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Effects and optimization of initial pH and sewage sludge compost content on leaching of lead and zinc in contaminated soil

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Abstract−We investigated the effects of initial pH ($2 \le pH_0 \le 6$) and sewage sludge compost content ($5 \le [SSC] \le 25$ g/kg) on leaching characteristics of lead (Pb) and zinc (Zn) in contaminated field soil. pH_0 and [SSC] significantly affected the leaching of Pb and Zn in soils contaminated with them. The pH in the solution increased as reaction time and [SSC] increased. The leached amounts of Pb and Zn were highest at $pH_0=2$ and increased with reaction time. As [SSC] increased, the leached amount of Pb decreased (50.4 mg/kg at control condition ([SSC]=0 g/kg); 22.9 mg/kg at [SSC]=25 g/kg at $pH_0=2$) and the leached amount of Zn increased (20.1 mg/kg at [SSC]=0 g/kg; 31.7 mg/kg at [SSC]=25 g/kg at $pH_0=2$). The change increased as pH_0 decreased. Within the design boundaries, minimum leaching of Pb (14.7 mg/kg) occurred at $pH_0=5.1$ and [SSC]=25 g/kg, and minimum leaching of Zn (5.0 mg/kg) occurred at $pH_0=5.1$ and [SSC]=5 g/kg.

Keywords: Biosolids, Heavy Metals, Optimization, Pb, Zn

INTRODUCTION

Contamination of soils by heavy metals is a common problem worldwide [1]. Mining and smelting of lead (Pb) and zinc (Zn) ores have resulted in extensive metal contamination of the hillsides and waterways near those operations [2]. Commonly-applied and emerging cost-effective soil amendments for immobilization of heavy metals include biosolids such as sewage sludge compost (SSC) [3].

Sewage sludge is concentrated wastewater composed of municipal liquid wastes after treatment. It is an inevitable by-product of wastewater treatment processes [4]. Methods to treat or dispose of the ultimate product of the sludge include using it as a soil conditioner or fertilizer [5,6]. Compost has great potential to retain trace elements in non-available forms due to several processes, including raising soil pH, complexation, precipitation, or a combination of them, thereby potentially reducing their overall bioavailability and toxicity and thus providing effective stabilization [7,8]. When SSC is applied to contaminated soil as a soil stabilizer, not only are the properties of the soil improved, but also the mobility of heavy metals in the mixtures, which is associated with the characteristics of the matrix, may be affected [5]. However, due to the nature and source of the sludge, it often contains pollutants such as heavy metals. The potential that heavy metals may leach from the sludge solids during soil application presents a major environmental concern [5]. Therefore, regulations have been introduced in many countries to impose strict limitations on the application of SSC [9]. SSC can be used to adjust soil pH and organic matter content to favor the sorption of heavy metals in a relatively stable form [10].

Organic matter is one of factors responsible for the mobility of heavy metals. When SSC is added to a soil, its carbon and nutrient contents increase. However, the binding of heavy metals is not very strong, and is highly dependent on pH [11]. Therefore, pH is one of the key parameters that determines the mobility of heavy metals in soils, sludge, and compost [12]. Leaching of heavy metals from soils due to acid rain percolation is a concern in many parts of the world, such as near mining areas. The pH of the rain varies depending on the location, but it can vary from highly acidic to neutral [1].

SSC utilization to remediate a contaminated soil is a promising approach because the increasing quantities of sewage sludge produced make its disposal a problem. pH is one of the key parameters that affects mobilization and retention of heavy metals in soils and waste materials [13]. Here, we present an experimental study to determine the effect of initial pH (pH_0) and SSC content ([SSC]) on leaching of Pb and Zn from the contaminated field soil and optimize the operating parameters to minimize the release of heavy metals. We focused on these metals because they showed higher concentrations than any other metals in the contaminated soil tested.

