

RETENTION OF Cd, Cu, Pb AND Zn BY WOOD ASH, LIME AND FUME DUST

TAIT CHIRENJE¹, LENA Q. MA^{2*} and LIPING LU²

¹*B108, Natural and Mathematical Sciences, The Richard Stockton College of New Jersey, Pomona, NJ 08240-0195;* ²*Soil and Water Science Department University of Florida Gainesville, FL 32611-0290*

(*author for correspondence, e-mail: tait.chirenje@stockton.edu)

(Received 19 December 2003; accepted 29 November 2005)

Abstract. Heavy metals are of interest due to their deleterious impacts on both human and ecosystem health. This study investigated the effectiveness of wood ash in immobilizing the heavy metals Pb, Cd, Cu and Zn from aqueous solutions. The effects of initial metal concentrations, solution pH, ash dose and reaction time on metal sorption, as well as the metal sorption mechanisms were studied. To investigate the effect of initial metal concentrations, solutions containing Cd, Zn (25, 50, 75, 100 or 125 mg L⁻¹), Cu (25, 50, 75, 100, 125, 150 or 175 mg L⁻¹) or Pb (250, 500, 750, 1000, 1250, or 1500 mg L⁻¹) were reacted with 10 g L⁻¹ ash for two hours. For the effect of pH, solutions containing 100 mg L⁻¹ of Cd, Cu or Zn or 1500 mg L⁻¹ of Pb were reacted with 15 g L⁻¹ ash over a pH range of 4 to 7. The wood ash was effective in immobilizing the four metals with a sorption range of 41–100 %. The amounts of metals retained by the ash followed the order of Pb > Cu > Cd > Zn. As expected, absolute metal retention increased with increasing initial metal concentrations, solution pH and ash dose. Metal retention by the ash exhibited a two-phase step: an initial rapid uptake of the metal followed by a period of relatively slow removal of metal from solution. Metal retention by the ash could be described by the Langmuir and Freundlich isotherms, with the latter providing a better fit for the data. Dissolution of calcite /gypsum minerals and precipitation of metal carbonate/sulfate like minerals were probably responsible for metal immobilization by the ash in addition to adsorption.

Keywords: heavy metals, sorption, immobilization, precipitation, fume dust

Introduction

Heavy metals are potential pollutants in both the aquatic and soil environments (Alloway and Ayres, 1993). The ubiquitous nature of heavy metals, their toxicity in trace quantities, and their tendency for bioaccumulation in the food chain make it pertinent to develop schemes to immobilize metals from wastewater and soils (Viraraghavan and Rao, 1991).

Various methods to remediate heavy metal contaminated soils and wastes exist, including thermal, biological, and physical/chemical treatments. However, most current treatment technologies are either too costly or only partially effective. For example, excavation and off-site disposal of contaminated soil cost \$270 to \$460 /Mg soil in 2000 (USEPA, 2001). The use of metal-accumulating plants to extract

metals (phytoremediation/phytoextraction) from soils is promising (Ma *et al.*, 2001; Salt *et al.*, 1995), but most of these plants exhibit limited growth and inefficient transfer of heavy metals from soil to plant under field conditions. Among the many in-place treatment technologies reported by Sims *et al.* (1986), which included soil flushing, immobilization, chemical degradation, biodegradation, and attenuation, in-situ immobilization of metal-contaminated soil was the most cost-effective remediation method. For example, the cost of remediating a lead battery-cracking site in-situ using a phosphate additive was approximately \$55/Mg soil in the early 1990s (Chowdhury *et al.*, 1994).

Natural, agricultural and industrial solid wastes have been used to immobilize metals in soils and waters (Namasivayam and Kadiruelli, 1997). Natural minerals such as Fe oxides, clay minerals and calcite have been tested in sorption studies (Coughlin and Stone, 1995; Roy, 1993; Zachara *et al.*, 1991). Ferrihydrite, a common surface coating of subsoil particles (Benjamin and Leckie, 1981), natural zeolite (Blanchard *et al.*, 1984), and more complex natural minerals such as kaolinite and glauconite (Holm and Zhu, 1994) have been shown to exhibit considerable capacity for adsorption of trace metals. Phosphate minerals, including hydroxyapatite, have also been demonstrated to effectively immobilize heavy metals such as Pb from aqueous solutions and metal contaminated soils (Ma *et al.*, 1993, 1995).

In recent years, there has been an increase in the use of agricultural and industrial solid wastes as adsorbents for the removal of heavy metals (Periasamy and Namasivayam, 1996). The advantage of using solid wastes is that it saves disposal costs while alleviating potential environmental problems. Numerous studies have shown that different ashes and sludges may effectively immobilize heavy metals from aqueous solutions (Calace *et al.*, 2002; Garcia-Sanchez and Alvarez-Ayuso 2002; Hassett and Eylands, 1999; Ferrero *et al.*, 1986). Wood ash, produced when wood fines (mostly planar shavings) and chip rejects (from screening operations) are burned as fuel to produce energy in boilers, consists of salts, oxides and hydroxides of Ca, Mg, Na and K (Unger and Fernandes, 1990; McGinnis, 1995) and trace metals in lesser proportions. Like coal fly ash, wood ash is fine in texture, consisting mainly of particles ranging in size from clay to silt, making it a prime candidate as a sorptive material. For example, Hassett and Eylands (1999) noted that Hg retention in coal combustion fly ash was dependent on temperature and organic carbon (OC) content. Rao *et al.* (2002) determined the removal of Cr and Ni from solutions using fly ash and observed that the Cr-Ni sorption capacity of fly ash was comparable to that of activated carbon under varying conditions of pH, particle size and initial Cr and Ni concentrations. These results were echoed by Hequet *et al.* (2001), who observed high Cu and Zn sorption capacities on fly ash.

