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Solubility of Trace Elements and Heavy Metals from Stabilized Sewage Sludge by Fly Ash

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Abstract Stabilized sewage sludge (SS) by fly ash (FA) and alkaline mine tailing as artificial soil, to be applied on the ecological rehabilitation at mining junkyard, offers a potential viable utilization of the industrial by-product, as well as solves the shortage of soil resource in mine area. In this study, trace element and heavy metal soil solution concentrations arising from fly ash, sewage sludge, mine tailing, and artificial soil mixtures were investigated in a laboratory incubation. It was found that total Cd, Pb, and Zn contents in artificial soils were significantly lower than the control standards for pollutants in sludges from agricultural use (GB 4284-84). Soil solution Cd and Pb concentrations were obviously reduced by mixing sewage sludge with alkaline fly ash. Initial soil solution Cd, Pb, and Zn concentrations in artificial soils were 1.773–14.672, 4.05–24.95, and 133–608 μg L^{-1}, respectively, and after 35-days incubation, soil solution Cd, Pb, and Zn concentrations gradually decreased and were approaching control levels by the end of the experiment, and finial soil solution were decreased to 0.037–0.365, 2.12–7.34, and 29–509 μg L^{-1}, respectively.

Keywords Stabilized sewage sludge · Fly ash · Mine tailing · Trace elements · Solubility

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In China, many abandoned mine lands need revegetation. In these abandoned mine lands revegetation is hindered by the lack of suitable topsoil (Wang and Cai 2006). The use of plowland soil for ecological remediation wastes both manpower and material resources, but also can not solve the soil resource shortage for ecological remediation (Shen et al. 2004).

Fly ash is a byproduct of coal fired power plants, and is composed of particulate matter collected from the flue gas stream. In China, 1.8×10^8 t fly ash (FA) from the generation of electricity was produced each year (Ben and An 2004). Land-filling is the traditional method of disposal of fly ash, however, the dual factors of increased cost and stricter legislation have prompted research into alternative methods of disposal or utilization of this waste material (Abbott et al. 2001; Kriesel et al. 1994). Over the last 25 years, numerous studies on the use of fly ash as a soil amendment have been performed (Adriano et al. 1980). Although benefits associated with the application of FA to soils have been reported, the poor acceptance of agronomic of FA is due to low organic C content, high salinity, and environmental concerns over potentially toxic elements (Carlson and Adriano 1993). Biosolids is a useful source of organic matter, a pool of a slow-release essential nutrients (nitrogen, phosphorus, sulphur and magnesium) and microorganisms. The mixing of an organic waster product such as with fly ash has been proposed to increase the macronutrient content of the resulting mixture while reducing odor and improving handling properties of the organic waste (Jackson and Miller 2000; Belmonte et al. 2006). Field trials utilizing FA/biosolids mixtures as fertilizers for maize produced comparable yields to conventional fertilization techniques. The results of a pot study showed that the coal ash, reservoir sediments and sewage sludge mixed in proper proportions could greatly promote plant growing and increase production (Shen et al. 2004). However, heavy metals content associated with the land application of FA and SS should be investigated. Many researchers have noted an increased availability of trace elements in fly ash-amended soil (Tolle et al. 1983). Adriano et al. (1980) reported that Cadmium uptake in sudangrass resulting from sewage sludge application was reduced in the presence of fly ash, and Cd, Zn, Mn uptake in tall wheat grass were reduced when SS was mixed with fly ash.

Trace metal availability is mostly a function of solubility, soil extractions solution should provide a reasonable technique for assessing whether a trace element is available for plant uptake or leaching. Trace element availability from land application of single FA or sewage sludge is well documented (El-Mogazi et al. 1988; Carlson and Adriano 1993; Gibbs et al. 2006; Belmonte et al. 2006). However, a few attempts were made to investigate trace element availability from land application of FA/SS mixtures and the feasibility of the FA/SS mixtures without natural soil used in the ecological remediation of the dumping site for mullock in China. This study will provide valuable information and data for the application of these artificial soils to mining areas.

Materials and Methods

The mine spoil material (MT) was collected from the Dagushan iron mine (123°03′36.6″E and 41°03′03″N) in Anshan City, Liaoning Province. Fly ash (FA) used in this study was obtained from a Power Plant of Anshan Steel Company and sewage sludge (SS) was from the North Waste Water Treatment Facility located in Haicheng city, China. Fly ash and mine tailing samples were air-dried before mixed with sewage sludge. The basic chemical properties of the fly ash, sewage sludge and mine tailing were determined shown in Table 1.

