Research Article

Study on the Stabilization of Lead in Soil with Phosphate Rock

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ABSTRACT

This study selected the most representative agricultural soil in Taiwan, prepared the Pb-contaminated soil via manual simulation, and added phosphate rock to the soil, whereby it could be used as a material for restoring Pb-contaminated soil. The objective is to explore the release of Pb in the simulated Pb-contaminated soil washed with various extractants and compare the results. Additionally, this study explores the release of Pb in test soil after appropriate amounts of phosphate rock were added to it.

First, the pH of the test soil, Lp series soil, indicates that it is strongly acidic because its parent material is rich in iron and aluminum oxides. The soil has a greater specific surface area compared to many clay minerals in Taiwan. This study conducted FE-SEM and EDS observation of the surface structure of the Pb-contaminated Lp series soil. The findings show that Al, Si, P, Ca, and Fe in the Lp series soil belong with elements adjacent to Pb. Regarding amounts of Pb released in the simulated Pb-contaminated soil washed with four extractants, the one washed with 0.05 M EDTA contains the highest amount of Pb released in it, i.e., approximately 76.6%; this high-efficient release of Pb may have to do with the complexation of EDTA. As for the release of Pb in the Lp series soil after phosphate rock was added to it, it reduces as the amount of phosphate rock added to it increases. This result suggests that an increase in the pH of the soil affects the stability of lead. In other words, when the pH of the soil solution increases, the stability of Pb in soil increases via ion exchange and complex reaction on soil surface.

Key words: phosphate rock, complexation, extraction, soil restoration

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1. INTRODUCTION

An important factor causing accumulation of heavy metals in many types of soil is finished products containing metals, wastewater, or waste generated as a result of industrial activities. Each industrial activity may produce metal waste [1-3]. Complicated physicochemical reactions occur among heavy metals in the soil system, including dissolution, complex reaction, adsorption, mobility, precipitation, diffusion, evaporation, bonding to organic matter, and absorption or adsorption by microorganisms. Some properties of soil such as pH and redox potential may control the parameters of these reactions [4]. Moreover, heavy metals in soil are highly cumulative and toxic with low mobility. They will not decompose and disappear due to biological effects. Thus, they may hinder crop growth, resulting in a low yield of crops. There may also be deterioration in agricultural product quality due to absorption and accumulation of heavy metals by crops. Human beings or animals consuming agricultural products can then be poisoned. In this case, Cd, Cr, Hg, Pb, and As are the most toxic heavy metals [5,6].

Solubility is a kinetic parameter of thermodynamics, which can be used to determine the content of soluble lead when the system reaches equilibrium. In a kinetic system, concentration levels of soluble lead depend on the formation of solid-phase lead compounds [6,7]. EL Bamiki et al. [8] pointed out in their study that the solubility of phosphate rock is the most important factor in lead removal. Furthermore, characterized by high efficiency and low cost, phosphate rock was deemed to be the source of phosphatic fertilizer in the past, which could effectively reduce the solubility of lead to a lower level. However, reduction degrees depend on the ability of phosphate rock to provide phosphorus to soil solutions. Mar and Okazaki [9] considered that the dissolution of phosphate rock increases the concentration levels of water-soluble calcium, phosphorus, and hydroxide ion. However, the

precipitation of pyromorphite reduces the concentration levels of phosphorus and hydroxide ion. In general, the higher the solubility of phosphate rock, the more significant impact it has on reducing the concentration level of water-soluble lead. The effectiveness of phosphate rock in stabilizing Pb in soil is dominated by the amount of soluble phosphorus. The reaction time and properties of phosphate rock and characteristics of soil itself are also important factors because they can directly affect the solubility of phosphate rock in soil and how phosphate rock reacts with lead in soil [10,11].

Based on the above reasons, this study used continuous extraction to observe changes in the morphological distribution of heavy metals in soil when various amounts of phosphate rock were added to the Pb-contaminated soil. An FM-SEM analysis was performed to determine the main elements accumulated in the Pb-contaminated soil. With these research methods, we could then evaluate the effects of phosphate rock on the restoration of the Pb-contaminated soil and feasibility of such restoration.

