



# Immobilization of high-Pb contaminated soil by oxalic acid activated incinerated sewage sludge ash<sup>☆</sup>



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## ABSTRACT

Identifying effective and low-cost agents for the remediation of Pb-contaminated soil is of great importance for field-scale applications. In this study, the feasibility of reusing incinerated sewage sludge ash (ISSA), a waste rich in phosphorus, under activation by oxalic acid (OA) for the remediation of high-Pb contaminated soil was investigated. ISSA and OA were mixed at different proportions for the treatment of the high-Pb contaminated soil (5000 mg/kg). The Pb immobilization efficacy was further examined by both the standard deionized water leaching test and the toxicity characteristic leaching procedure (TCLP). The overall results showed that the use of the ISSA alone and an appropriate mixture of the ISSA and OA could effectively reduce the leachability of Pb from soil. 20% ISSA together with 30% OA (0.2 mol/L) reduced leached Pb concentration by 99%. The main stabilization mechanisms were then explored by different microstructural and spectroscopic analytical techniques including SEM, XRD and FTIR. Apparently, OA released phosphate from the ISSA and Pb from soil via acid attack, which combined and precipitated as stable lead phosphate minerals. However, excessive OA could cause high leaching of phosphate and zinc from the ISSA. Overall, this study indicates that ISSA could be used together with OA to remediate high-Pb contaminated soil, but careful design of mix proportions is necessary before practical application to avoid excessive leaching of phosphate and zinc from the ISSA.

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## 1. Introduction

Soil contaminated by lead (Pb) is of great concern because Pb is poison and can accumulate in human body through the food chain threatening the human health (Blanchar, 2001; Igalavithana et al., 2019). In China, the Pb content in approximate 1.5% of soil on the ground surface exceeds the limit set by the authority (Ministry of Environmental Protection, 2014). It was reported that the Pb concentration in the Pearl River Delta exceeded 150 mg/kg, and that Pb

concentration in around  $3.6 \times 10^4$  hm<sup>2</sup> of main farmland soil was over 300 mg/kg exceeding the safe level (Zhang et al., 2019). The severe soil pollution problem, caused by low awareness in environmental protection during industrialization and urbanization, has pressed many local authorities to formulate soil pollution remediation plans to treat Pb-contaminated soil (Zhang et al., 2019).

Stabilization is a method extensively used to remediate Pb-contaminated soil. Generally, a stabilization agent is applied to reduce the solubility, bioavailability and mobility of Pb (Chen et al., 2021; Yin et al., 2006). This method has attracted great attention in both research and field applications due to its low cost, low carbon-footprint, simple operation and high compatibility (Li and Poon, 2017; Wang et al., 2018a). The commonly used stabilization agents include cement, fly ash, blast furnace and steel slag, red mud, phosphate rock, etc (Du et al., 2014; Guo et al., 2021; Liu et al.,

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2018). Particularly, cement-based S/S received tremendous attentions for Pb contaminated soils, sludges, and so on via precipitation, physical and chemical fixation (Guo et al., 2020, 2021; Wang et al., 2020). Nevertheless, the production of cement is regarded as energy-intensive and of high-carbon footprint (Li et al., 2018b). Except from cement, phosphate-based compounds such as phosphate rock and phosphoric acid have been widely investigated and even recommended to immobilize Pb contaminated soil since they have the potential to transform Pb to stable forms such as pyromorphite  $[Pb_5(PO_4)_3(OH, Cl, F \dots)]$  (Cao et al., 2009; Jiang et al., 2012; Li et al., 2016; Palansooriya et al., 2020; Yang et al., 2001; Zeng et al., 2017). It was reported that the application of the phosphate rock to treat Pb-contaminated soil induced the formation of phosphate minerals, which effectively reduced the water solubility, phytoavailability and bioaccessibility of soil Pb (Cao et al., 2009). However, some phosphate rock contains very little phosphate, which limits its stabilization efficacy (Zhang et al., 2018). Phosphoric acid, together with KCl acting as a chloride ion donor could reduce the solubility and bioaccessibility of Pb in highly contaminated soil (Pb content > 4000 mg/kg) due to the formation of a compound similar to chloropyromorphite (Yang et al., 2001). Generally, an effective immobilization of Pb using phosphate-based compounds requires an acidic environment to increase the solubility of both the phosphate phase and the Pb related phase (Su et al., 2015). A plenty of studies showed that the combined use of acid and phosphate-based compounds were effective in reducing the solubility of Pb in soil. Zhang et al. (2018) reported that the oxalic acid (OA) activated phosphate rock became more effective in transforming Pb in soil from the non-residual fraction to the residual fraction thus enhancing the stabilization efficiency of the rock. A phosphate-binder (comprising OA-activated phosphate rock, monopotassium phosphate and reactive magnesia) could effectively reduce the leachability of Pb from the polluted soil due to the formation of stable Pb-related precipitates such as fluoropyromorphite  $(Pb_5(PO_4)_3F)$  as revealed by XRD analysis (Du et al., 2014).

