

Feasibility of Natural Zeolite for Heavy Metal Stabilization in Municipal Solid Waste Incineration Fly Ash: A Novel Approach

Mitali Nag*, Amirhomayoun Saffarzadeh, Takayuki Shimaoka

Department of Urban and Environmental Engineering, Faculty of Engineering, Kyushu University, Fukuoka, Japan

Email: *nag-m@doc.kyushu-u.ac.jp

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Abstract

The current study investigated the sorption process of heavy metals, especially lead (Pb^{2+}) and Zinc (Zn^{2+}), in Municipal Solid Waste Incineration (MSWI) fly ash applying natural zeolite, namely mordenite, as an inexpensive adsorbent to assess its feasibility for the treatment of fly ash. Batch experiments were performed to investigate the effects of the influential parameters, such as metals initial ion concentration, dosage of adsorbent, liquid to solid (L/S) ratio, and equilibrium concentration of metal on the immobilization of Pb^{2+} and Zn^{2+} , in a novel approach. Heavy metals removal efficiency increased with increasing the dosage of mordenite influenced by the media-specific surface area. Heavy metals adsorption is ascribed to various mechanisms of ion exchange and adsorption processes. The Langmuir and Freundlich isotherm models were investigated using the adsorption data. The adsorption process describes better in the Freundlich isotherm model compared to the Langmuir isotherm model with a high determination coefficient (R^2), especially for the adsorption of Pb^{2+} . In addition, the affinity of mordenite to Pb^{2+} was shown to be higher than that of Zn^{2+} . This allows the use of mordenite to capture of Pb^{2+} in MSWI fly ash. Results raise expectations about using mordenite as a low-cost material for treating MSWI fly ashes. The results show that heavy metal (Pb^{2+} and Zn^{2+}) removed by mordenite adsorbent is practical and effective. In order to achieve the higher efficiency on heavy metal stabilization in MSWI fly ash, additional experiments are necessary.

Keywords

Natural Zeolite, Mordenite, Heavy Metals, Fly ash, Adsorption

1. Introduction

Municipal solid waste incineration (MSWI) has become an essential technology for sustainable waste management in modern societies. The main advantages of MSWI are pollution reduction from landfills, reduced land utilization, and reduced fossil fuel usage (Brunner & Rechberger, 2015). MSWI generally produces two main types of ashes: bottom ash (BA) and fly ash (FA). Both BA and FA generally contain large amounts of leachable heavy, and the less leachable heavy metals in BA exist as carbonates. On the other hand, FA shows undesirable pH and contains soluble salts. It also has more volatile and potentially toxic trace metals (Zn, Pb, Ba, Cu, Ni, Hg, As, Cd, and Cr) in leachable forms (Quina et al., 2018). Therefore, BA is usually used to substitute for quartz sand cement production (Liu et al., 2018). Conversely, FA is handled as hazardous waste and always requires pretreatment before disposal in landfills. Therefore, although much research has been done on the uses of FA and its effects on soil, plants, and in the environment (Basu et al., 2009; Gupta et al., 2002), the proper handling and disposal of FA remain as a serious environmental problem.

In Japan, incineration FA is managed as general waste under special regulations. Therefore, direct landfilling or ocean dumping of FA is illegal. Instead, through intermediate treatments, FA is encapsulated and stabilized by removing contaminants. The most common methods of treating FA are cement solidification, advanced separation, treatment with chemical reagents, melting, and solidification. However, most of the stabilization techniques have some drawbacks (Zhu et al., 2018). For example, chemical treatment and advanced separation are efficient techniques for FA treatment, but technical and economic constraints limit the implementation of large-scale projects (Liu et al., 2018). The melting process also requires high costs for the construction of associated facilities. Moreover, Diliberto et al. (2018) suggest that few treatment technologies have been identified as zero-waste treatment, most of which require FA pretreatment and are unsuitable to be used at incineration plants. Therefore, the main drawbacks are the use of additional operational processes and raw materials.

For managing and stabilizing the MSWI FA, new stabilization treatment techniques using waste and by-products have been promoted in recent years. FA mixed with rice husk (Bosio et al., 2014), silica fume (Rodella et al., 2017), residues of electrolytic manganese (Zhan et al., 2018), biochemical effluents (Xu et al., 2018), red mud (Li et al., 2019), sewage sludge ash (Benassi et al., 2019), and waste fishbone (Nag et al., 2020; Mu et al., 2018) as some of the most recent treatment technologies.