2. MATERIALS AND METHODS

2.1 Sources of test soil

This study selects Taiwanese soil (Lopei series soil, Lp series soil) as the sampling soil sample. The sample soil was obtained from Neipu Township in Pingtung County, Taiwan. It is a kind of oxidized diluvium soil containing abundant iron and aluminum oxides and is characterized by fine texture. Its high iron and aluminum oxide content makes it an ideal catalyst carrier. This kind of soil is ideal for planting pineapples.

2.2 Preparing the Pb-contaminated test soil

This study prepared the Pb-contaminated soil by adding lead nitrate solution to the test soil at the ratio of 1:1 (w/v). An appropriate amount of the test soil was air-dried before an equal amount of deionized water was added to it and the mixture well stirred. The Pb-contaminated soil was formed after the mixture was left to stand and air-dried for approximately one month. This study used lead nitrate solution with a concentration of 7000 mg/L.

2.3 Preparing various extractants

This study selected four agents as the extractants for heavy metals. (i) 0.1 M $Ca(NO_3)_2$: 23.62g of $Ca(NO_3)_2 \cdot 3H_2O$ was dissolved using deionized water and the quantity set to 1 L. (ii) 0.05 M EDTA (pH 7.0): 14.61g of EDTA was dissolved using deionized waster, its pH adjusted to 7.0 using acetic acid or ammonia solution, and the quantity set to 1 L. (iii) 0.1 M HCl: 8.3 mL of strong HCl (12M HCl) was added to deionized water and the quantity set to 1 L. (iv) Aqua regia: a mixture of nitric acid and hydrochloric acid at a ratio of 1:3.

2.4 FE-SEM and EDS analyses of the Pb-contaminated soil

Scanning Electron Microscopes (SEMs) are widely applied for various purposes. When combined with an energy dispersive spectrometer (EDS), an SEM can be used for qualitative, quantitative, point, and line analyses, as well as mapping. An SEM was used in this experiment to observe the surface structure changes of受Pb汙染之test soil. An SEM was used in this experiment to observe changes in the surface structure of the Pb-contaminated test soil. An EDS was used to observe the elemental distribution in the kish graphite structure and its properties.

2.5 Application of phosphate rock

This study took 50 g of Lp series soil on six occasions and placed each of them in a 250-mL Erlenmeyer flask, to which 0, 4, 8, 12, 16, and 20 g of phosphate rock powder (imported from Jordan by Taiwan Fertilizer Co., Ltd.) were separately added. Each sample was tested in triplicate before the soil with a field capacity (the amount of water held in the soil) of 23.9% was added to it. The mixture was oscillated for 10 days in a temperature controlled shaker at 25℃, then taken out for subsequent experiments.

2.6 Adsorption reactions in the Pb-contaminated test soil

This study took 5.0 g of Lp series soil and placed it in a centrifuge tube, to which lead nitrate solution (at a solid to liquid ratio of 1:5) with an 8 g/L concentration was added. The mixture was oscillated for 0.5, 1, 2, 4, 8, 12, 24, 36, 48, 60, and 72 h, respectively, in a shaker at 25℃. An analysis of lead concentrations in the mixture was performed after it was filtered using the Gelman Science Type A/E 47 mm filters to obtain the amount of Pb being released when the adsorption reaction in the soil reaches equilibrium [12].

3. RESULTS AND DISCUSSION
3.1 Analysis of oxides of different elements in the composition of Lp series soil
Table 1 shows the results of an analysis of the elemental composition of the Lp series soil. In terms of texture, the Lp series soil only contains 14.6% of sand, but a higher amount (53%) of clay. Its pH (= 4.21) indicates that it is strongly acidic because its parent material is rich in iron and aluminum oxides [13]. The Lp series soil has a specific surface area of 179.13 m^2/g, which is greater than that of many clay minerals in Taiwan. This characteristic suggests that its texture is finer than that of soil in other areas in Taiwan and that it has a higher degree of weathering [14]. This study further explores the cation exchange capacity (CEC) of the Lp series soil. With a CEC of 11.96 cmole/kg, the Lp series soil has a relatively low degree of compaction; its organic matter content is generally less than that of soil in other areas in Taiwan [15].