MATERIALS AND METHOD

1. Materials

Contaminated field soil was collected from an agricultural area located about 200 km southeast of Seoul, Korea. This area is affected by an abandoned Au-Ag-Pb-Zn mine [14] that has become a main source of toxic metals such as Pb and Zn, because huge amounts of tailings were left without countermeasures on a slope [15]. Sewage sludge and SSC were obtained from a municipal wastewater treatment plant in Mungyeong, South Korea. Collected soil and SSC were air-dried, and then ground to pass through a 2-mm sieve.

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2. Leaching Test

Batch leaching tests were conducted in a shaking incubator (25 °C, 150 rpm). Each sample consisted of 10 g of sieved soil/SSC mixture and 100 mL of HNO_3 solution in a 250-mL Erlenmeyer flask [17]. Samples were taken at reaction times of 0.5, 1, 3, 6, 12, 24, 48, and 72 h [12]; pH was not regulated during the tests.

3. Experimental Design for Response Surface Analysis

Response surface analysis (RSA) was used to evaluate the relative significance of pH_0 and [SSC], and to determine the conditions under which leaching of Pb and Zn is minimum within the experimental range of the pH_0 and [SSC]. We used central composite design that consisted of a 2×2 (pH_0×[SSC]) orthogonal design augmented by five replicates at the center point. A sequential procedure of collecting data, estimating polynomials, and verifying the adequacy of the model was used. Least squares regression was used to estimate the parameters of the response surface.

Initial conditions were based on realistic environment parameters. The pH of rain varies from 2 to 7 [1], so we used $2 \leq pH_0 \leq 6$. In Korea the maximum application of SSC is 4 tons per 1,000 m^2 per year [9], and the average thickness of the plow layer is 15 cm [16]; assuming that the soil weighs 1 ton/m^3, this disposal rate is 26.7 g/kg. Therefore, we used 5≤SSC≤25 g/kg. Conditions at the center point were pH_0=4 and [SSC]=15 g/kg. Observations at the center point were replicated to estimate the experimental error. Data at reaction time of 72 h were used for RSA.

4. Analytical Methods

pH was determined in extracts (1 g sample : 5 mL water) by using a pH electrode (Istek, Inc., Model 735P, Korea). Moisture content of samples was determined by difference after drying to constant weight at 105 °C in a hot-air oven. Organic matter or volatile solid (VS) content was determined by difference after combustion in a muffle furnace at 550 °C for 2 h. Total nitrogen was determined by using the Macro-Kjeldahl method [18]. Phosphorus pentoxide (P_2O_5) was measured in dried samples (1 g) after mineralization using 10 ml of a mixture of 60% $HClO_4$ (9 mL) and 98% H_2SO_4 (1 mL). Phosphorus was measured colorimetrically using ultraviolet-visible spectrophotometer (T-60, Sunileyela) at 470 nm.

Concentrations of heavy metals (Pb, Zn, Cu, Mn, Cr, Fe, Cd, and Ni) were determined using 0.5 g of sample digested for 5 min at 175 °C using 10 mL of 70% HNO_3 solution in a microwave accelerated reaction system (CEM, USA) equipped with temperature and pressure sensors within the cavity and a turntable with pressure-sealed vessels (Omni) of 100 mL each [19]. The heavy metals in the digested samples were analyzed using atomic absorption spectrophotometry (Analytik Jena AA300) in an air-acetylene flame.

RESULTS AND DISCUSSION

1. Physicochemical Properties of Contaminated Field Soil, Dewatered Sludge, and Sewage Sludge Compost

The contaminated soil was a sandy loam (15.4±3.1% clay, 35.9±4.9% silt, and 48.7±1.9% sand). It was moderately acidic (pH 5.4±0.1), and contained 4.0±0.4% organic matter, 1,571.4±160.0 mg Pb/kg, and 443.0±2.8 mg Zn/kg (Table 1). The dewatered sewage sludge was alkaline (pH 8.1±0.1), and contained 80.7±0.7% VS (dry basis), 23.7±0.1 mg Pb/kg, and 603.0±0.1 mg Zn/kg (Table 1). The SSC had pH 6.6±0.1, 59.9±0.1% VS (dry basis), 35.3±0.1 mg Pb/kg, and 786.9±0.1 mg Zn/kg.

