{m}-2\text{mm}$) competitively promoted Pb stabilization after 28 days. Pb stabilization capacity obtained 4.57 and 4.63 mg/g in <math><600\mu\text{m}</math> and $600\mu\text{m}-2\text{mm}$ FB sizes, respectively, while 0–2 mm reached 4.18 mg/g.

Table 2. Adsorption isotherm constants

FB sample Sizes	Langmuir isotherm				Freundlich isotherm		
	Q	b	R ²	R _L	K _f	n	R ²
<math><600\mu\text{m}</math>	5.50	19.76	0.97	0.001	6.20	3.45	0.96
$600\mu\text{m}-2\text{mm}$	4.99	28.21	0.99	0.001	5.40	5.03	0.99
0–2 mm	5.24	27.29	0.99	0.001	6.97	3.77	0.98

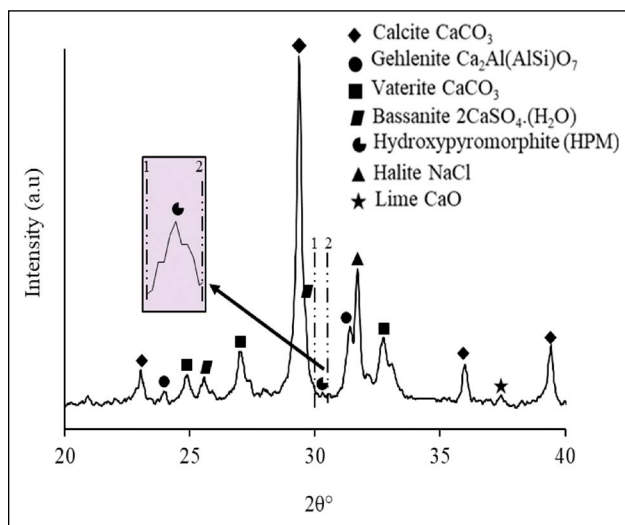


Figure 5. The XRD pattern of fly ash after treatment with FB-HA (0–2 mm).

Adsorption Isotherms

The Langmuir model was effectively narrated the sorption data with all higher values of R², and the R_L values lie in <math>0 < R_L < 1</math>. This indicates that the isotherm is favorable according to Table 2. The R_L values are calculated by following Equation 5:

$$R_L = \frac{C_0}{1 + K_L C_0} \tag{5}$$

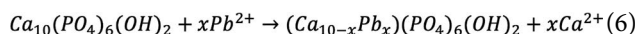
where C₀ (mg/L) is the initial metal concentration and K_L (L/mg) is the Langmuir constant related to adsorption energy. The R_L value indicates that the shape of the isotherm is unfavorable (R_L>1), linear (R_L=1), favorable (0<R_L<1), or irreversible (R_L=0).

One of the most extensively used mathematical descriptions is the Freundlich isotherm. This isotherm can be applied to experimental data for a wide range of metal concentrations. The Freundlich isotherm provides an expression that encompasses the surface heterogeneity and the exponential distribution of active sites, and their energies.

Table 2 shows the Freundlich adsorption equation constants (k_f and n) for metal cations at different fishbone sizes. An n-value in the range of 2–10 exhibits good adsorption, but n<1 slightly inhibits the adsorption capacity at lower equilibrium concentrations. In case of different fishbone sizes, the calculated n values between 3 and 5, indicate favorable

adsorption of Pb on to FB-HA. According to literature [18], illimitable surface coverage is reckoned mathematically, which specifies the multilayer sorption on the surface as because this isotherm cannot predict any saturation of the sorbent by the sorbate. Apatite in fishbone is comparable to hydroxyapatite based on Ca content and is therefore suitable for removing heavy metal ions from IFA. In addition to synthetic hydroxyapatite, bones from fish waste have been studied as a potential source of calcium phosphate for heavy metal stabilization [19–22]. Hydroxyapatite is superior to apatite ore because of its purity and much less unwanted metal substitution.

The ion-exchange and dissolution-precipitation processes are the two most common mechanisms proposed in capturing heavy metals with HA [23]. Through an ion-exchange mechanism, the metal adsorbs to the surface of HA or diffuses inward, releasing Ca by expelling more insoluble endogenic Ca ions. The low solubility of heavy metal phosphates drives the exchange reaction towards the release of Ca ions. In the dissolution-precipitation mechanism, Ca is first dissolved with phosphate ions, and heavy metal ions precipitate by uniform (in solution) or non-uniform (on the remaining solid HA) nucleation [24, 25]. Both mechanisms can explain that the certainty of the sorption reaction is notably retarded since the initiatory HA surface is covered with less soluble phosphate. Following the ion exchange, a new sparingly soluble metal phosphate builds a casing that confines the subsequent dissolution of the underlying Ca ions and interrupts the exchange reaction. It resembles the effect of heavy metal phosphate casing of HA particles due to non-uniform precipitation [26]. Depending on the degree of crystallinity, specific surface area, density, and composition of hydroxyapatite certain amounts of heavy metal ions removed in each mechanism [27]. The parameters, such as pH, initial metal concentration, rate of addition, and temperature, also play a substantial role [28–32]. In general, both of the above mechanisms are strong evidence of Pb precipitation and the formation of hydroxypyromorphite (HPM), a very stable Pb compound in the environment as shown in Equation 6.