Table -1 Results of an Analysis on the Basic Properties of the Tk and Lp series soil

soil	Water content %	pH	CO$_3^{2-}$ %	CEC cmole/kg	Specific surface area (m^2/g)	Particle Size (%)			texture	organic matter content %
						sand	silt	clay		
Lp series soil	3.33	4.21	0.63	11.96	179.13	14.6	32.4	53.0	clay	1.28

3.2 FE-SEM and EDS analyses of the Pb-contaminated Lp series soil
Figures 1 and 2 show the use of FE-SEM and EDS to observe the surface structure of the Lp series soil. The analysis results suggest that Al, Si, P, Ca, and Fe in the Lp series soil are elements adjacent to Pb. Moreover, elements such as Ti, Ni, Cu, and Au are also present in the Lp series soil. Adjacent elements refer to elements whose peaks can be observed using the EDS, but their distribution shown in the electron microscope images obtained using x-ray mapping does not necessarily correspond to that of Pb. If the distribution of the adjacent elements fully matches that of Pb, they will be called "associated elements." The electron microscope images shown in Figure 1 indicate Al, Si, P, and Ca as elements associated with Pb, followed by K, Mg, and Fe.
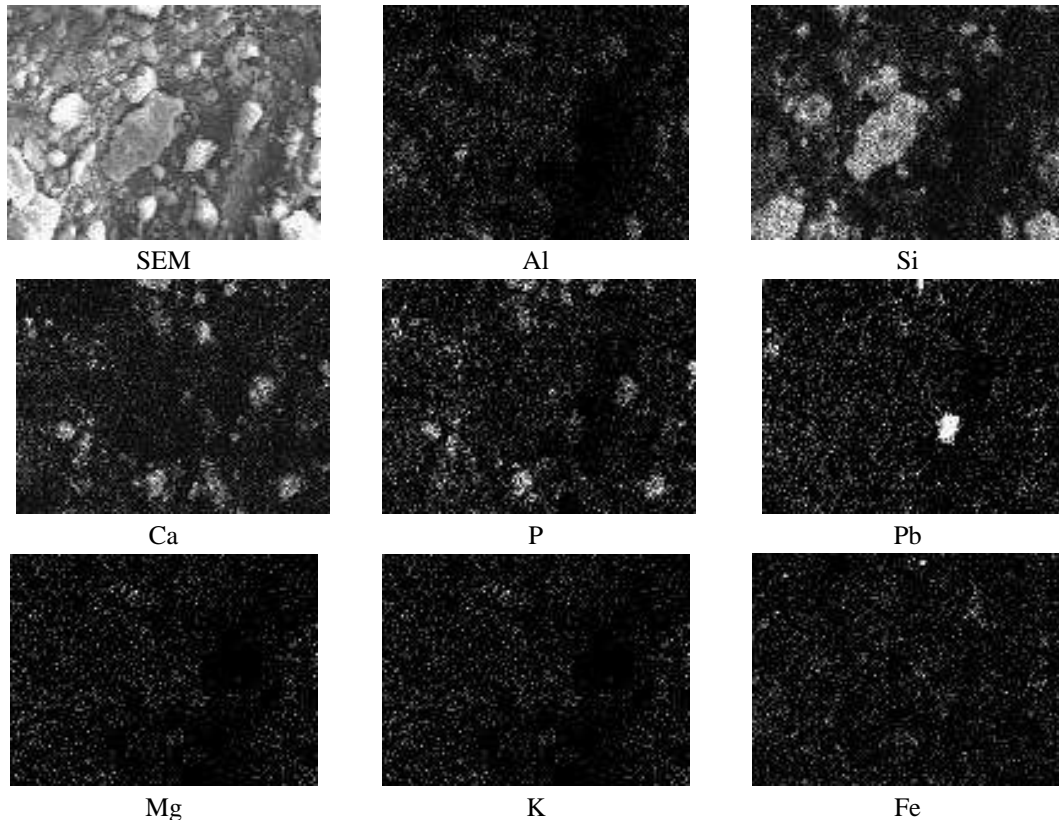