The objectives of this research were to study the influence of metal concentrations, solution pH, sorbent dosage and reaction time on metal sorption process by wood ash and investigate the associated metal sorption mechanisms to advance our understanding of in-situ mobilization of metals.

Materials and Methods

MATERIALS

Wood ash and other industrial by-products; wood sludge and lime, and fume dust, were tested for their ability to sorb heavy metals in a preliminary study. The wood ash, sludge and lime used in this study were by-products of a plywood plant from Brunswick, Georgia. The fume dust was a by-product of a steel company from Niagara Falls, New York. The samples used were all in air-dry condition and fine enough to pass through a 1-mm screen. Selected characteristics of the sorbents are summarized in Table I.

Deionized distilled water was used to prepare all solutions and suspensions. Metal solutions for Cd, Cu, Pb and Zn were prepared by dissolving 2.743g of $\text{Cd}(\text{NO}_3)_2$, 3.661 g of $\text{Cu}(\text{NO}_3)_2$, 15.99g of $\text{Pb}(\text{NO}_3)_2$ or 4.551g of $\text{Zn}(\text{NO}_3)_2$ into 20mL of 2M HNO_3 , and the solutions were then diluted to 1L with deionized distilled water to yield a stock solutions containing 1000 mg L^{-1} of Cd, Cu, or Zn, or $10,000 \text{ mg L}^{-1}$ of Pb. The stock solutions were further diluted to obtain solutions containing 0 to 50 mg L^{-1} of Cd, Cu, Pb or Zn.

A preliminary experiment was conducted to select the most effective material for metal sorption. Solutions containing 75 mg L^{-1} of Cd, Cu, Pb or Zn were reacted with ash, lime, sludge or fume dust at a dosage of 10 g L^{-1} for two hours.

SORPTION EXPERIMENTS USING WOOD ASH

The effects of initial metal concentration, pH, reaction time, and ash dosage were tested using the following procedures:

- (a) Initial metal concentrations: Solutions containing Cd, Zn ($25, 50, 75, 100$ or 125 mg L^{-1}), Cu ($25, 50, 75, 100, 125, 150$ or 175 mg L^{-1}) or Pb ($250, 500, 750, 1000, 1250,$ or 1500 mg L^{-1}) were reacted with 10 g L^{-1} ash for two

TABLE I
The sorption of the different elements[†] onto the materials used in the study

	mg/kg						g/100 g				
	K	P	Zn	Cu	Mn	Na	Ca	Mg	N	OM	pH
Lime	82.7	4020	8.3	5.50	93.7	7610	40.8	0.40	0.01	1.70	9.80
Ash	4920	2320	180	42.2	860	2950	4.20	0.71	0.07	25.0	8.90
Fume dust	3000	540	1770	43.0	85.8	970	0.14	0.08	0.03	3.20	7.00
Sludge	150	224	67.3	22.4	209	3140	5.50	0.60	0.05	80.6	9.50

[†]K, Zn, Cu, Mn, Na, Ca, and Mg were determined on a Tehrmall Jarell Ash ICP atomic emission spectrophotometer and N (total N) and P were determined on a segmented flow autoanalyzer.

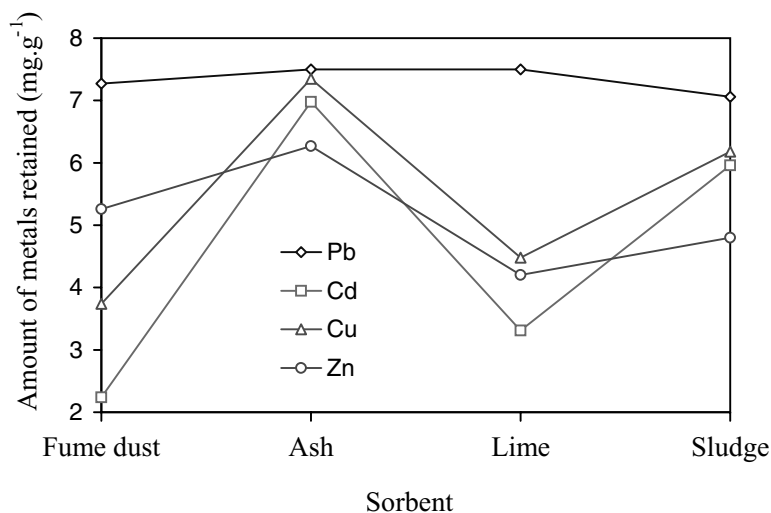


Figure 1. Metal sorption by four industrial by-products after reaction with 75 mg L⁻¹ Pb, Cu, Zn or Cd for two hour at 10 g sorbate L⁻¹.

hours. Intentionally higher Pb concentrations were used in this study due to the effectiveness of the ash in sorbing Pb (Figure 1).

- (b) pH: Solutions containing 100 mg L⁻¹ of Cd, Cu or Zn or 1500 mg L⁻¹ of Pb were reacted with 15 g L⁻¹ ash over a pH range of 4 to 7. The pH was adjusted using 0.1N HNO₃ or NaOH.
- (c) reaction time: Solutions containing 125 mg L⁻¹ of Cd, Cu or Zn or 1500 mg L⁻¹ of Pb were reacted with 10 g L⁻¹ ash for 2.5 to 240 minutes.
- (d) ash dosage: Solutions containing 125 mg L⁻¹ of Cd, Cu or Zn or 1500 mg L⁻¹ of Pb were reacted with 5 to 20 g L⁻¹ ash for two hours.

In the preliminary study, four industrial by-products (ash, lime, and sludge from a wood company, and fume dust from a steel company) were reacted with aqueous Pb, Cu, Cd or Zn to determine the most effective sorbent.