The sewage sludge used in the experiment was composted in outdoor for several days after collected. When the water content of SS was 55–60%, it was well mixed with dry fly ash and mine tailing. Then the mixture materials were air-dried and ground to pass through a 2-mm sieve. Mixtures of FA/SS were prepared at the ratios of 3:1 (A), 2:1 (B), 1:1 (C) and 0.5:1 (D) respectively; FA/SS/MT were prepared at only one ratio of 2:1:1 (E). All treatments of stabilized SS (or called artificial soil) were listed in Table 2.

One thousand grams of every dry artificial soil sample was placed in a plastic bucket. The details of treatments A, B, C, D, and E are listed in Table 2. Three replicates were designed. All treatments were wet to the moisture of 17% (*W/W*) by adding deionized water and re-wet to this moisture content throughout the incubation period, on the day prior to every soil solution sampling. The plastic buckets were open to the atmosphere (25°C), but were strictly controlled to avoid any leaching. By this approach, the authors minimized the effect of soil loss during sampling, and thus were better able to keep each treatment at an equivalent moisture content for the duration of the study.

The soil solution was periodically extracted (Days 1, 5, 7, 15, 22 and 35) from the incubated treatments, by centrifugation. One hundred grams of moist soil was sampled from each plastic bucket and then was put into a plastic bottle and 10 ml deionized water was added. Although the artificial soil was at 17% moisture content, it was still necessary to add a further 10 ml of deionized water to the soil sample prior to centrifugation, to extract a sufficient volume of the soil solution. Sufficient time was allowed for this added water to percolate into the soil, because the soil was still below field holding capacity and this was a rapid process. The artificial soil was centrifuged at 3,000 r/min for 25 min. After centrifugation, the soil solution in the bottle was filtered (0.22 μm). The solid cake collected on

Table 2 Artificial soils (A–E) of sewage sludge mixed with mine tailing and fly ash in weight proportions

Composition	Treatments				
	A	B	C	D	E
Fly ash	3	2	1	0.5	2
Sewage sludge	1	1	1	1	1
Mine tailing	0	0	0	0	1

Table 1 Basic physicochemical properties of the compositions

Composition	OM (%)	Available N (mg kg^{-1})	Olsen P (mg kg^{-1})	Available K (mg kg^{-1})	pH	Cd (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})
Coal fly ash	2.66	0.55	115.92	169.49	10.88	0.66	38.36	4.75
Sewage sludge	36.69	216.71	324.33	1,531.43	7.65	3.71	362.84	157.04
Mine tailing	0.54	3.15	70.28	312.24	8.71	–	–	–

– Represent undetectable

the filter paper was carefully returned to the corresponding bucket and remixed evenly with the bulk remaining soil.

Aliquots of the filtered soil solution were taken for measurement of the cations of Ca, Mg in the leachates by means of ion chromatography (IC-1010 China). Measurements of pH and Eh were made on a slurried (1:1 soil/H_2O) sub-sample of the incubated soil. Cd, Pb, and Zn contents in artificial soil solutions were analyzed by means of atomic absorption spectrophotometry (AA-6300, Shimadzu, Japan).

SPSS 12.0 statistical package was employed for Statistical analysis. Analysis of variance was used to test for significant differences in trace element solubility in individual treatments and interactive effects of the mixed waste treatments.

Results and Discussion

Mixing of fly ash and alkaline mine tailing with municipal sewage sludge resulted in an increase in soluble Ca and Mg. Treatment D (the ratio of FA to SS was 1:2) exhibited the largest solution Ca concentration (439.67 mg L^{-1}) (Fig. 1), and treatment C (FA:SS = 1:1) exhibited the largest solution Mg concentration (304.56 mg L^{-1}) (Fig. 2) by the end of the incubation. Finial solution Ca concentrations in FA/SS mixtures were much greater than that in both FA-alone and MT-alone treatments.

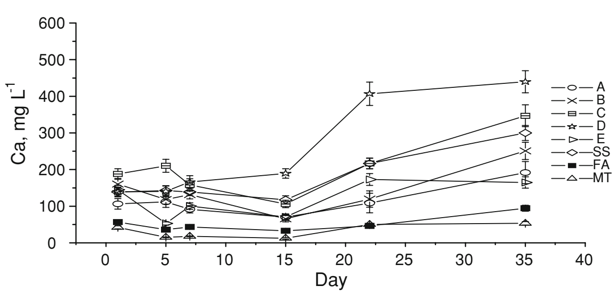

Fig. 1 Solution Ca concentration in artificial soil (*SS* sewage sludge; *FA* fly ash; *MT* mine tailing; *A–E* artificial soil treatments). *Error bars* represent one standard deviation