Recently, nanoparticles have attracted considerable interest owing to their distinct properties. Nanoparticle atoms can spontaneously bind with other atoms because most of the atoms on the surface of nanoparticles are unsaturated. Nanoparticles as adsorbents attract increasing interest for their applications due to their high adsorption capacity, ease of operation, and rapid adsorption process (Claesson & Philipse, 2007). Natural and synthetic zeolites have been applied as

porous nanomaterials in water and wastewater treatment because of their well-defined porous structure and excellent cation exchange and sorption characteristics. Zeolites are hydrated aluminum-silicate minerals consisting of SiO_4 and AlO_4 tetrahedra bonded by sharing oxygen atoms. Natural zeolites are expected to have a broad extent of utilization owing to their unique three-dimensional porous structures. Natural zeolites belonging to the cation exchanger group because their primary structural unit, silicon, is isomorphically replaced by aluminum, resulting in an excess negative charge on the zeolite surface. Numerous studies have confirmed the excellent performance of zeolites in removing metal cations from wastewater (Margeta, Logar, Siljeg, & Farkas, 2013; Wang & Peng, 2010; Princz et al., 2005). Natural zeolites are often found in natural deposits associated with glassy volcanic rocks and are obtainable at low cost (Tominaga, 2001; Ohnuma, 1967; Japan Society for the Promotion of Science, 1994). Natural zeolites are employed in many fields including agronomy and horticulture because of their excellent ion exchange capacity, absorptivity, water retention characteristics, and economical (Dimitrova et al., 2006; Tsai et al., 2003; Haimidi et al., 1999; Shao et al., 2002; Sadjadi et al., 2007; Sohrabnezhad et al., 2007, 2008). Through regulating the ratio of aluminum (Al) to silicon (Si), a variety of zeolites with tuned channel structures and ion exchangeability can be attained. Mordeinite zeolites with low Si-Al ratios are rich in free Na^+ owing to the presence of many electronegative AlO_4 tetrahedra (Chaouati et al., 2016; Lotti et al., 2015). Mordeinite is extensively familiar to dispel multivalent ions due to its strong ion exchangeability, excellent hydrophilicity, and reasonable price (Liu et al., 2013; Arancibia-Miranda et al., 2016; Huang et al., 2018). However, studies on heavy metals stabilization from MSWI fly ash by Japanese natural zeolites such as mordenite have not yet been carried out. Mordenite belongs to a family of medium-silica zeolites and is considered to have an excellent ion exchange ability and this has been ascertained by several researches (Król et al., 2013). The ideal composition of mordenite mineral is $\text{Na}_8\text{Al}_8\text{Si}_{40}\text{O}_{96}\cdot n\text{H}_2\text{O}$ and a structure clarified in the Cmcm space group (Pourahmad et al., 2010). The Si/Al modulus of mordenite is about five but varies within a narrow range depending on its origin and formation states. The exchangeable cations are mostly sodium and rarely potassium (Wojciechowska et al., 2019).

Numerous studies have been conducted to stabilize heavy metals in water and wastewater treatment by using different types of natural zeolites (Tasić et al., 2019; Babel & Kurniawan., 2003; Nah et al., 2006; Bose et al., 2002). However, to authors' knowledge, no studies have been performed yet to stabilize heavy metals in MSWI fly ash using natural zeolite. This study presents a promising novel and simple approach for heavy metal stabilization using natural zeolite materials (here, mordenite). Mordenite (fine particles) were used to remove Pb^{2+} and Zn^{2+} from two admixtures determined by the L/S ratio at different doses of mordenite, and the experimental conditions were studied and optimized. The novelty of this method is that the untreated MSWI fly ash was used in its original state

and the mixture of the fly ash and mordenite was in solid and gel-like condition instead of aqueous condition. Several studies have been done to stabilize heavy metals usually in aqueous condition by different types of natural and synthesized zeolites (Sočo & Kalemekiewicz, 2013; Wang et al., 2009; Hałas et al., 2017; Mamlis & Katsou 2013; Basaldella et al., 2007). In addition, this fly ash treatment method can be applied directly to thermal plants and the treated fly ash can be used as raw material for construction and other purposes. The sorption isotherms were also modeled. This study investigated the feasibility of using mordenite to stabilize Pb^{2+} and Zn^{2+} from MSWI fly ash in the presence of other cations. In addition, the selectivity of mordenite for Pb^{2+} was compared with other heavy metals such as Zn^{2+} .

2. Materials and Methods

2.1. Fly Ash Collection

MSWI fly ash was obtained from two anonymous stoker-type incineration plants (S and R) that treat the MSW produced by the City F, Japan. FA sample, mixed with $Ca(OH)_2$, collected from the air pollution control (APC) unit where fabric filters are used. After collection, the samples were kept in air-tight repositories.

2.2. Mordenite Preparation

Mordenite with the chemical formula $(Ca, Na_2, K_2) Al_2Si_{10}O_{24} \cdot 7H_2O$ is a zeolite mineral, and it is one of the six most commercially available zeolites. We acquired mordenite from a local market in Japan. The zeolite sample was crushed, ground into powder state, and dried at $80^\circ C$ before proceeding the experiment.