ANALYSES

All suspensions were filtered through 0.45 μm Nucleopore polycarbonate membrane filters. The filtrates were analyzed for Pb, Cd, Cu and Zn using an atomic absorption spectrophotometer (Model 2380, Perkin Elmer, Pittsburgh, USA). The pH values of the solutions were measured with an Orion pH meter (AccuModel 20, Denver, USA). The soil organic matter was determined using the Wakley Black method. A Shimadzu TOC analyzer was also used to determine the dissolved, inorganic and total organic carbon in the samples following digestion. The solid phases

were analyzed using an X-ray diffractometer (XRD, Nicolet XRD Madison, WI) using $\text{CuK}\alpha$ radiation of aluminum powder mounts to determine the mineral phases in the ash before and after the sorption experiment. The samples were scanned with $\text{Cu K}\alpha$ radiation at $2^\circ 2\theta$ per min. The surface morphology and elemental distribution of the solid phase were analyzed using a scanning electron microscopy (SEM/EDAX, JSM-6400/TN500, Jeol, USA). All analyses were carried out in duplicate.

Results and Discussion

Among the four materials tested in the preliminary study, wood ash was the most effective sorbent (Figure 1). It was unclear why the wood ash was the most effective in immobilizing metals because the most important factors influencing metal sorption are pH, particle size, OC, inorganic carbon (IC), and clay content (McBride, 1994). Among the four materials tested, the papermill lime had the highest pH (9.8) and the highest Ca concentration (408 g kg^{-1}), and the papermill sludge had the highest content of organic matter (OM, 801 g kg^{-1} ; Table I). The fume dust had the highest clay contents (464 g kg^{-1}). Among the four metals tested, Pb was sorbed the most and Cd and Zn had the least sorption onto these materials (Figure 1). In fact, Pb was adsorbed in nearly the same amounts in all materials. Based on these observations, wood ash was selected in this experiment because of its effectiveness in immobilizing all four metals.

SORPTION ISOTHERMS

Both the Langmuir and Freundlich sorption models were used to fit metal sorption by wood ash to evaluate the mechanistic parameters associated with the sorption process.

The Langmuir isotherm: The Langmuir isotherm assumes uniform energy of sorption onto the surface and no transmigration of sorbate on the surface (Benjamin and Leckie, 1981; Jain and Ram, 1997). It is derived from:

$$X/M = KbC/(1 + KC) \quad (1)$$

where X/M is the amount of metals sorbed per unit weight of sorbent, C is the equilibrium concentration of the sorbate, K is a concentration factor (also called a distribution coefficient or partition coefficient), and b represents the maximum amount that can be sorbed. Based on the b values of the Langmuir model, the maximum sorption capacity (mg g^{-1}) for the four metals followed the order: Pb (101) > Cu (11.6) > Cd (8.4) > Zn (7.5), which was consistent with the actual data in Figures 2A and B (Table II). However, based on K values of the Langmuir model, distribution coefficients for the four metals followed the order: Pb > Cd > Cu >

TABLE II
Characteristic parameters and correlation coefficients of data by the Freundlich and Langmuir equations

Element	Freundlich			Langmuir		
	1/n	K (l/g)	R ²	b (mg/g)	K (l/mg)	R ²
Pb	9.53	73.8	0.998	101	2.42	0.912
Cd	6.39	5.03	0.984	8.40	1.29	0.985
Cu	6.06	6.92	0.993	11.6	1.12	0.943
Zn	6.13	4.12	0.997	7.50	0.65	0.966

Zn (Table II). Based on the Langmuir model, the reported distribution coefficients of Pb and Zn for bed sediments were 0.64 and 0.12 L mg⁻¹ (Jain and Ram, 1997) and that of Cu for coirpith carbon was 0.44 L mg⁻¹ (Namasivagam, 1997). In our experiment, the distribution coefficients of Pb, Zn, and Cd were 2.42, 1.12, and 0.65 L mg⁻¹ (Table II), which were much greater than those reported for sediment and coirpith carbon, indicating that the wood ash is a more effective sorbent than both sediment and coirpith carbon for these metals under the conditions of our study.

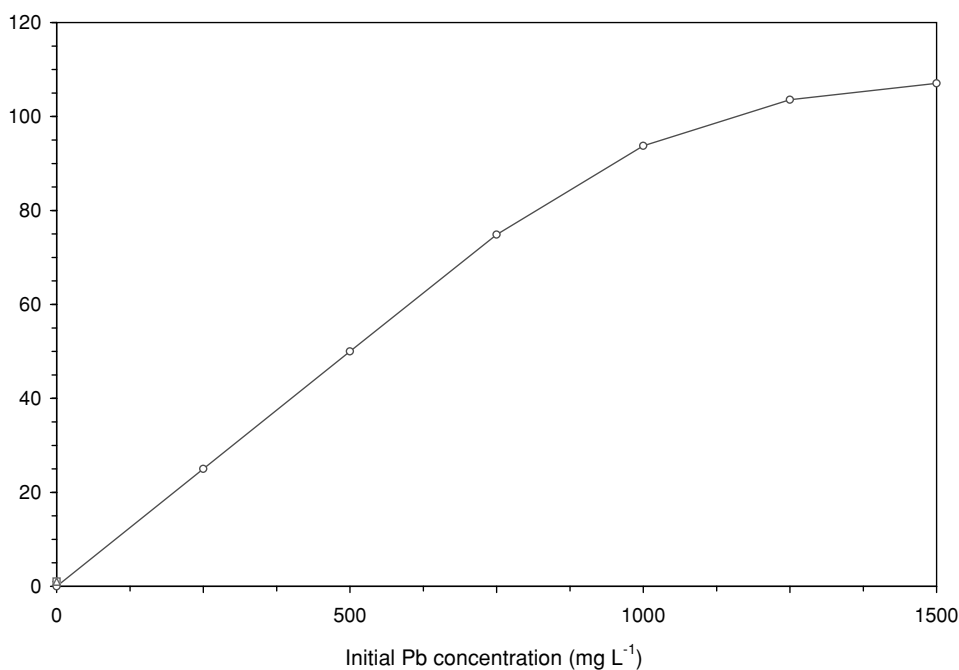


Figure 2. Effects of initial metal concentrations on metal immobilization by the wood ash after reaction for two hours at 10 g ash L⁻¹.