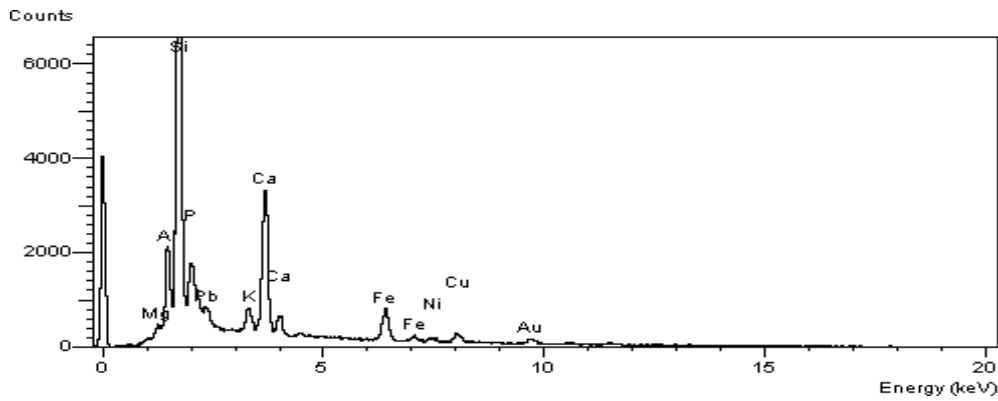*Figure 1: FE-SEM analysis of the Pb-contaminated Lp series soil*

Figure 2: EDS analysis of the Pb-contaminated Lp series soil

3.3 Time required for the adsorption of lead by the test soil to reach equilibrium

The objective of conducting an adsorption kinetic experiment is to find the reaction time needed for reaching adsorption equilibrium. Figure 3 shows the adsorption of Pb by the Lp series soil that varies with time. The result of the adsorption kinetic experiment suggests that the adsorption of Pb by the Lp series soil can reach equilibrium within 24 h, which corroborates those of two respective studies. First, Rajapaksha et al. [16] pointed out that the adsorption of Cu, Cd, and Pb by soil can reach equilibrium within 24 h. Second, Yang et al. [17] considered that the adsorption of Pb by soil can reach equilibrium within 24 h. Thus, 24 h is set as the reaction time needed for reaching equilibrium for subsequent adsorption experiments conducted in this study.
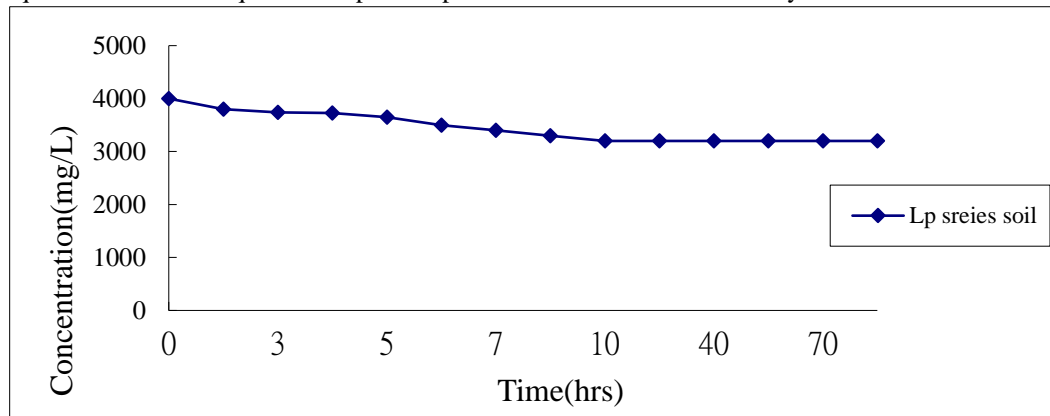

Figure 3: Adsorption of Pb by the test soil that varies with time

3.4 An analysis of the basic properties of phosphate rock

Table 2 shows the results of an analysis of the physicochemical properties of phosphate rock. According to the results, the pH of the phosphate rock indicates that it is moderately alkaline with low organic matter content. The phosphate rock contains 6.6% of carbonate, a concentration lower than carbonate concentrations in soil in other areas in Taiwan. The amount of carbonate is one of the important factors affecting whether the phosphate rock can be dissolved. The solubility of the phosphate rock increases as the amount of carbonate substituting for phosphate in it increases [18,19].