The contaminated soil was more acidic than the SSC, so increasing the fraction of SSC could decrease the acidity of the water slurry of soil (Table 1) [5]. The VS in the SSC was 15 times higher than organic matter in the soil. Zn was the most abundant element in the dewatered sludge and SSC. Zn content was higher in the sludge than in the contaminated soil. P_2O_5 was 4.4 times higher in the SSC (2,676.3 mg/kg) than in the contaminated soil (600.3 mg/kg). The sewage sludge in this study had high content of Cr,

Table 1. Physicochemical properties of contaminated field soil, sewage sludge, and sewage sludge compost

Characteristic			Material		
			Contaminated field soil	Sewage sludge	Sewage sludge compost
pH			5.4±0.1	8.1±0.1	6.6±0.1
Total nitrogen (%)			1.2±0.1	3.2±0.1	3.1±0.1
P_2O_5 (mg/kg)			600.3±5.6	2,368.7±9.5	2,676.3±17.4
Proximate (%)	Water		-	81.2±0.1	26.8±0.6
	Volatile solid	Wet basis	-	15.1±0.2	43.8±0.3
		Dry basis	-	80.7±0.7	59.9±0.1
	Ash		-	3.6±0.1	40.1±0.1
Total heavy metal (mg/kg)		As	N.D.[a]	N.D.	N.D.
		Cd	0.9±0.4	N.D.	N.D.
		Cr	9.1±0.3	126.3±0.1	242.3±0.1
		Cu	63.0±0.9	264.5±0.1	605.6±0.5
		Hg	0.2±0.1	N.D.	N.D.
		Ni	59.6±0.8	21.1±0.1	26.3±0.1
		Pb	1,571.4±160.0	23.7±0.1	35.3±0.1
		Zn	443.0±2.8	603.0±0.1	786.9±0.1

[a]N.D.: not detected

Cu, and Zn but relatively lower content of As, Cd, Hg, Ni, and Pb [20]. The pH of the sludge favors sorption of the heavy metals in a relatively stable form, and its organic matter content changes the soil's chemical parameters [10].

2. Effects of pH and Sewage Sludge Compost Content on Leaching Behavior in Contaminated Soil

2-1. pH

The final pH (pH_{72}) in each solution after 72 h of reaction time increased with [SSC] as a result of the high pH (6.6±0.1) of the SSC (Fig. 1 and Table 1). At pH_0=2, pH_{72} increased to 3.2 at control condition ([SSC]=0 g/kg), 3.5 at [SSC]=5, 3.6 at [SSC]=15, and 4.5 at [SSC]=25 g/kg (Fig. 1). At pH_0=4, pH_{72} increased to 5.8 at [SSC]=0, 6.2 at [SSC]=5, 6.4 at [SSC]=15, and 6.7 at [SSC]=25 g/kg. At pH_0=6, pH_{72} were similar to those at pH_0=4. Because buffering capacity increased with [SSC], the time required to increase pH decreased as [SSC] increased [21]. Metal leachability decreases