The Freundlich isotherm: The Freundlich isotherm is represented as:

$$X/M = KC^{1/n} \quad (2)$$

where X/M is the amount of solute sorbed per unit weight of sorbent, C is the equilibrium concentration of solute remaining in the solution, K and $1/n$ are Freundlich constants related to sorption capacity and sorption intensity, respectively. Based on the K values of the Freundlich model, the sorption capacity followed the order: $Pb > Cu > Cd > Zn$ (Table II), which was consistent with the order based on the Langmuir model. However, a different order ($Cu > Zn > Cd > Pb$) was observed using the sorption intensity ($1/n$) of the Freundlich model. Jain and Ram (1997) showed that the order based on K values was different from that based on $1/n$ values for Pb and Zn sorption by sediments. It seemed both models described metal sorption by the wood ash satisfactorily as reflected by the relatively high fitting correlation coefficients ($r^2 > 0.91$) of the sorption data. However there were some differences between the actual data and the parameters derived from the models. Metal sorption on calcite is described well by the Freundlich and Langmuir (Kinniburgh, 1986), and two-part Langmuir equations. The nonlinearity of metal sorption over the entire sorbate concentration range and good fit to the Freundlich isotherm attests to the non-uniformity or heterogeneity of sorption sites (Benjamin and Leckie, 1981) on the calcite surface.

EFFECTS OF INITIAL METAL CONCENTRATIONS ON METAL SORPTION BY THE ASH

The amount of Pb sorbed by the wood ash initially increased rapidly with increasing Pb concentrations and slowed down when Pb concentrations reached 750 mg L^{-1} (Figure 2B). The increases were more modest for Cu , Cd and Zn (Figure 2A). The amounts of metals sorbed by the ash followed the order: $Pb > Cu > Cd > Zn$, which was also observed for amorphous iron oxyhydroxide by Benjamin and Leckie (1981). Zachara *et al.* (1991) stated that ionic radius is an important factor influencing metal sorption selectivity on calcite. This was especially important for one of the materials, ash, which had high concentrations of calcite. The ionic radii of Pb , Cd , Zn and Cu are 0.118, 0.097, 0.074, and 0.073 nm (Puls and Bohn, 1988; McConnell, 1973), respectively. Normally, cations with larger ionic radii preferentially displace cations with smaller ionic radii. Based on ionic radii, the predicted order of bonding preference was: $Pb > Cd > Zn > Cu$, which was in general agreement with our observation with the exception of Cu .

In addition to ionic radii, the solubility of metal carbonates and hydroxides may also be an important factor in determining metal sorption since they may form during the sorption reactions. Carbonate formation is especially important in materials like ash, which have high salt content. The solubility products of metal carbonates

followed an increasing order of PbCO_3 ($10^{-12.95}$) < CdCO_3 ($10^{-11.29}$) < ZnCO_3 ($10^{-9.82}$) < CuCO_3 ($10^{-9.61}$) < CaCO_3 ($10^{-8.34}$), and those of metal hydroxides followed an increasing order of Cu(OH)_2 ($10^{-20.3}$) < Zn(OH)_2 ($10^{-16.9}$) < Pb(OH)_2 ($10^{-15.3}$) < Cd(OH)_2 ($10^{-14.4}$) < Ca(OH)_2 ($10^{-5.2}$) (McBride, 1994). The order predicted based on carbonate solubility was identical to that based on ionic radii, where the order based on hydroxides provided little trend for comparison.

The solubility product (K_{sp}) of the salt:



is given by the relationship: $K_{\text{sp}} = [\text{A}][\text{B}]$. A high K_{sp} indicates high solubility. Using the concentration of Cu used in this study, the likelihood of forming precipitates of the compounds discussed above and CuO (tenorite), and $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ (malachite) was calculated and the only precipitates determined to be possible were those of tenorite and malachite. Under the conditions of our study, tenorite and malachite precipitated but there was a very small probability of other compounds precipitating under the conditions of our study.

EFFECTS OF pH ON METAL SORPTION BY THE ASH

As expected, metal sorption increased significantly with increasing solution pH (data not shown). This may be attributed to less competition from protons for sites on the ash particle at higher pH. In addition, both dissolved organic C (DOC) and carbonate in solution increased with increasing solution pH. Among the three metals with same initial concentrations, Zn was the most sensitive to solution pH changes, followed by Cu and Cd (Figure 3). There was no significant increase in the amount of Pb immobilized by the ash compared to an increase in Zn from 88 to 97% ($\alpha = 0.05$).

As pH increased, carbonate concentrations decreased after reaction with Zn, whereas little change in carbonate concentrations was observed after reaction with Cd. Reduction in carbonate concentrations may have been a result of formation of hydrozincite, whose formation took both OH^- and CO_3^{2-} out of solution and increased with increasing pH. On the other hand, carbonate concentrations remained constant as pH increased from 4 to 6. Carbonate concentrations increased significantly as pH increased from 6 to 7 after reaction with Cu or Pb.

Hydrozincite ($\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$) is less soluble than ZnCO_3 , but more soluble than Zn(OH)_2 (McBride, 1994). Among the four metals studied, CdCO_3 had the lowest solubility after PbCO_3 and Cd(OH)_2 had the highest. Cadmium, thus, was strongly associated with CO_3^{2-} over the entire pH range studied and was only slightly affected by solution pH (Figures 3A & B). This possibly explains why pH had less effect on Cd than other three metals. Similar observations were reported by McBride (1979).