Similar to phosphate rocks, incinerated sewage sludge ash (ISSA), a by-product from the incineration of sewage sludge, was found to be able to remove heavy metals especially Pb from aqueous solutions (Pan et al., 2003; Wang et al., 2019a, 2019b). One of the main mechanisms of Pb removal by ISSA was the precipitation of pyromorphite under acidic environment (Wang et al., 2019a). In addition, ISSA, with some pozzolanic reactivity could immobilize Pb in soil with the combined use of Portland cement (Li and Poon, 2017), and heavy metals in marine sediments with the addition of lime (Li et al., 2019; Zhou et al., 2019). The application of ISSA has been recognized as a cost-effective means for immobilization of Pb in soil. The effectiveness may be enhanced if phosphate could be released from ISSA, which could then combine with Pb to form stable lead phosphate precipitates. Du et al. (2014) presented a new binder, KMP, composed of oxalic acid-activated phosphate rock, which was confirmed to be effective in stabilization of Pb/Zn contaminated soils due to the formation of phosphate-based products. Nevertheless, studies on stabilizing heavy metal contaminated soils with ISSA are limited. Based on this concept, it was believed that the combined use of ISSA with acid could achieve

a higher Pb stabilization efficacy compared with ISSA alone. It was already known that acids including sulphuric acid, phosphoric acid, OA and others could release phosphate from ISSA (Fang et al., 2020). OA was selected in this study because of its phosphate extraction effectiveness, ability to chelate metals and friendliness to the environment (Debela et al., 2013; Fang et al., 2018a; Jiang et al., 2012; Su et al., 2015). In addition, potential adverse effects induced from phosphate and the likelihood of introduction of toxic elements to the soil were considered low with the use of OA (Zeng et al., 2017).

The aim of this study was to investigate the feasibility of combined use of ISSA and OA for effective remediation of high-Pb contaminated soil. The specific targets include a) optimizing the mix design for effective immobilization of Pb in soil, b) identifying the immobilization mechanisms, and c) evaluating potential environmental risks through a series of laboratory experiments.

## 2. Materials and methods

### 2.1. Materials

The soil used was a silty clay obtained locally in Hong Kong. The soil was composed of 13% sand, 62% silt, and 25% clay size fractions on a dry mass basis (determined by wet sieving and hydrometer tests). The soil sample was dried, ground and then sieved through a 2 mm sieve before used in tests. The chemical compositions of the soil determined by X-ray fluorescence analysis (XRF, Rigaku Supermini, 2000) are shown in Table 1. The as-received soil had a pH of 7.34 (1:5 dry soil: DI Water). According to the regulations in Hong Kong, the Pb concentration in the collected soil did not exceed the threshold (258, 255, 229 & 857 mg/kg for urban residential, rural residential, industrial, and public parks respectively) for remediation works (EPD, 2007). The soil was therefore spiked by adding a prescribed amount of  $Pb(NO_3)_2$  solutions to get a high-Pb contamination level (5000 mg/kg) according to the classification given in the Guidance Manual for Use of Risk-Based Remediation Goals (RBRGs) for Contaminated Land Management (EPD, 2007). The spiked soil was braised for 10 days ( $23 \pm 2$  °C, 95% humidity) to allow  $Pb(NO_3)_2$  and the soil to react adequately (Li and Poon, 2017).