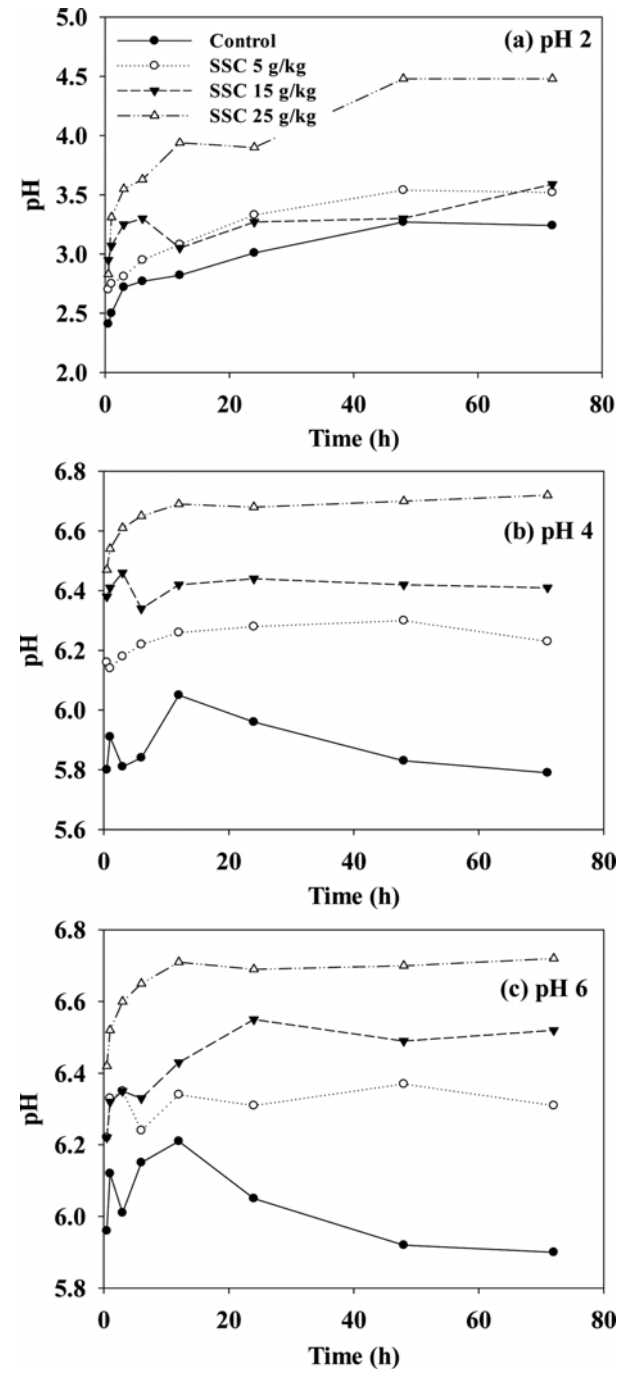

Fig. 1. Time-dependent pH changes in reaction solutions of pH 2 (a), 4 (b), and 6 (c) with sewage sludge compost content of 0, 5, 15, and 25 g/kg.