Zirino and Yamamoto (1972) demonstrated that solution pH significantly affects

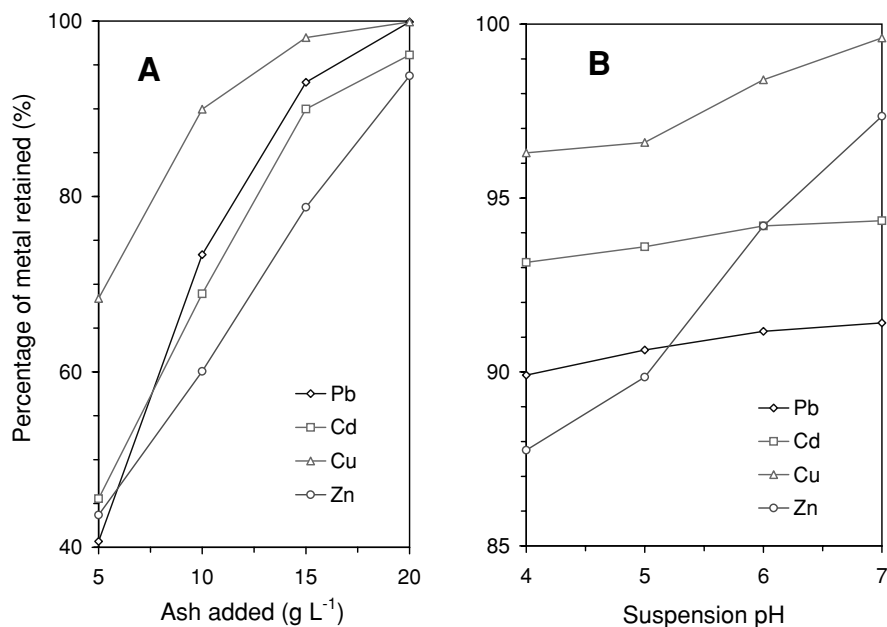


Figure 3. The effect of the amount of (A) ash added and (B) suspension pH on percentage of metal adsorbed by the wood ash after reaction with 100 mg L⁻¹ for Cu, Cd and Zn and 1500 mg L⁻¹ for Pb for two hours.

metal species distribution and as a result affects metal sorption. Baes and Mesmer (1976) reported that $\text{Cu}_4(\text{OH})_2\text{CO}_3$ is a more stable species for Cu at lower pH than organically complexed Cu, which is a more important phase when solution pH is above 6. In our study, total carbonate concentrations increased significantly when solution pH increased from 6 to 7 after reaction with 100 mg L⁻¹ Cu (Figure 3B). This suggested that $\text{Cu}_4(\text{OH})_2\text{CO}_3$ was an important species at pH < 6, whereas other forms of Cu (e.g. organically complexed Cu) became more important species at pH > 6. Among the four metals studied, PbCO_3 was the most insoluble mineral and Pb had the highest initial concentrations (1,500 vs. 100 mg L⁻¹). As a result, PbCO_3 was precipitated after Pb reaction with the ash. As expected, Pb sorption on calcite increased with increasing pH. The pH of CaCO_3 suspensions was high enough to precipitate most of the added Pb (90–91%).

EFFECTS OF ASH DOSAGE ON METAL SORPTION BY THE ASH

Percent metal immobilization increased significantly as the amount of ash added increased (Figure 3A). Ash dosage of 15 g L⁻¹ (Pb, Cd, Cu) and 20 g L⁻¹ (Zn) was required to immobilize 90% of the respective metals. However, metal sorption per unit weight of sorbent decreased from 120 to 75, 13 to 9, 12 to 6, and 12 to 6 mg

g^{-1} for Pb, Cu, Cd and Zn, respectively, when the amount of ash added increased from 5 to 20 g L^{-1} . Ferrero and Prait (1986) reported that the sorbed amount of Pb, Cu, Cd and Zn was 12.8, 20, 29.9 and 15 (mg g^{-1}) at coal ash dosage of 5 g L^{-1} . This study showed the potential of wood ash as a sorbent, especially for Pb.

EFFECT OF REACTION TIME ON METAL SORPTION BY THE ASH

Metal sorption by the ash was very rapid for the first 30 minutes (Figure 4B). After 5 minutes the amounts of Pb, Cu, Cd and Zn sorbed by the ash were 51.4, 8.8, 6.8 and 5.7 (mg g^{-1}), respectively, which accounted for 42%, 71%, 77% and 66% of the total metals sorbed in 4 hours (Figure 4B). This was attributed to the instantaneous utilization of the most readily available sorbing sites on the ash surface. Two sorption stages in the Ca isotopic exchange between calcite and aqueous solutions were been observed by Moller and Sastri (1973). The first stage of Ca uptake was due to surface exchange, which was completed within 16 hours, whereas the slower exchange process was a result of "lattice penetration and recrystallization". In our study, Scanning Electron Microscopy Energy Dispersive X-ray analysis (SEM/EDAX) results indicate the formation of cerussite after the ash reacted with 1500 mg L^{-1} Pb for four hours and 30 minutes, respectively (Figure 5A & B). It is clear that cerussite peaks increased while calcite peaks decreased as reaction time increased from 30 minutes (Figure 5A) to four hours (Figure 5B). This suggested that formation