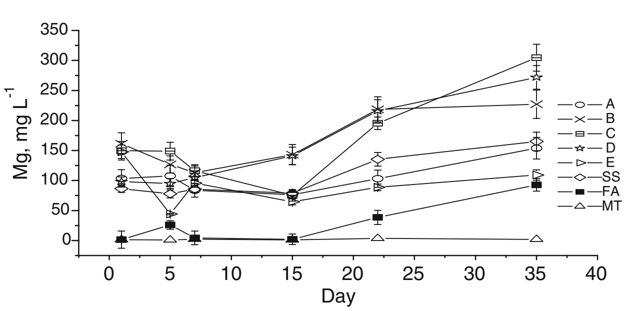

Fig. 2 Solution Mg concentration in artificial soil

Additionally, soluble Ca in artificial soil treatments increased with proportion of FA decreasing in mixtures. Final solution Ca concentration for artificial soil treatments were: D(FA:SS = 1:2) > C(FA:SS = 1:1) > B(FA:SS = 2:1) > A(FA:SS = 3:1); final solution Mg concentration were: C > D>B > A.

The results of this study together with other research shows that mixing fly ash with either poultry litter or sewage sludge could increase soil solution Ca and Mg concentrations and lead to a less dispersive system (Jackson and Miller 2000). During the incubation studies, soil solution Ca and Mg concentrations (Figs. 1, 2) notably improved in a manner similar to that observed for solution EC (Zhang et al. 2007). It is possible that fly ash is composed of fine particles containing silica (SiO_2), magnesium oxides (MgO), calcium oxides (CaO), and small quantities of other oxides (Abbott et al. 2001). When sewage sludge was mixed with fly ash, the neutralization reactions in the mixtures are:

$$CaO + H_2O = Ca(OH)_2 + 2H_2O \quad (1)$$

$$Ca(OH)_2 + 2H^+(soil) = Ca^{2+}(soil) + 2H_2O \quad (2)$$

$$MgO + H_2O = Mg(OH)_2 + 2H_2O \quad (3)$$

$$Mg(OH)_2 + 2H^+(soil) = Mg^{2+}(soil) + 2H_2O. \quad (4)$$

In reactions (1)–(4), two hydrogen ions in the artificial soil were exchanged for one calcium or magnesium (Carlson and Adriano 1993). The increase in the bulk solution concentration of these two cations was closely linked to nitrification processes (nitrification releases H+ into soil solution) and the resultant pH changes in the artificial soil treatments (Zhang et al. 2007). The decrease in pH associated with nitrification increased exchangeable acidity, thus, the variable charge portion of the cation exchange capacity (CEC) of the soil was reduced resulting in increased bulk solution concentrations of Ca and Mg (Van Breemen et al. 1984; Jackson and Miller 2000).

Total Cd contents in artificial soil treatments showed Cd values obviously below the control standard contents that recommended by China Ministry of Agriculture (0103/1984) for agricultural land application of biosolids (GB 4284-84) (Zhang et al. 2007). Results obtained from incubation experiment indicated that soil solution Cd concentrations in all treatments were also low, with the highest Cd concentration (in SS treatment) being only 18.61 μg L^{-1} (Fig. 3). During the incubation, solution Cd concentration for SS treatment gradually decreased and achieved constant after 22 days. However, mixing fly ash with sewage sludge extremely reduced the solubility of Cd in sewage sludge. Initial solution Cd concentrations in mixtures were lower than that in SS treatment. Moreover, in the period of 1–5 days, there was an order of magnitude

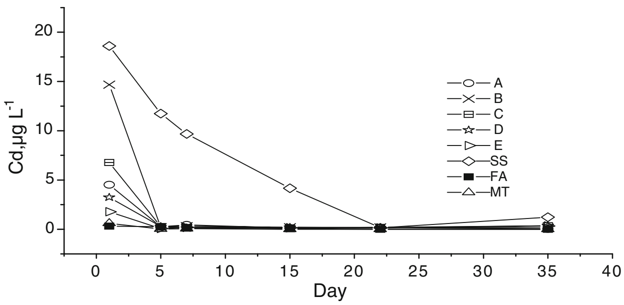

Fig. 3 Solution Cd concentration in artificial soil

decrease in solution Cd concentrations for FA/SS mixtures. It is possible that alkaline fly ash is a ferro–alumin–silicate mineral containing substantial quantities of magnesium oxides (MgO), and calcium oxides (CaO) (Carlson and Adriano 1993; Ben and An 2004). Soluble Cd in sewage sludge may be strongly adsorbed by these oxides under alkaline condition when SS was mixed with fly ash.