The sorption mechanism on this topic has been reviewed details in elsewhere [17, 33].

Cheung et al. [22] used bone char to absorb heavy metals in solutions. Bone char is mainly comprised of HA and also contains 9–11% (by weight) carbon, accounting 50% of the total specific surface area of 100 m² g⁻¹. The sorption mechanism could be imposed to at least three pathways that found by their observations: i) ion exchange of divalent metal ions with HA; ii) sorption of metal ions onto HA surface trellis; and iii) sorption of metal ions onto the surface of carbon.

Calcium compounds in fishbone are mainly in the form of hydroxyapatite with low solubility. Furthermore, hydroxyapatite is embedded in the collagen matrix [34], making contact with the solution very difficult. Therefore, calcium in fishbone is very difficult to dissolve in water or acidic solutions. Calcium solubility in the solution increases as the particle size of the fishbone decreases. This may be due to the increased specific surface area and destruction of the collagen matrix. Therefore, it was suggested that reduced particle size in fishbone might promote metal absorption. Similar results were also obtained in this study with an FB particle size of less than 600 μm.

Figure 5 shows the mineral composition of a fly ash sample treated with mixed particle size FB-HA (0–2 mm). After treatment with FB-HA, the XRD pattern confirmed the occurrence of primitive HPM. However, since IFA has various principal mineral phases, the HPM peaks were not clear. Calcite (CaCO₃) and halite (NaCl) as major phases were confirmed in the IFA treated with FB-HA. Other minor or trace mineral phases, such as basanite (2CaSO₄·H₂O), vaterite (CaCO₃), and lime (CaO), were also detected. Sylvite (KCl) disappeared in the treated fly ash (Fig. 5), due to its high solubility, and new phases, such as bassanite [2CaSO₄·H₂O], vaterite (CaCO₃), and HPM, were developed in the system. Gehlenite [Ca₂Al(AlSi)O₇], a common Ca-rich mineral in incineration residues, was also detected.

The distribution of major elements in the fly ash treated with FB-HA (28 days) was determined using the elemental mapping technique. Ca, Si, and P (infer to bound with O) are the major elements extensively exist in the IFA particles. Despite the presence of hydrate phases in fly ash, light elements like hydrogen (H) cannot be directly measured by the EDX technique. Pb and Zn (Fig. 6) were found to be homogeneously distributed in the treated IFA particles. It is difficult to detect the newly-constituted compounds in the host medium, particularly the immensely scattered or as ultrafine aggregates [17].

Figure 7 shows the FT-IR spectrums of selected sample of fly ash S, before and after treatment with FB-HA (28 days) in the 400–4000 cm⁻¹ scanning range. Compared to the original fly ash sample S, the IR spectra suggested that no other phases developed after heavy metal stabilization. Stretching and bending vibrations of silicates were observed around 910–1020 and 400 cm⁻¹, sulfate anions around 1100–1150 and 600–650 cm⁻¹ and carbonate anions around 870 cm⁻¹ and 1420 cm⁻¹. The variation peaks of phosphate (PO₄³⁻) were prominent around 541 cm⁻¹, 592 cm⁻¹, and 1100 cm⁻¹. The bands of resembling intensities were ascribed to anhydrite (CaSO₄) at 596, 617, 675, 1118, and 1157 cm⁻¹ of wavelengths. Formation of anhydrite caused by the dehydration of gypsum, basanite, or both [35]. The IR spectra also confirmed the existence of gehlenite (485, 815, 860, 980, 880, and 922 cm⁻¹), basanite (1154 cm⁻¹), and calcite (1442 cm⁻¹ and 874 cm⁻¹) in fly ash sample (S).