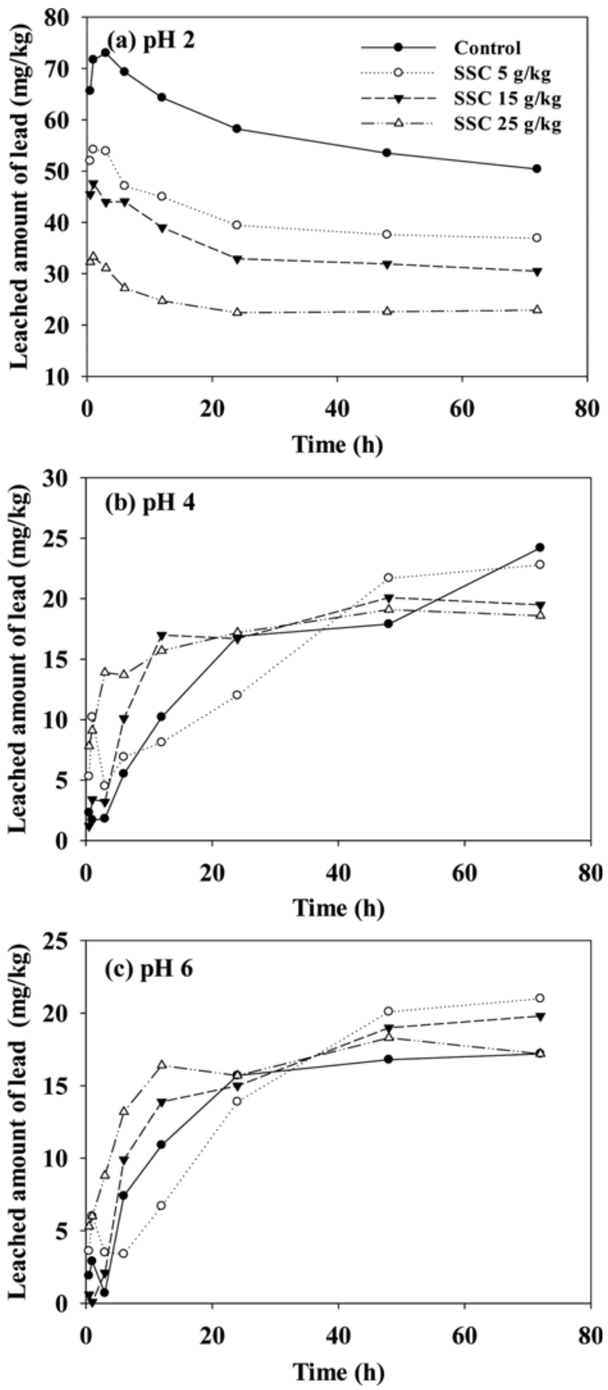

Fig. 2. Time-dependent lead leaching in reaction solutions of pH 2 (a), 4 (b), and 6 (c) with sewage sludge compost content of 0, 5, 15, and 25 g/kg.

as pH increases [21,22], so the increase in pH in the presence of SSC might retard metal leaching.

At all values of pH_0, solution pH increased rapidly during the first 0.5 h of reaction time, and then generally increased slowly after 1 h (Fig. 1). pH_{72} depended on pH_0 and [SSC]. At pH_0=2, pH_{72} increased from 3.2 at [SSC]=0 to 4.5 [SSC]=25 g/kg. In contrast, at pH_0=4 and 6, pH_{72} was 5.8-6.7 regardless of [SSC]; i.e., the initial acidity of the solutions was neutralized by the high pH of the SSC.