2.3. Bulk Compositional Analysis

X-ray fluorescence (XRF), device was used for analyzing the bulk element compositions of fly ash samples (S and R). The element/ion concentrations in the leachate obtained from batch leaching tests were analyzed by an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, 720 ICP-OES) following acid digestion with analytical grade nitric acid [HNO_3]. Leaching test was performed by standard Japanese Leaching Test (JLT-46). JLT-46 was conducted in polypropylene bottle with the L/S ratio of 10:1, shaking for 6-hours at 200 rpm. Tests were run in duplicate and the mean value was provided with standard error.

2.4. Mineral Phase Detection

X-ray diffractometer (XRD) technique was used for analyzing the mineral phase of fly ashes and mordenite. The mineral phases were ascertained by using Jade 6.0 software. Scanning Electron Microscope coupled with an Energy Dispersive X-ray (SEM-EDX) detector (Hitachi SU-3500) was used to perform a detailed phase analysis of FA and mordenite before and after the experiments in back-

scattered electron (BSE) mode. The specific surface area and pore volume of the samples measured by the B.E.T. nitrogen adsorption technique.

2.5. Batch Adsorption Studies

As shown in **Table 1**, every set of experiment contained twelve bottles (including replicate), and each bottle contained fly ash (S and R) with different dosages of mordenite and two L/S ratios. The tests were conducted under a static condition in 250-ml polypropylene bottles settled at room temperature for 24 h. The admixtures were graded into gel-like (L/S = 1.5 mL/g) and solid-like (L/S = 0.5 mL/g) admixtures. Deionized water was added to each bottle to increase the total leachant to 100 mL, after 24 h of settlement period. The admixtures were then subjected to a standard Japanese leaching test (JLT-46). To obtain the leachate, bottles were centrifuged at 3000 rpm for 20 min. The solid and liquid parts were separated by vacuum filtration through a 0.45 μm pore-size membrane. Each test was run in duplicate, and the results were provided as mean values with standard errors.

Batch tests were initiated with various doses of mordenite under a settling time of 24 hrs. The values of metal (Pb^{2+} and Zn^{2+}) uptake were calculated using the following Equation (1):

$$R_M = \left(1 - \frac{M_e}{M_0}\right) \times 100 \quad (1)$$

here R_M = metal removal efficiency (%), M_0 = initial metal ion concentration in the solution (mg/L), M_e = final metal ion concentration in the solution (mg/L).

The adsorption capacity was defined and calculated as the amount of heavy metal stabilized per unit mass of mordenite using Equation (2):

$$q_e = (C_0 - C_e) * \frac{v}{m} \quad (2)$$

here q_e = adsorption capacity (mg/g), C_0 = initial metal ion concentration in the solution (mg/L), C_e = final metal ion concentration in the solution (mg/L), m = weight of adsorbent (g), v = volume of solution (L).

Table 1. Experimental condition.

FA Sample	L/S (mL/g)	FA (g)	Zeolite (g)	Deionized-water (mL)	Settling time (h)
S	0.5	10	1, 2, 3, 5, 8, 10	5	24
	1.5			15	
R	0.5	10	1, 2, 3, 5, 8, 10	5	24
	1.5			15	

2.6. Calculation of Adsorption Isotherm Constants

The sorption data were tested with two widely used isotherms, namely, Langmuir and Freundlich. Adsorption of metal ions onto mordenite was modeled by Langmuir isotherms. The linear form of the Langmuir isotherm model is shown in Equation (3):

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (3)$$

here C_e is the equilibrium metal concentration in the solution (M), q_e is the number of metal ions adsorbed onto the zeolite, and Q and b are the Langmuir constants related to sorption capacity and sorption energy, respectively.

The Freundlich isotherm presumes two conditions - firstly that sorption takes place on a heterogeneous surface through a multilayer adsorption mechanism and secondly, that the adsorption amount increases with the concentration according to the following Equation (4):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

here C_e indicates the equilibrium metal concentration (mg/L), and q_e indicates the amount of metals adsorbed per unit mass of mordenite (mg/g). K_f is a constant associated to bonding energy, $1/n$ is the factor of heterogeneity and n (g/L) estimates the deviation from linearity of adsorption. Constants of Freundlich equilibrium were calculated from the graph plotted in $\log q_e$ versus $\log C_e$. The state of non-linearity specifies by the n value; when n equal to 1, adsorption is linear; when $n < 1$, adsorption is a chemical process; when $n > 1$, adsorption is a physical process (Int, 2019).