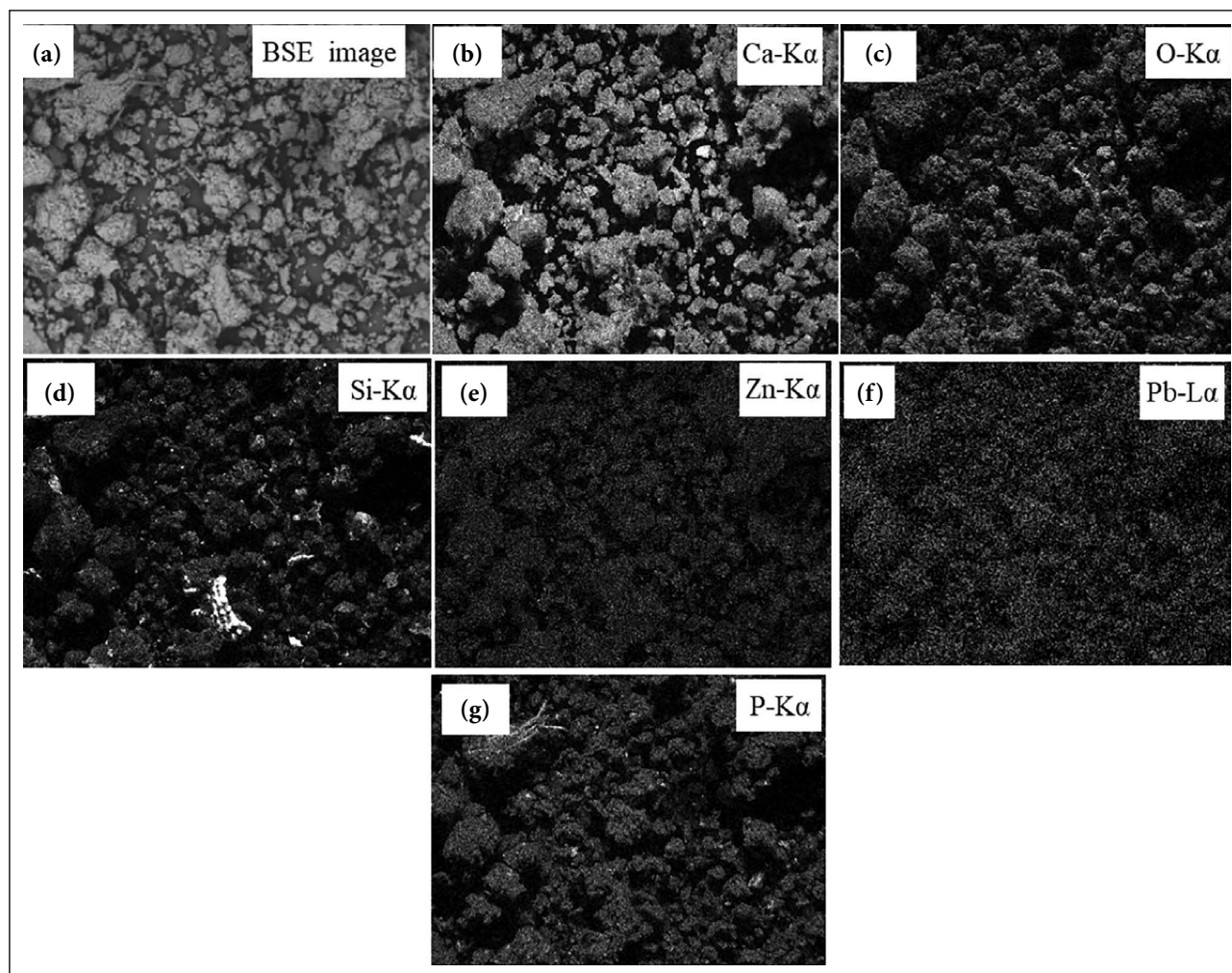


Figure 6. The BSE image (a) and characteristic X-ray images (b to g) of different elements in fly ash treated with FB-HA (0–2 mm).

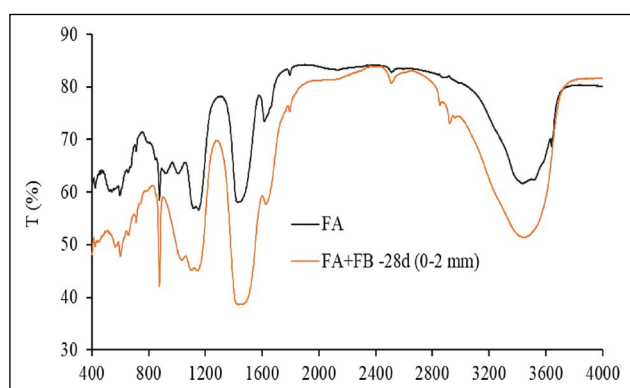


Figure 7. FT-IR spectra of fly ash before and after treatment with FB-HA (0–2 mm size) (28 days).