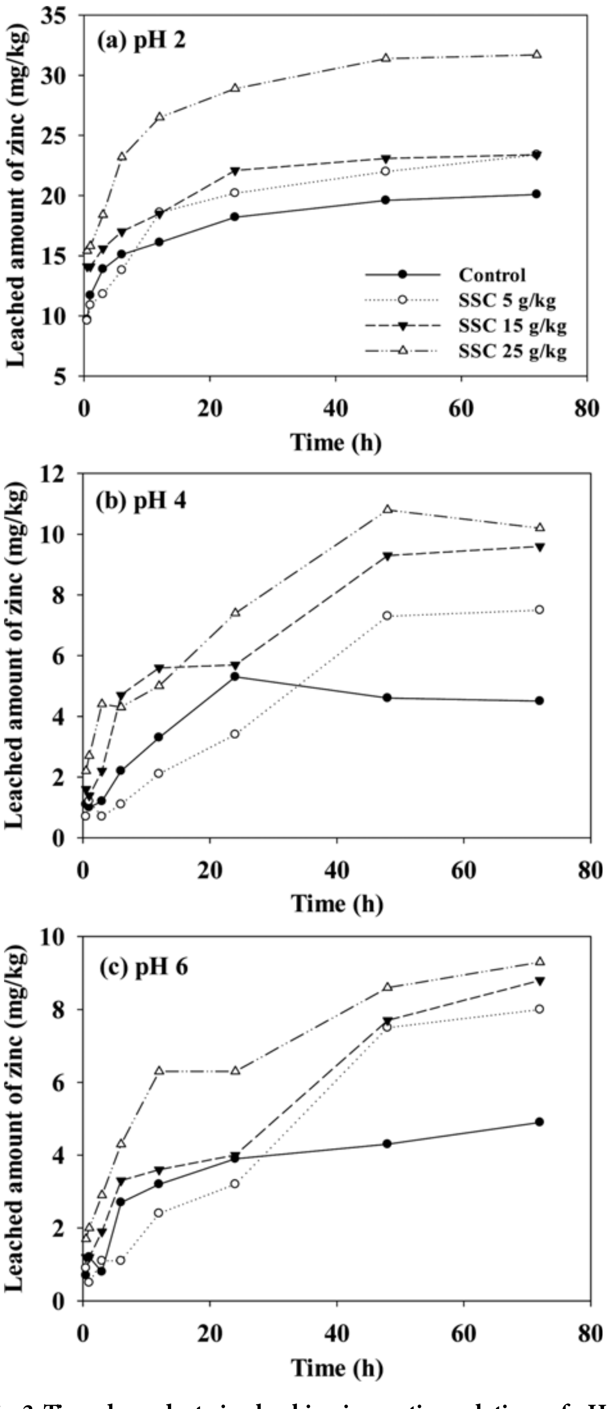

Fig. 3. Time-dependent zinc leaching in reaction solutions of pH 2 (a), 4 (b), and 6 (c) with sewage sludge compost content of 0, 5, 15, and 25 g/kg.

2-2. Lead Leaching

Pb leachability generally decreased as [SSC] increased (Fig. 2). This relationship might be caused by the high organic matter content or by P_2O_5 (Table 1), which is insoluble at acidic pH and that provides sorption sites for Pb [11,23]. The highest leachability of Pb (50.4 mg/kg) was observed at [SSC]=0 g/kg in the solution with pH_0=2 [1]. The increase in mobility of cationic metals as pH decreases is the result of dissolution of metal-hydroxides, -oxides, -carbonates, or -phosphates, and to diminished adsorption at cation exchange surfaces [13].

The leaching behavior of Pb depended on pH_0. At pH_0=2, the maximum occurred within 1 to 3 h of reaction, and decreased thereafter (22.9-36.9 mg/kg after 72 h). At pH_0=4 and 6, the amount of Pb leached increased with reaction time (18.6-24.2 and 17.2-21.0 mg/kg after 72 h, respectively), and changed only marginally regardless of [SSC]. Finally, the amount of Pb leached reached a quasi-steady state at all pH_0 and [SSC]. Several studies also reported that moderate leaching of heavy metals around the neutral pH-range and increased leaching at low pH are pH-dependent leaching trends [13,23].

SSC shows higher remediation potential for Pb than for Zn [7]. Compared with many other heavy metals the mobility of Pb in soils is the lowest [5]. Pb has the highest affinity for organic matter, but its stability in soils generally decreases as pH decreases [8,24]. In the present study, SSC might participate in reducing in metal concentrations by increasing the soil's organic matter content [24]. Also, phosphate-rich compounds (Table 1) applied to Pb-contaminated soils can form pyromorphite-type minerals ($Pb_5(PO_4)_3X$; X=F, Cl, B, or OH) and thereby effectively limit Pb availability [2,24-26].

2-3. Zinc Leaching

Zn leachability generally increased as [SSC] increased (Fig. 3). At all pH_0 the leached amount of Zn generally reached a quasi-steady state with no significant further increase regardless of [SSC]. The leached Zn amount (20.1-31.7 mg/kg in 72 h) was highest at pH_0=2 in this study [11] and the highest leachability of Zn was observed at [SSC]=25 g/kg. pH also significantly affected

Table 2. Experimental design and observed amount of leached lead and zinc

Trial	Independent variables		Observed leached amount (mg/kg)	
	Initial pH	Sewage sludge compost (g/kg)	Lead	Zinc
1	2	5	36.9	23.4
2	6	5	21.0	8.0
3	2	25	22.9	31.7
4	6	25	17.2	9.3
5[a]	4	15	19.5±3.0	9.6±1.8
6	2	15	30.5	23.4
7	6	15	19.8	8.8
8	4	5	22.8	7.5
9	4	25	18.6	10.2

[a]Center point was replicated five times (average±standard deviation)

leaching of Zn in a various soil-SSC mixture [5]. This result is also explained by the general increased mobilization of elements at low pH [13]. Zn can precipitate with anions like phosphates, and can form complexes with organic ligands [26]. Cation exchange and complexation by organic ligands may be the main factors that control Zn mobility in acidic soils [26]. However, Zn is rather mobile and is easily out-competed for adsorption sites by other cations like Pb, Cr, Cu, and Ni [7,8,26]. In dewatered sludge and SSC, Zn has higher exchangeable, reducible, and oxidizable fractions than does Pb [27]. The presence of one contaminant (e.g., Pb) might decrease the stabilization efficiency of the other (e.g., Zn) due to competition for sorption sites (Figs. 2(a) and 3(a)).