Table -2 An analysis of the basic properties of phosphate rock

Name of element	Concentration
pH (PR:H_2O = 1:1)	7.9
Organic matter	4.92 g/kg
Carbonate as CO_2	6.6%
Total phosphorus (P_2O_5)	24.52%
Citric-acid soluble phosphorus	415 mg/L
Available phosphorus (Olsenˈs sodium bicarbonate method)	13.2 mg/L
Chloride as Cl	0.03% max.
Iron & Aluminium Oxide	1.5% max.
Fluoride as F	3.6% max.
Moisture	3% max.

3.5 A comparison of the amounts of Pb released in the simulated Pb-contaminated soil washed with various extractants

Figure 4 shows a comparison of the amounts of Pb released in the Pb-contaminated test soil washed with various extractants. According to the results, the Pb-contaminated test soil washed with 0.05 M EDTA has the highest amount of Pb released in it. The total amount of Pb released in the test soil is approximately 76.6% (3050/3980 = 0.766), which may have to do with the complexation of EDTA. Lumiste et al. [19] postulated that when EDTA reacts with water-soluble Pb, it can easily exist in the form of a complex: $Pb-EDTA^{2-}$. Thus, a soil solution containing EDTA can increase Pb removal efficiency. In other words, contaminant removal mechanisms are closely related to complexation. Moreover, Steele and Pichtel [20] pointed out that as high as 82% of Pb can be released in soil washed with EDTA, which has little relevance to the concentration level of EDTA itself. In this study, the amount of Pb released in the Pb-contaminated soil washed with 0.1 M HCl is 72.9% (2900/3980=0.729), which may be because that it has a lower pH and enhanced removal capability and ion exchange capacity [21]. The amount of Pb released in the Pb-contaminated soil washed with 0.1 M $Ca(NO_3)_2$ is 65.3% (2599/3980=0.653). Although this amount is not as high as that of Pb released in the Pb-contaminated soil washed with 0.05 M EDTA and 0.1 M HCl, it is considered a high release rate. This result has to do with the ability of carbonate (CO_3^{2-}) to retain more heavy metals in soil, which corroborates that of Shah et al.'s study [22]. They used the Pb-contaminated soil prepared via manual simulation to conduct an experiment on Pb adsorption and perform a morphological analysis of lead. The findings suggest that soil containing CO_3^{2-} can absorb more heavy metals. In other words, when $Ca(NO_3)_2$ is added to soil, Pb will be released from the soil and retained in $Ca(NO_3)_2$.
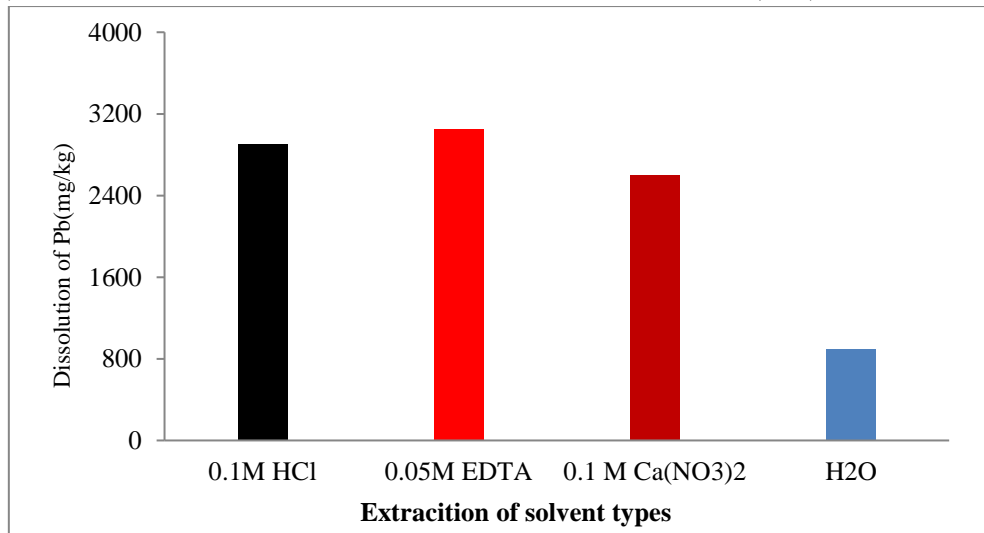