Utilizing waste fishbone for metal stabilization from in fly ash can reduce the use of chelate, a complex and expensive chemical [36]. Thus, the technique has prospects as a cheap and environmentally friendly approach. In this study, a low dosage of FB-HA was used. Therefore, the amount of ul-

mate mixture (fishbone and fly ash) would be lower than the amount of cement-treated fly ash, which can decelerate the occupation of landfill space. Furthermore, this study demonstrated that fishbone stabilized heavy metals such as Pb as one of the main hazardous heavy metals in fly ash, though the application is case-dependent. Additionally, the reuse or recycling of waste fishbone will be enhanced and therefore reduce the need for its disposal.

There are several advantages to using fishbone HA. Hydroxyapatite can sequester heavy metals and precipitate as minerals that are not biological. HA is considered the ideal non-specific surface sorbents for species that do not precipitate separately and the most economical reactionary medium for many metals [7].

CONCLUSIONS

This study revealed that size-fractionated fishbone (<600 μm and 600 μm–2 mm) was individually more efficient in Pb stabilization than non-fractionated FB (0–2 mm)

over longer contact periods. The finer fishbone fraction achieved the highest Pb removal efficiency (94–96%) over long settling periods due to the uniformity of the fishbone particles and possibly the extensive surface area. Fishbone particles in the size range of 0–2 mm are considered suitable for stabilizing Pb in both short (78%) and long (86%) settling periods. Under any circumstances, Pb stabilization was achieved using only 10% FB-HA. In addition, the use of waste fishbone can increase its recycling rate and reduce the need for disposal. Thus, this technique is expected to be a cheap and environmentally friendly approach. Instead of using a wide size range of FB (0–2 mm), size-fractionated FBs (<600 μm and 600 μm –2 mm) can be used to achieve significant Pb immobilization (>95%) at longer contact time between IFA and FB. Equilibrium adsorption data were best fitted with both Langmuir and Freundlich isotherm models. The R_L values of Langmuir isotherm in the present investigation were less than one and the n values of Freundlich isotherm lie between 3 and 5, suggesting the favorable adsorption of Pb onto FB-HA. The findings also suggest that fishbone meal, a locally attainable and an inexpensive adsorbent, is technically feasible for stabilizing heavy metals in MSWI fly ash.

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DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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APPENDIXS

Appendix 1. Definition of analytical quality control samples used in laboratory analysis

QC type	Definition	Frequency	Used to evaluate	Limits	Corrective action
Performance test standard (PT)	Certified reference standard	Per analytical method or manufacturer's specifications	Accuracy, precision	Per manufacture's specifications	Affected samples and associated quality control must be reanalyzed following successful instrument recalibration
Continuing Calibration (CC)	Standard solution at a concentration in the center of the calibration curve	Every 10 samples	Accuracy, comparability	80–120%	Analysis cannot proceed unless CCs pass. All samples/ QA after the last passing CC must be re-analyzed
Laboratory Control Sample (LCS)	Standard solution from a different vendor than that of the calibration standard spiked with compounds of interest into a clean water matrix	Every analytical batch or 20 samples, whichever is more frequent	Accuracy, comparability	80–120%	Perform instrument maintenance and prepare new standard solution if necessary. Samples and associated QA must be re-analyzed
Instrument or Analytical Blank (Lab Blank)	Clean water matrix, free of analyte. Analyzed in same manner as samples	Every analytical batch or 20 samples, whichever is more frequent	Accuracy	Measured value less than MDL ^a or RL ^b	In some cases, target compound values may be subtracted out, in other analyses target compounds present in blank must be flagged as contamination and may not be subtracted out
Laboratory Duplicate (Lab Dup)	Analytical duplicate	Every analytical batch or 20 samples, whichever is more frequent	Comparability, precision	RPD ^c <25% (n/a if native concentration of either sample <RL)	Rerun sample. If second result is not within limits, report with qualifier

a: MDL: Method detection limit; b: RL: Reporting limit; c: RPD: Relative percent difference.

Appendix 2. Summary of laboratory QA/QC for analyzed samples

QA/QC test	Fly ash, fishbone XRD	Fly ash XRF	Fly ash, fishbone SEM-EDX	Fly ash, treated fly ash samples FT-IR	JLT-46, treated samples ICP
Total number of samples analyzed*	10	2	6	4	26
Completeness of samples collected (%)	100	100	100	100	100
Samples completed on time (%)	100	100	100	100	100
CC's (%)	100	100	100	100	100
LCS passing (%)	100	100	100	100	100
Lab dup passing (%)	100	100	100	100	98.5
Lab blanks passing (%)	100	100	100	100	100
Overall (%)	100	100	100	100	99.8

*: Including duplicates.