3. Optimization for Minimal Leaching of Heavy Metals

For both metals, nine trials including the center point (Table 2, Trials 1-5) were run first to test the adequacy of a first-order model describing the response surface of leaching. The first-order regression had a poor r^2; i.e., was not adequate to approximate either metal. To test higher-order models, four augmentation points (Table 2, Trials 6-9) were run and the results were included in the analysis. Increasingly-complex polynomials from linear to quadratic were tested to model the augmented data set. The adequacy of each model was assessed based on the r^2, regression p-value, and lack-of-fit (LOF) and the simplest model of best fit was used to describe the response surface of leached metal (mg/kg soil).

For Pb, the model was:

$$\text{Leached Pb}=55.60-12.44\text{pH}_i-0.37[\text{SSC}]+1.22\text{pH}_i^2 \quad (r^2=0.82,\ p<0.01) \tag{1}$$

This equation's LOF was not significant ($p>0.05$). Plots of residuals showed small variance with no pattern or trend (data not presented); thus the variances were random and homogeneous [28]. pH_0 ($p=0.004$) and [SSC] ($p=0.011$) significantly affected Pb leaching. Pb leaching was more sensitive to changes in pH_0 than to changes in [SSC]. Pb leachability decreased as pH_0 and [SSC] increased. To determine the conditions that minimize the Pb leaching, the partial derivatives of Eq. (1) were set to zero with respect to the independent variables.

For Zn, the model was:

$$\text{Leached Zn}=55.92-20.43\text{pH}_i+0.21\text{SSC}+2.01\text{pH}_i^2$$

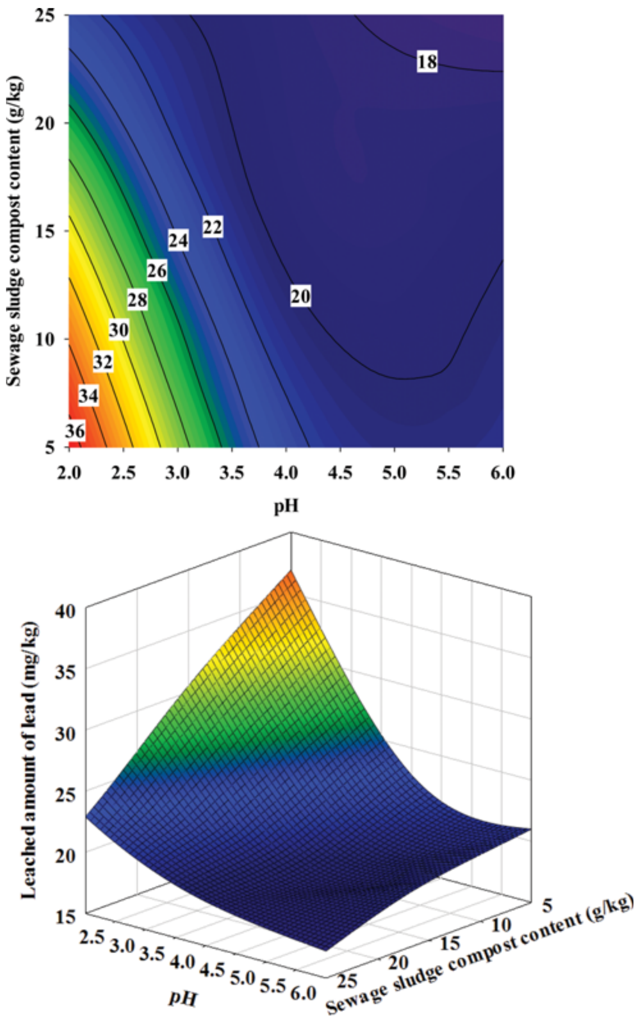

Fig. 4. Two- and three-dimensional contour plots of leached amount of lead with respect to initial pH and sewage sludge compost content within the design boundaries.