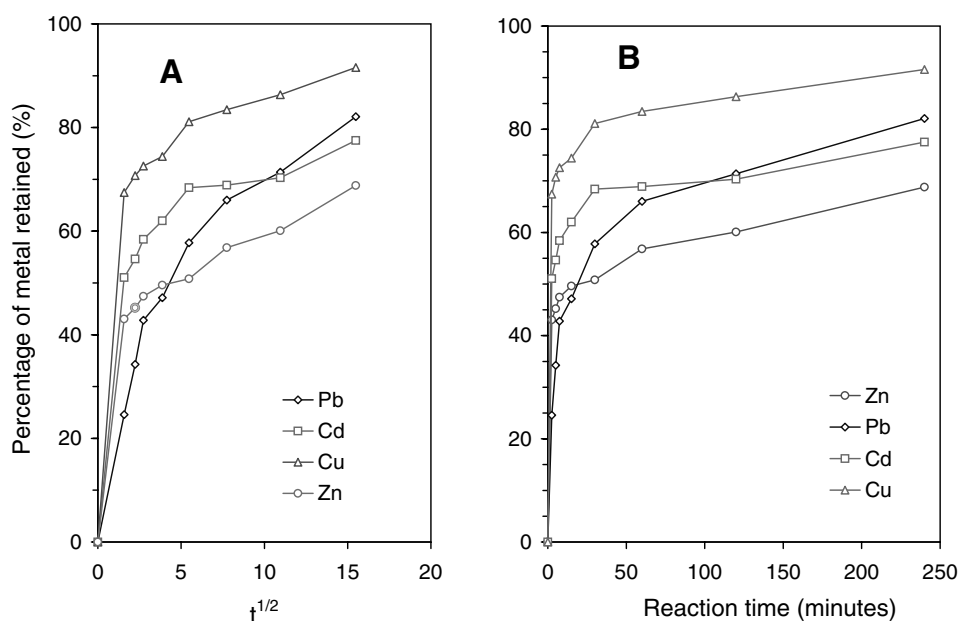


Figure 4. The effect of time on percentage of metal adsorbed by wood ash.

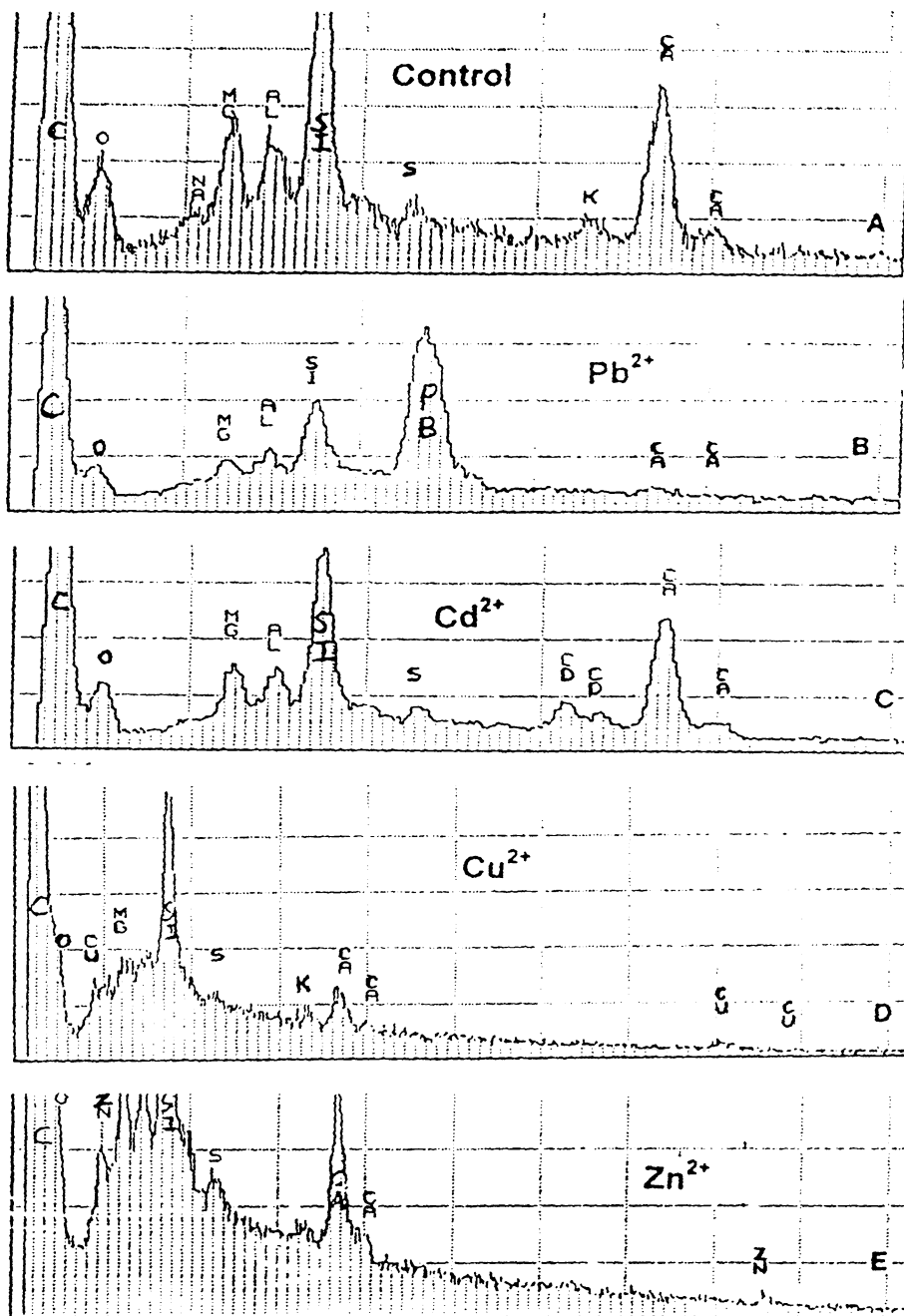


Figure 5. SEM/EDAX patterns of the ash (A) before and after sorption reaction. (A) control sample; (B), (C), (D), (E) ash sample after reaction with $1500 \text{ mg L}^{-1} \text{ Pb}^{2+}$, $150 \text{ mg L}^{-1} \text{ Cd}^{2+}$, Cu^{2+} and Zn^{2+} solution for half hour. Q represented quartz; CA calcite; G gypsum; CE cerrusite (B) using four hour reaction time.