Figure 4: Amounts of Pb released in the Pb-contaminated soil washed with various extractants

3.6 Effects of adding phosphate rock to the Pb-contaminated test soil on the release of Pb in the soil

Table 3 shows a comparison of the results and amounts of Pb released in soil after the four extractants added with phosphate rock react with the Pb-contaminated soil. According to the results, the amount of Pb released in the contaminated soil decreases as that of phosphate rock added to the contaminated soil increases, i.e., they are negatively correlated. The reason for this is that an increase in the pH of the soil affects the stability of lead [13]. To put it another way, when the pH of the soil solution increases, the stability of lead in soil increases via ion exchange and complex reaction on soil surface. This finding corroborates that of Schuffert et al.'s study [23]. They pointed out that the amount of Pb released in soil decreases as that of phosphate rock added to the soil increases. In terms of the amounts of Pb released in soil washed with the four extractants, Table 3 shows that the soil washed with 0.05 M EDTA has the highest amount of Pb released in it after phosphate rock was added to it, followed by that washed with 0.1 M HCl, 0.1 M $Ca(NO_3)_2$, and H_2O. This finding corresponds to that of the experiment conducted in Section 3.5, i.e., the soil washed with 0.05 M EDTA contains the highest amount of Pb released in it. This study added appropriate amounts of phosphate rock to the Pb-contaminated soil, which could increase the amounts of Pb released in the soil. Extractant EDTA can effectively reduce the stability of lead in soil while not damaging the soil structure.

Table -3 Results and amounts of Pb released in soil after various extractants added with phosphate rock react with the Pb-contaminated soil

Amount of phosphate rock added (g)	Amount of Pb released			
	0.1M HCl	0.05M EDTA	0.1M Ca(NO$_3$)$_2$	H$_2$O
0	2610±27 (66)	2907±58 (73)	1975±48 (50)	843±10(2.1)
4	1027±21 (26)	2663±25 (67)	1097±13 (28)	1.1±0.0
8	637±25 (16)	2377±15 (60)	1007±3 (25)	ND
12	260±17 (6.5)	2197±45 (55)	972±8 (24)	ND
16	93±6 (2.3)	2087±42 (52)	908±24 (23)	ND
20	68±20 (1.7)	1913±15 (48)	837±13 (21)	ND

4. CONCLUSION

This study used the most representative agricultural soil in Taiwan, prepared the Pb-contaminated soil via manual simulation, and added phosphate rock to the soil, whereby it could be used as a material for restoring Pb-contaminated soil. It explores the release of Pb in the Pb-contaminated soil washed with various extractants and compares the amounts of Pb released in the soil. The test soil selected for this study was Lp series soil, a soil used for agriculture in southern Taiwan, which only contains 14.6% of sand, but 53.0% of clay. It is thus suitable to be used as a material for restoring soil contaminated by heavy metals. An adsorption kinetic experiment was conducted and its findings suggest that the adsorption of Pb by the Lp series soil can reach equilibrium within 24 h. A comparison of the amounts of Pb released in the Pb-contaminated soil washed with four extractants was made. The results indicate that the Pb-contaminated soil washed with 0.05 M EDTA contains the highest amount of Pb released in it because EDTA can easily exist in the form of a complex: Pb-EDTA^{2-} when it reacts with water-soluble Pb. Thus, a soil solution containing EDTA can increase Pb removal efficiency. Finally, this study added appropriate amounts of phosphate rock to the Pb-contaminated soil, which could increase the amounts of Pb released in the soil. Among the four extractants, EDTA can effectively reduce the stability of Pb in soil while not damaging the soil structure.

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