3. Results and Discussion

3.1. Elemental Composition and Leachable Elements of Fly Ash

The principal elements present in fly ash more than 1% (wt.) are Ca, Cl, Si, Al, Zn, Na, K, Mg, Ti, P, and S. Elements less than 1% (wt.) are grouped into minor and trace elements. **Table 2** shows the major and minor elements in both S and R fly ashes. For acid gas attenuation (especially HCl), slaked lime $[\text{Ca}(\text{OH})_2]$ was originally mixed with fly ash. Therefore, fly ash samples contained significantly high concentrations of Ca and Cl, 33% - 45% and 22% - 26%, respectively. It was also noticed that the content of Zn and Pb was significantly higher than that of other elements. Therefore, considering the environmental toxicity, these two metals were selected as the main target in this study.

Similar to Pb^{2+} , Zn^{2+} may react with substances like i.e., oxygen or acids to form potentially toxic compounds, but Zn in metallic form is relatively harmless. The initial Pb^{2+} and Zn^{2+} concentrations were obtained by the standard Japanese Leaching Test (JLT-46), also presented in **Table 2**.

3.2. Mineral Compositions of Fly Ashes and Mordenite

Figure 1(a) presents the XRD pattern of mordenite zeolite. The XRD profile of mordenite is accords with the patterns described in the literature (Schmidt et al., 2000; Hincapie et al., 2004; Shaikh et al., 1993; Treacy & Higgins, 2001), confirming that this product is a crystalline mordenite zeolite. SEM-EDX was also used to analyze the composition of the mordenite powder, and the micrograph is shown in **Figure 1(b)**. The elemental composition of mordenite (**Figure 1(b)**)

Table 2. Bulk elemental composition of fly ash sample S and R.

FA (components)	S (%)	R (%)
SiO ₂	6.62	10.59
Al ₂ O ₃	3.93	2.21
Fe ₂ O ₃	1.22	0.70
TiO ₂	1.14	0.58
MnO	0.05	0.02
P ₂ O ₅	1.26	0.54
CaO	33.07	45.19
MgO	2.73	2.45
Na ₂ O	12.24	4.17
K ₂ O	5.31	2.71
Cl	22.29	25.65
Pb	0.42	0.33
Sb	0.16	0.13
Cu	0.12	0.09
Zn	2.62	1.39
S	1.98	1.86
LOI	4.60	1.15
Pb in leachate (mg/L)	48.50	100.89
Zn in leachate (mg/L)	4.88	6.13

shows that Si, Al, and Ca are the main cations, and other elements are present at lower concentrations. The specific surface area and pore volume of mordenite are shown in **Table 3**. It can be seen that mordenite zeolite has a surface area of 62 m²·g⁻¹. The pore volume demonstrates that mordenite is a porous material with a pore volume of 0.034 cm³·g⁻¹ with microspores.

The mineral phases of the original FA samples from sources S and R are shown in **Figure 2(a)**. The principal phases are found halite (NaCl) and sylvite (KCl) that are considered the main sources of Cl, which is very abundant in fly ash (**Table 2**). Ca-rich minerals including calcite (CaCO₃), anhydrite (CaSO₄), lime (CaO), and mayenite (Ca₁₂A₁₄O₃₃) were identified as minor phases, which inclusively illustrate the noteworthy Ca concentration in fly ash (**Table 1**). However, IFA is a synthetic material and is not completely crystalline. As a result, the XRD technique cannot track out phases with lower amount or amorphous components (Madsen et al., 2011). **Figure 2(b)** shows the mineralogical composition of IFA after treating with mordenite (mordenite dosage of 100%). **Figure 2(b)** shows distinct mordenite peaks and other major mineral