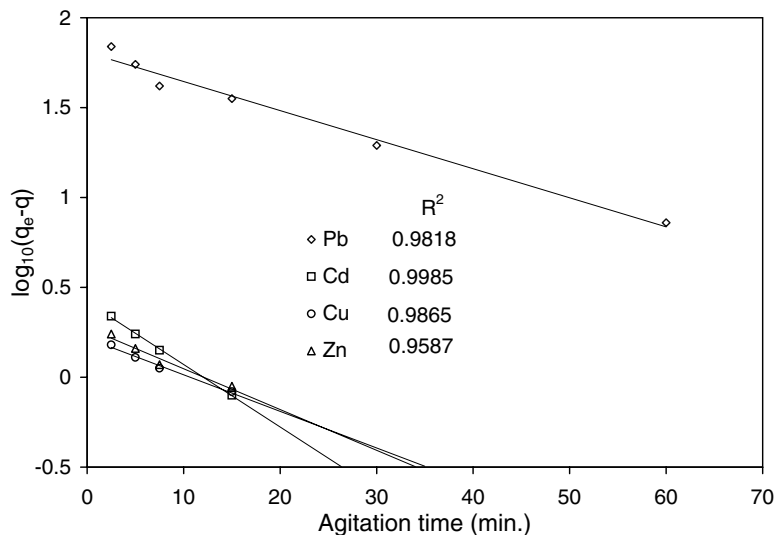


Figure 6. Linear plots of Log ($q_e - q$) vs t for Pb, Cd, Cu and Zn.

of cerussite was at the expense of calcite. Significant amount of Pb in the ash was detected by SEM/EDAX after the ash reacted with 1500 mg L^{-1} Pb for four and a half hours (data not shown).

The kinetics of Pb, Cd, Cu and Zn sorption on the ash followed first order rate equation given by Lagergreen (Namasivayam and Ranganathan, 1993):

$$\text{Log}(q_e - q) = \log q_e - k_{ad}t/2.3 \quad (3)$$

Where, q and q_e are the amounts of metal adsorbed (mg g^{-1}) at time t (min) and at equilibrium time, respectively, and k_{ad} is the sorption constant ($1/\text{min}$). Linear plots of $\text{Log}(q_e - q)$ vs t show the applicability of the above equation for metal sorption by the ash (Figure 6). K_{ad} values calculated from the slopes of the plots were $\text{Pb} (1.61 \times 10^{-2}) < \text{Zn} (2.00 \times 10^{-2}) < \text{Cd} (2.20 \times 10^{-2}) < \text{Cu} (3.43 \times 10^{-2})$ (L/min), which was in the same order as that in Figure 4B. Other parameters that determine the sorption rate, such as agitation (or flow) rate in the aqueous phase, sorbent structural properties, metal ion properties (e.g., hydrated ionic radius), initial concentration of metal ions, and chelate-formation rate (Denizli *et al.*, 1997) may also have played a role in this study and more research is needed to verify these results.

Conclusion

Wood ash is capable of immobilizing Pb, Cd, Cu and Zn effectively from aqueous solutions. Among the four metals studied, the quantity of metals sorbed by the

ash decreased in the order: Pb > Cd > Cu > Zn. The sorption data suggest that sorbent dose is the most important parameter in metal sorption onto the ash. The immobilization process was rapid, nearing completion in 30 minutes. Metal sorption by the ash was probably due to ion exchange between metal ions in the aqueous solutions and Ca²⁺ on the surfaces of calcite and gypsum in the ash, which resulted in the formation of calcite-gypsum-like minerals.

Acknowledgements

We wish to thank Dr. Willie Harris for his assistance in using SEM and XRD.