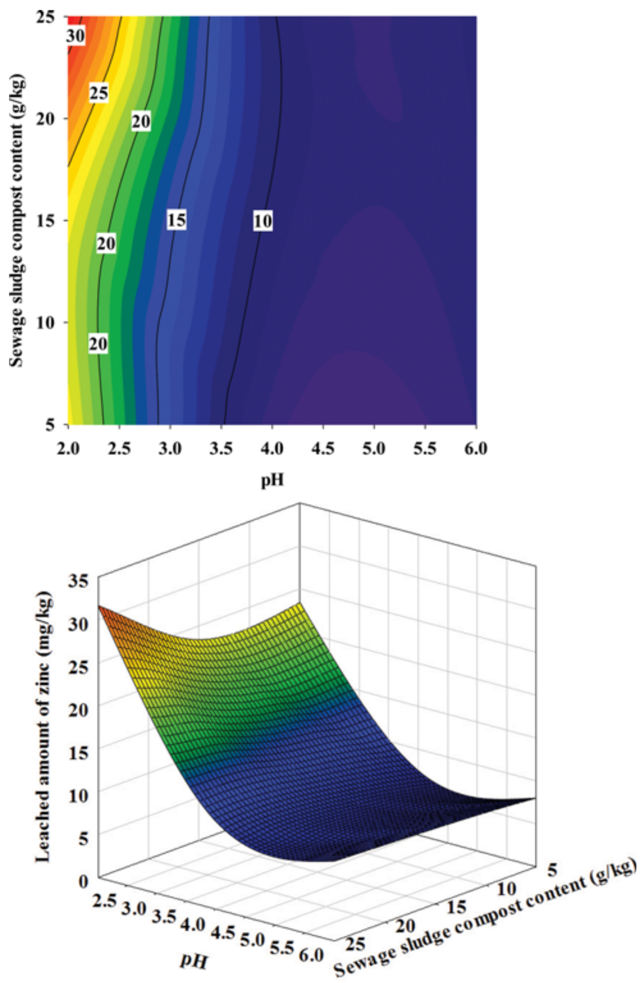

Fig. 5. Two- and three-dimensional contour plots of leached amount of zinc with respect to initial pH and sewage sludge compost content within the design boundaries.

$(r^2=0.95, p<0.0001)$ (2)

This equation's LOF was not significant ($p>0.05$). pH_0 ($p<0.001$) and [SSC] ($p=0.040$) affected Zn leaching significantly. Zn leaching was also more sensitive to changes in pH_0 than to changes in [SSC]. Zn leaching decreased as pH_0 increased and as [SSC] decreased.

The leaching rates of Pb and Zn were minimal at the same pH but at opposite [SSC]. Pb leaching was lowest (14.7 mg/kg) at pH_0=5.1 and [SSC]=25 g/kg (Fig. 4). Zn leaching was lowest (5.0 mg/kg) at pH_0=5.1 and [SSC]=5 g/kg (Fig. 5). The response surface of Zn forms a trough at pH 5.1, so the leaching rate is relatively insensitive to [SSC] at this pH.

CONCLUSIONS

Under strongly acidic conditions (pH_0=2), addition of SSC (5-25 g/kg) to contaminated soil significantly decreased the amount of leached Pb, but increased the amount of leached Zn. RSA determined that pH_0 and [SSC] affected the leached amount of Pb and Zn significantly, and that this leaching was more sensitive to changes in pH_0 than to changes in [SSC]. Within the design boundaries, minimum leaching of Pb (14.7 mg/kg) occurred at pH_0=5.1 and [SSC]=25 g/kg, and minimum leaching of Zn (5.0 mg/kg) occurred at pH_0=5.1 and [SSC]=5 g/kg. These results suggest that SSC is a potentially effective conditioning agent for contaminated soil that contains Pb, in particular at strongly acidic pH.

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