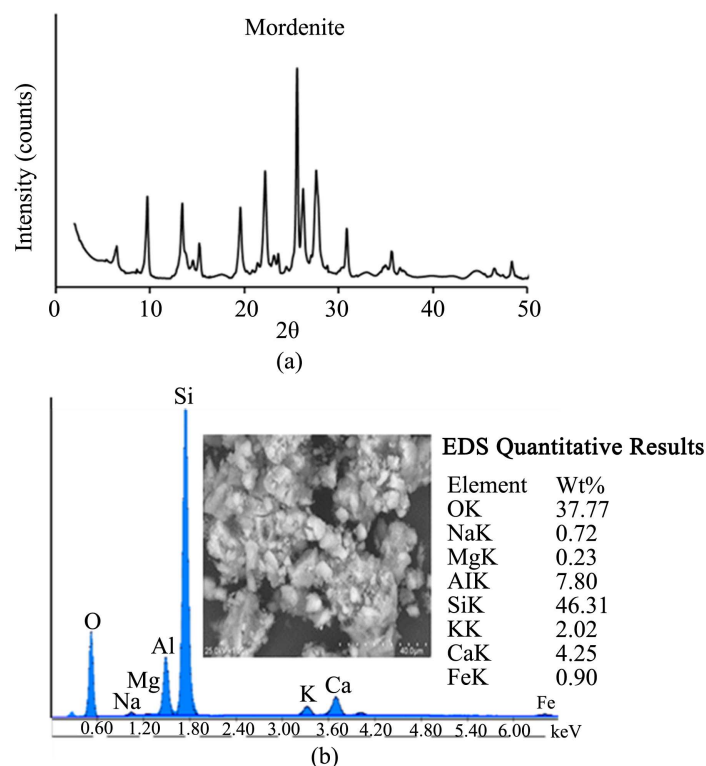


Figure 1. (a) XRD pattern of mordenite; (b) Scanning Electron Microscopy (SEM) micrograph of mordenite and associated analytical data.

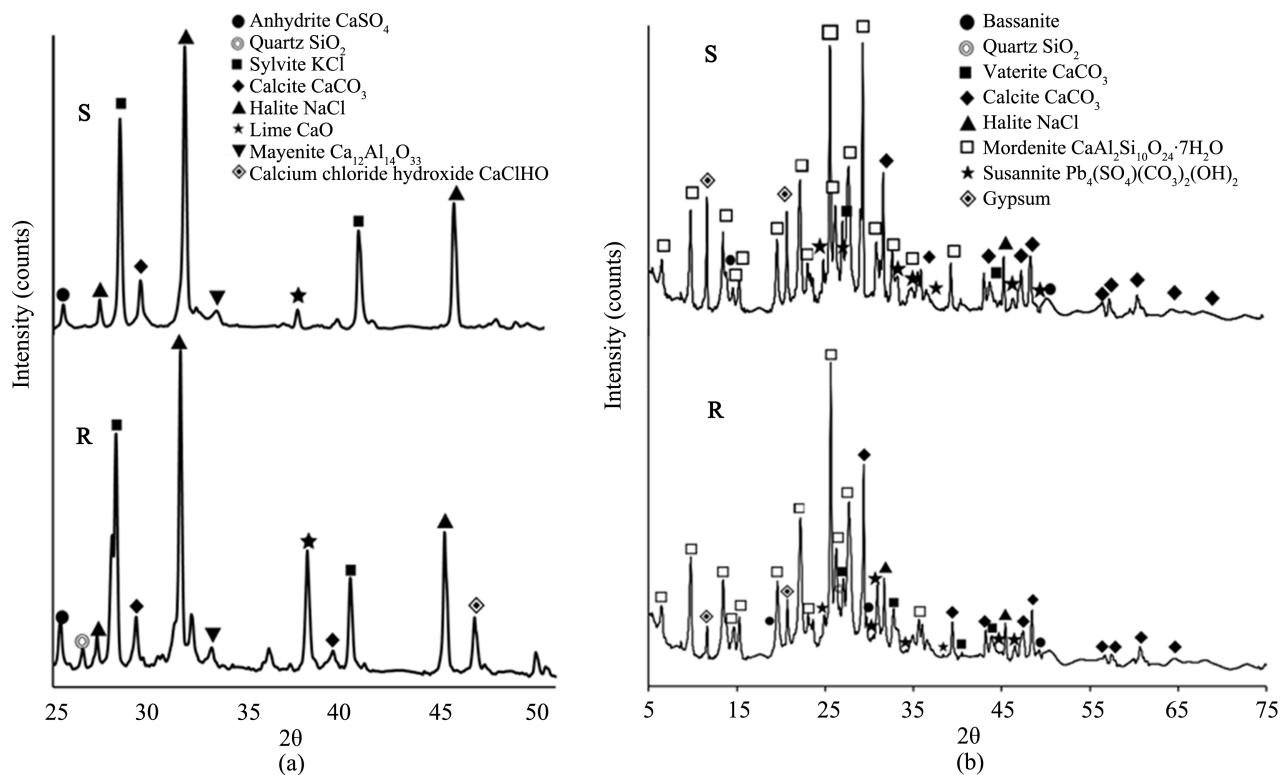


Figure 2. (a) XRD spectra of IFA S and R before treatment; (b) XRD spectra of fly ashes S and R after treatment with mordenite (100%).

Table 3. Textural properties of mordenite.