References

- Alloway, B. J. and Ayres, D. C.: 1993, Chemical principles of environmental pollution. Blackie Academic & Professional, London.
- Baes, C. F. and Mesmer, R. E.: 1976, The hydrolysis of cations. John Wiley & Sons. New York.
- Benjamin, M. M. and Leckie, J. O.: 1981, 'Multiple-site adsorption of Cd, Cu, Zn and Pb on amorphous iron oxyhydroxide.' *J. Coll. Int. Sci.* **79**, 209–221.
- Blanchard C., Manuanyl M. and Martin, G.: 1984, 'Removal of heavy metals from waters by means of natural zeolites.' *Wat. Res.* **18**, 1501–1507,
- Calace, N., Nardi, E., Petronio, B. M. and Pietroletti, M.: 2002, 'Adsorption of phenols by papermill sludges.' *Environ. Pollut.* **118**, 315–319.
- Chowdhurt, A. K., Stanforth, R. R. and Warren, R. S.: 1994, 'In Situ Remediation of Contaminated Soil at a Lead-Acid Battery Cracking Site Using Phosphates', I&EC special symposium, Atlanta, GA, ACS.
- Coughlin, B. R. and Stone, A. T.: 1995, Nonreversible adsorption of divalent metal ions (Mn, Co, Ni, Cu, and Pb) onto goethite: effect of acidification, Fe (II) addition and picolinic acid addition. *Environ. Sci. Technol.* **29**, 2445–55.
- Denizli, A., Salih, B. and Piskin, E.: 1997, 'New sorbents for removal of heavy metal ions: diamine-glow-discharge treated polyhydroxy ethylmethacrylate microspheres.' *J Chromatography A.* **773**, 169–178.
- Ferrero, F. and Prati, M. P. G.: 1986, 'Coal fly ash alginate for the removal of heavy metals from aqueous solutions.' *Annali di Chimica* **86**, 125–132.
- Garcia-Sanchez, A. and Alvarez-Ayuso, E.: 2002, 'Sorption of Zn, Cd, and Cr on calcite. Application to purification of industrial wastewaters.' *Min. Engin.* **15**, 539–547.
- Hassett, D. J. and Eylands, K. E.: 1999, 'Mercury capture on coal combustion fly ash.' *Fuel* **78**, 243–248.
- Holm, T. R. and Zhu, X.: 1994, 'Sorption by kaolinite of Cd²⁺, Pb²⁺ and Cu²⁺ from landfill leachate-contaminated groundwater.' *J. Contam. Hydrol.* **16**, 271–287.
- Jain, C. K. and Ram, D.: 1997, 'Adsorption of lead and zinc on bed sediments of the river kali.' *Wat. Res.* **31**(1), 154–162.
- Kinniburgh, D. G. 1986, 'General purpose adsorption isotherms.' *Environ. Sci. Technol.* **20**, 895–904.
- Ma, L. Q., Komar, K., Tu, C., Zhang, W., Cai Y. and Kennelly, E.: 2001, 'A fern that hyperaccumulates arsenic: A hardy, versatile fast-growing plant helps remove arsenic from contaminated areas.' *Nature* **409**, 579.
- Ma, Q. Y., Traina, S. J., Logan, T. J. and Ryan, J. A.: 1993, 'In situ Pb immobilization by apatite.' *Environ. Sci. Technol.* **27**, 1803–1810.

- Ma, Q. Y., Logan, T. J., Traina, S. J.: 1995, 'Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks.' *Environ. Sci. Technol.* **29**, 1118–1126.
- McBride, M. B.: 1994, 'Environmental Chemistry of Soils,' Oxford University Press: Oxford.
- McBride, M. B.: 1979, 'Chemisorption of cadmium on calcite surface.' *Soil Sci. Soc. Am. J.* **44**:26–28.
- McConnell, D.: 1973, 'In. V. Herausgegeben (ed.) Applied Mineralogy. Apatite: its crystal chemistry, mineralogy, utilization, and geologic and biologic occurrences.' New York, Springer-Verlag.
- McGinnis, G.: 1995, 'Wood ash in the Great lakes region: Production, characterization and regulation.' Great lakes Regional Biomass Energy Program, Michigan.
- Moller, P. and Sastri, C. S.: 1973, 'Exchange studies on single crystals of calcite using ^{45}Ca as the tracer.' *Inorg. Nucl. Chem. Lett.* **9**, 759–763.
- Morse, J. W.: 1986, 'The surface chemistry of calcium carbonate minerals in natural waters: An overview.' *Mar. Chem.* **20**, 91–112.
- Namasivayam, C. and Kadiruelli, K.: 1997, 'Agricultural solid wastes for the removal of heavy metals: Adsorption of Cu(II) by coirpith carbon.' *Chemosphere.* **34**(2), 377–399.
- Namasivayam, C. and Ranganathan, K.: 1993, 'Waste Fe(III)/Cr(III) sludge as adsorbent for the removal of Cr(VI) from aqueous solution and chromium plating industry wastewater.' *Environ. Pollution.* **82**, 255–261.
- Periasamy, K. and Namasivayam, C.: 1996, 'Removal of copper (II) by adsorption onto peanut hull carbon from water and copper plating industry wastewater.' *Chemosphere.* **32**, 769–789.
- Rao, M., Parwate, A. V. and Bhole, A. G.: 2002, 'Removal of Cr and Ni from aqueous solution using bagasse and fly ash.' *Waste Manage.* **22**, 821–830.
- Roy, W. R.: 1993, 'Sorption of cadmium and lead by clays from municipal incinerator ash-water suspensions.' *J. Environ. Qual.* **22**, 537–43.
- Salt, D. E., Blaylock, M., Kumar, N. P. B. A., Dushenkov, V., Ensley, B. D., Chet, I. and Raskin, I.: 1995, 'Phytoremediation: a novel strategy for the removal of toxic metals from the environment using plants.' *Biotechnology* **13**, 468–474.
- Sims, R., Sorensen, D., Sims, J., McLean, J., Mahmood, R., Dupont, R., Jurinak, J. and Wagner, K.: 1986, 'Contaminated surface soils in-place treatment techniques.' Noyes Publications: Park Ridge.
- Unger, Y. L. and Fernandes, I. J.: 1990, 'Short-term effects of wood-ash amendment on forest soils.' *Water Air Soil. Pollut.* **49**, 315–328.
- United States Environmental Protection Agency (USEPA): 2001, 'Remediation technologies screening matrix, reference guide version 4.' <http://www.frtr.gov/matrix2/section4/4-29.html>
- Van Bladel, R., Halen, H. and Cloos, P.: 1993, 'Calcium-Zinc and Calcium-Cadmium exchange in suspensions of various types of clays.' *Clay Miner.* **28**, 33–38.
- Viraraghavan, T. and Rao, G. A. K.: 1991, 'Removal of cadmium and chromium from wastewater using fly ash.' 45th Purdue University industrial waste conference proceedings, Purdue University, Lewis Publishers, Inc.
- Zachara, J. M., Cowan, C. E. and Resch, C. T.: 1991, 'Sorption of divalent metals on calcite.' *Geochim. Cosm. Acta.* **55**, 1549–1562.
- Zirino, A. and Yamamoto, S.: 1972, 'A pH-dependent model for the chemical speciation of copper, zinc, cadmium and lead in seawater.' *Limnol. Oceanography.* **17**(5), 661–671.