Total Pb contents in artificial soil treatments were also much lower than the Control standards for pollutants in sludges from agricultural use (GB 4284-84) (Zhang et al. 2007). Water-soluble metal fractions may be useful in the evaluation of metal mobility since they can identify with confidence the composition of soil solutions (Larsen and Widdowson 2006). The solution Pb concentration was qualitatively similar to Cd solubility over the duration of the incubation study (Fig. 4). Initial concentrations in mixtures were significantly lower than that in SS treatment. In the period of day 1 to day 5, soil solution Pb concentrations were significantly declined to the lowest point. After this, soluble Pb concentrations slightly increased and achieved stable level by the end of the incubation. Final soil solution Pb concentrations in artificial soils were 2.12–7.34 μg L^{-1}. The low artificial soil solution Pb concentrations reflect the general insolubility of this element in soil systems despite the presence of soluble complexing agents (Jackson and Miller 2000).

Zinc is a micronutrient and is needed by plants in small quantities and use as catalyst in numerous biological processes. Excessive quantities of Zn can render biosolids hazardous to human health, plant, and animal life (McGrath and Cunliffe 1985; Gupta and Gupta 1998). In general, soils that contain greater than 300 mg kg^{-1} extractable Zn is considered to be phytotoxic to plants (Levy et al. 1999; Brallier et al. 1996). Previous study showed total Zn contents in artificial soil treatments were extremely lower than the Control Standard (GB 4284-84). The highest content (140.87 mg kg^{-1}) was detected in D treatment (FA:SS = 1:2), while lowest total Zn content (32.26 mg kg^{-1}) was in E treatment (FA:SS:MT = 2:1:1; Zhang et al. 2007). Brallier et al. (1996) and Levy et al. (1999) reported that soils contain >300 mg kg^{-1} extractable Zn is considered to be phytotoxic to plants. Thus, the extractable Zn in artificial soil treatments was much lower than threshold levels that may cause phytotoxicity.

Additional problems related to zinc pollution are changed in the Zn speciation. Larsen and Widdowson (2006) reported that in soil amended with zinc-enriched sewage sludge, an increase was observed of easily available Zn species from 3%–21%. Thus, change of soluble Zn concentration in waste mixtures should be investigated before they were used in mine areas. From the incubation study, it was found that initial solution concentrations of Zn in artificial soil treatments were from 133 to 608 μg L^{-1} (Fig. 5). Soluble Zn in both FA-only and MT-only treatments was extremely low and even undetectable after 5 days incubation. Mixing fly ash with sewage sludge increased the solution Zn concentration compared to FA treatment. In addition, concentrations of soluble Zn increased with the increment of percentage of SS in mixtures. When the ratio of SS to FA was 2:1, solution Zn concentration in D treatment was 100 μg L^{-1} higher than that in SS treatment. During the incubation study, soil solution Zn concentrations for artificial soil treatments slightly decreased and achieved the stable level after 22 days. Results of the pot experiment indicated that FA/SS mixtures contained low solution Zn concentration and would not lead to Zn pollution for the ground water when these mixtures were applied as artificial soil on remediation in mine areas.

Mixing fly ash with sewage sludge increased the solution Ca and Mg concentrations. Total Cd, Pb, and Zn

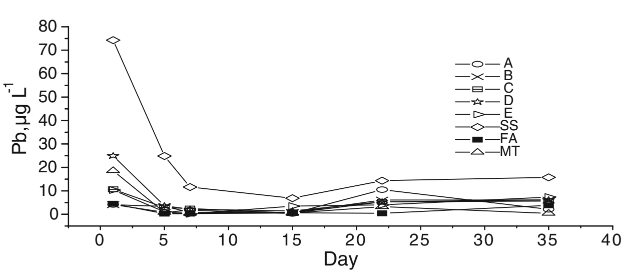

Fig. 4 Solution Pb concentration in artificial soil

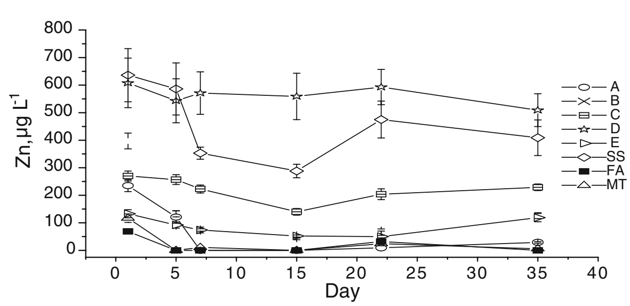

Fig. 5 Solution Zn concentration in artificial soil

contents in artificial soils were significantly lower than the Control standards for pollutants in sludges from agricultural use (GB 4284-84, 1985). The results obtained form incubation experiment suggested that alkaline fly ash stabilized soluble Cd and Pb from sewage sludge. Finial soil solution Cd, Pb, and Zn concentrations in artificial soils were 0.037–0.365, 2.12–7.34, and 29–509 μg L^{-1}, respectively. This indicated that application of these artificial soils composed of fly ash and sewage sludge would not lead to Cd, Pb, and Zn contamination and could be used for ecological reconstruction in mining areas.

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