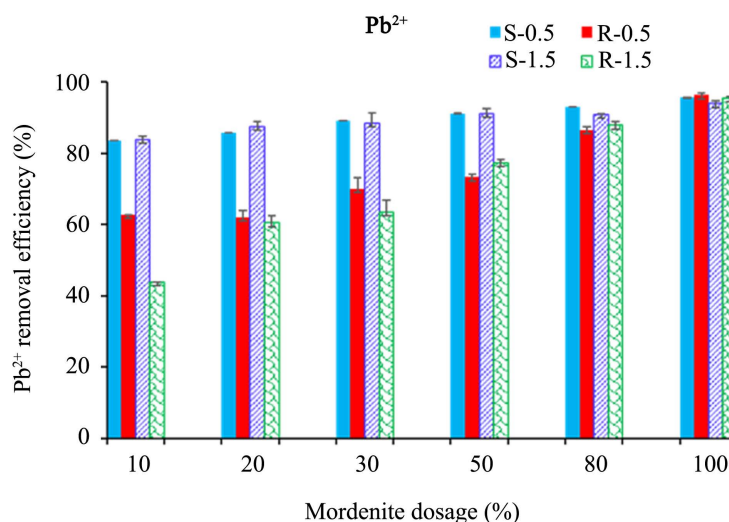
Sample	S_{BET} (m ² /g)	V_{Tot} (cm ³ /g)	D_{BET} (nm)	Si/Al ratio
Mordenite	62.1	0.034	2.24	6

phases in IFA samples treated with mordenite. According to the results, calcite (CaCO₃) and halite (NaCl) are ascertained as major phases, and the other minerals such as vaterite (CaCO₃), basanite [2CaSO₄·(H₂O)], gypsum (CaSO₄·2H₂O), quartz (SiO₂) were exist as minor or trace phases in the mordenite-treated FA. Besides, sylvite (KCl), a highly soluble mineral, disappeared. In contrast, susannite Pb₄(CO₃)₂(SO₄)(OH)₂, a Pb-bearing mineral closely related to leadhillite and macphersonite, was probably formed in the fly ashes samples after treatment, next to vaterite (CaCO₃), bassanite [2CaSO₄(H₂O)]. Susannite is easily confused with leadhillite. When leadhillite is heated, it reversibly transforms to susannite in the temperature range of 50 °C - 82 °C (Bindi & Menchetti, 2005).

3.3. Effect of Mordenite on Pb²⁺ and Zn²⁺ Stabilization

3.3.1. Effect of Adsorbent Dosage

The effect of different doses of adsorbent (mordenite) on both admixtures specified by the L/S ratio (L/S = 0.5 mL/g and L/S = 1.5 mL/g) was studied. In both conditions, the removal efficiency of Pb²⁺ gradually increased with increasing the mordenite dosage. However, as shown in **Figure 3**, the solid-like condition (L/S = 0.5 mL/g) was slightly better than the gel-like condition. The results showed that an adsorbent dosage of 10% - 20% stabilized about 83% - 87% of Pb²⁺ in both mixtures of sample S. However, as the adsorbent dosage gradually increased, the removal efficiency of Pb²⁺ from sample S was steadily improved. Sample R also showed the same trend of removal efficiency as sample S. However, the removal efficiency of sample R was lower than that of sample S (more than 20%) in both conditions until the adsorbent dosage reached 50%. This may

**Figure 3.** The trend of Pb²⁺ removal efficiency as a function of mordenite addition.

be due to the screening effect of the adsorbent, which protects the adsorption site of the adsorbent by shortening the intercellular distance due to the aggregation of unit cells as the amount of adsorbent increases (Ghogomu et al., 2013). However, a significant Pb^{2+} removal efficiency (more than 95%) was achieved at 100% adsorbent in all cases.

In the case of the Zn^{2+} removal efficiency in the solid-like condition (S-0.5), the removal efficiency gradually increased with increasing the amount of zeolite, reaching about 80% after adding 80% and 100% mordenite, shown in Figure 4. Furthermore, the Zn^{2+} removal efficiency of fly ash samples increased with the addition of 10% mordenite in the solid-like condition. On the other hand, in the gel-like condition of sample R (R-1.5), Zn^{2+} leaching was significantly enhanced with up to 30% of mordenite and started to stabilizing with 50% mordenite.

After 24 h settlement, the removal efficiency of Zn^{2+} from sample S was 51% - 80% when treated in the solid-like state and 7% - 61% when treated in the liquid-like state. Since the leachability of Zn^{2+} in the mixture is accelerated in the liquid-like state, sample R also showed higher removal efficiency in the solid-like state (13% - 60%) than the liquid-like state (3% - 54%). It is worth noting that sample R showed a Zn^{2+} removal efficiency of more than 54% when 100% mordenite was used. Therefore, it suggests that both Zn^{2+} and Pb^{2+} can be stabilized effectively at a particular L/S ratio if enough adsorbent is supplied within only 24 h of settlement.

The uptake of heavy metal is attributed to several mechanisms in the ion-exchange process and the adsorption process. In the ion exchange process, metal ions must migrate through the pores of the zeolite mass and the channels of the lattice to be replaced by exchangeable cations mainly calcium and sodium. Diffusion is speedier within the pores and slower if the ions migrate within channels of lesser diameter (Erdem et al., 2004). In this case, uptake of metal ions can be attributed mainly to ion exchange reactions in the microporous minerals of the zeolite sample.

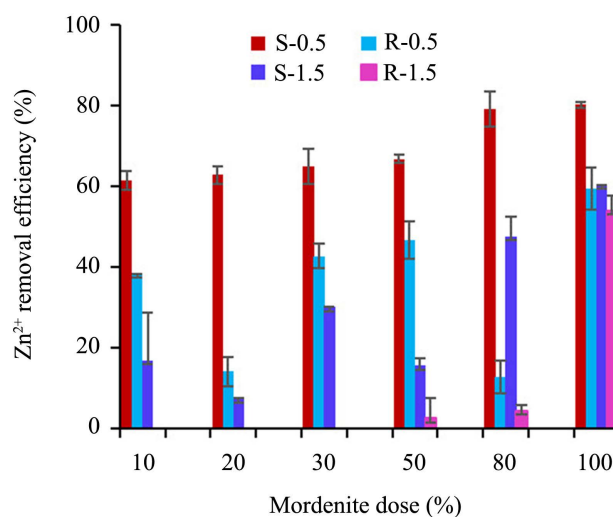


Figure 4. The trend of Zn^{2+} removal efficiency as a function of mordenite addition.

3.3.2. Effect of Initial Concentration

Removal efficiencies of Pb^{2+} and Zn^{2+} depicted earlier that help to indicate the effect of a particular natural zeolite (i.e., mordenite) on the immobilization of heavy metals in the fly ash samples. Therefore, it can be used as an indicator to estimate the appropriate dosage of mordenite for each specific condition. However, since the content of heavy metals in MSWI fly ash from various sources varies over a wide range, the heavy metal removal efficiency may not be a suitable reference value to be directly used in fly ash samples from other sources. Therefore, in order to estimate the different effects of mordenite, the adsorption capacity of mordenite for heavy metal stabilization was employed. The effect of the initial concentration of Pb^{2+} and Zn^{2+} ions on adsorption capacity in fly ash was also evaluated using different doses of mordenite adsorbent and two different admixtures with a contact time of 24 hours.

The experimental results (Figure 5) showed that the maximum Pb^{2+} sorption capacity was obtained when the mordenite added was relatively small (10%). Simultaneously, the amount of heavy metal captured per unit mass of mordenite gradually decreased as the amount of mordenite added increased. In addition, the higher initial concentration of Pb^{2+} was strongly improved the adsorption capacity, suggesting that sufficient Pb^{2+} supply highly contributed to the stabilization.

This is attributed to the fact that the higher the initial concentration of Pb^{2+} in the mixture/solution, the more activity is obtained. The available adsorbed ions are taken up quickly at the adsorption site because the probability of collision increases as the concentration increases (Ghogomu et al., 2013). Therefore, the adsorption capacity of the adsorbent is higher in the initial stage, which is attributed to the smaller concentration of the adsorbent during the adsorption process, most likely because of the more available active adsorption sites (Najua et al., 2008).

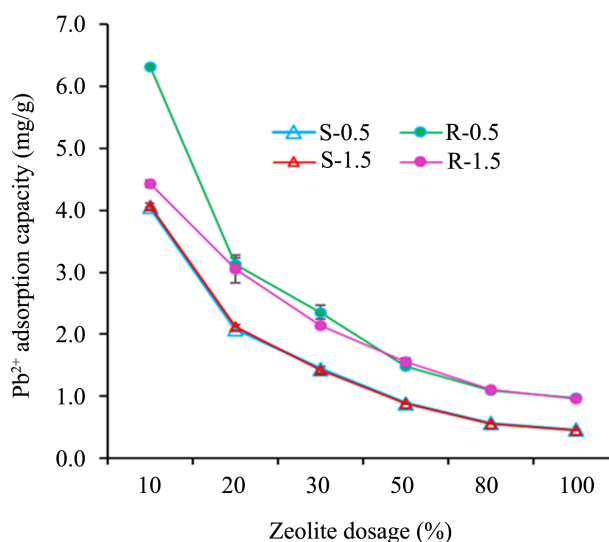


Figure 5. Pb^{2+} adsorption capacity by mordenite.

The enhance the adsorption capacity with the initial concentration increase of Pb^{2+} can be attributed to the increased interaction between the substituted Pb^{2+} and adsorbent (Shao et al., 2002). The maximum adsorption capacity of morde-nite was observed at the initial adsorbate concentration of 100.89 mg/L for sample R (Figure 5). In the solid-like condition, the maximum adsorption capacity of sample R was 6.32 mg/g, which was more than twice (>2.3) that of sample S (4.05 mg/g) with only 10% mordenite. It is also evident that sample R with a higher initial concentration of Pb^{2+} ion achieved higher adsorption capacity than sample S in all other cases. Therefore, the initial concentration and mixing conditions significantly affected the adsorption capacity of Pb^{2+} . We also found that IFA can be treated in the presence of a small amount of water instead. On the other hand, the maximum adsorption capacity of Zn^{2+} was 0.30 mg/g for sample S and 0.10 mg/g for sample R in the solid-like condition, shown in Figure 6. In the liquid-like condition, the leaching of Zn^{2+} from the mixture was more pronounced, and the adsorption capacity ranged from 0.02 to 0.08 mg/g.

3.4. Adsorption Isotherms

A linear plot was obtained by plotting C_e/q_e against C_e over the entire concentration range of the metal ions studied. However, the Langmuir model could not effectively explain the sorption data, especially for Zn^{2+} (data not shown), due to the low R^2 values (Table 4).

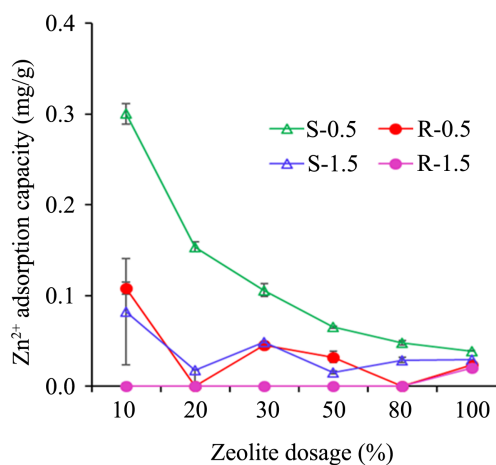


Figure 6. Zn^{2+} adsorption capacity by mordenite.

Table 4. Langmuir and Freundlich isotherms parameters.

FA Sample	Heavy metals	L/S	Langmuir Isotherm			Freundlich Isotherm			
			Q	b	R^2	R_L	K_f	n	R^2
S	Pb	0.5	1.89	0.28	0.73	0.07	9.48	0.62	0.90
		1.5	0.91	11.43	0.70	0.08	34.88	0.43	0.91
R	Pb	0.5	11.75	1.64	0.09	0.01	2.75	1.61	0.69
		1.5	7.37	0.88	0.38	0.01	3.16	1.72	0.84

One of the extensively used sorption isotherm is the Freundlich isotherm, usually fits well with experimental data.

In case of fly ash sample R, the n values were found to be 1.61 and 1.72 for L/S ratios of 0.5 and 1.5, respectively, indicating the physical adsorption of Pb^{2+} ions onto mordenite powder. The values of n for sample S were 0.62 and 0.43 for L/S ratios of 0.5 and 1.5, respectively, which were favorable for chemical adsorption process. **Table 4** shows the constants (k_f and n) and the regression coefficients R^2 values of the Freundlich adsorption equation for metal cations on natural zeolite. On the other hand, both Langmuir and Freundlich isotherms did not fit the adsorption data well for Zn^{2+} ion. This is because these isotherms do not speculate the sorbent by the sorbate. Therefore, mathematically, an extensive surface coverage is enumerated, specifying multilayer adsorption on the surface (Hasany et al., 2002).

4. Conclusion

Mordenite is a natural zeolite with outstanding promise for heavy metals stabilization especially lead and zinc in MSWI fly ash. The removal efficiency of Pb^{2+} and Zn^{2+} increased with increasing the amount of mordenite added. However, the highest Pb^{2+} adsorption capacity was recorded with high initial concentration of Pb^{2+} (100.9 mg/L) in solid-like condition (L/S = 0.5) with only 10% mordenite. On the contrary, the maximum Zn^{2+} adsorption capacity was recorded with an initial Zn^{2+} concentration of 4.88 mg/L under similar conditions. The Langmuir and Freundlich isotherm models were investigated using the adsorption data. The adsorption process describes better in the Freundlich isotherm model compared to the Langmuir isotherm model with a high determination coefficient (R^2), especially for the adsorption of Pb^{2+} . In addition, the affinity of mordenite to Pb^{2+} was shown to be higher than that of Zn^{2+} .

So far, the obtained results have shown that heavy metal (Pb^{2+} and Zn^{2+}) removal by mordenite is technically feasible and seems to be very effective. The treated fly ash can be used as raw material for construction.

In this study, preliminary investigations acquired the auspicious results of using an inexpensive natural zeolite as an environmentally friendly approach for stabilizing Pb^{2+} and Zn^{2+} in MSWI fly ash. Consequently, further researches have planned to explore the detailed mechanism of heavy metal stabilization by mordenite in MSWI fly ash and drive forward to achieve high efficiencies.

Conflicts of Interest

The authors declare that there is no conflict of interest.

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