The ISSA was collected from the modern sewage sludge incineration plant operated in Hong Kong. The chemical compositions of the ISSA are also shown in Table 1. The ISSA contained some heavy metals but it could be classified as a non-hazardous solid waste due to the low leaching potential of these metals from ISSA as confirmed from the Toxicity characteristic leaching procedure (TCLP) (Li et al., 2017).

To increase the stabilization efficacy, different methods for pre-treatment of the ISSA, including ball milling and acid washing, were adopted. Batch adsorption experiments were conducted to evaluate the effects of pre-treatment methods on the ability of the ISSA to remove Pb and to explore the potential removal mechanisms. The as-received, ball milled and acid washed ISSA were denoted as Coarse, Fine and Residual ISSA. The specific experiment methodology is shown in Supplementary Information Text S1.

**Table 1**  
Chemical compositions of the soil and ISSA.

Oxides (%)	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	SO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CuO	ZnO	PbO	Others
Soil	2.93	0.2	35.0	54.5	0.1	2.49	0.2	0.2	0.2	–	3.8	–	–	0.1	0.04
ISSA	4.4	2.9	17.2	31.7	10.8	2.0	9.3	0.7	0.1	–	17.8	0.1	0.3	–	2.7
Residue	–	2.1	11.3	37.0	1.8	1.6	8.1	0.8	–	16.2	20.7	0.08	0.27	–	0.05

**Table 2**  
Mix design of samples with different stabilization materials.

Sample ID	Soil (g)	ISSA (g)	Water (mL)	OA	
				Volume (mL)	Concentration (mol/L)
CK	20	0	0	0	0
0.2O	20	0	0	6	0.2
2O1	20	4	6	0	0
2010.1O	20	4	0	6	0.1
2010.2O	20	4	0	6	0.2
2010.5O	20	4	0	6	0.5
1010.5O	20	2	0	6	0.5
3010.5O	20	6	0	6	0.5

## 2.2. Design of material mixes for stabilization of Pb-contaminated soil

The mix design for the investigation of stabilization effect is shown in Table 2. The OA used was of analytical grade. Briefly, an amount of 20 g contaminated soil was first blended with different amounts of ISSA (2, 4 and 6 g, except the control mixes), and then with 6 mL OA of different concentrations (0.1, 0.2 and 0.5 mol/L). After thorough mixing, the mixtures were stored in a chamber (Temperature:  $23 \pm 2$  °C, Humidity  $50 \pm 1\%$ ) for 7 days. Different sample IDs represent different treatments of the soil (CK represent no treatment). The numbers before I and O represent the weight percentage of the ISSA and the concentration of OA respectively. For example, 2010.1O means that the amount of ISSA added was 20% of the soil by weight, and the concentration of OA added was 0.1 mol/L.

## 2.3. Test methods

The leaching potential of Pb in the soil was tested by two different methods as described in a previous study (Li et al., 2017). The TCLP was adopted to determine the toxicity of the samples. The samples were mixed with acetic acid solution (with a pH of 2.88) at a liquid to solid (L/S) ratio of 20 mL/g in capped polypropylene bottles, which were then placed in a rotary tumbler and rotated at 30 rpm for 18 h. The other method was a standard deionized water (DI) leaching test based on BS EN 12457–2 which is often used to check the suitability of disposing a waste material in a landfill (EN 12457–2, 2002; Macías et al., 2012). In this test, samples were mixed with deionized water at a L/S ratio of 10:1, and agitated for 24 h followed by a sequential extraction process to find the partition of Pb and other heavy metals in the samples. This method classifies the leachates into five fractions as follows:

- F1: Exchangeable (extracted by 1.0 mol/L  $\text{CaCl}_2$  at L/S of 15 mL/g);
- F2: Carbonate (extracted by 1.0 mol/L NaOAc with a pH value of 5.0 at L/S of 15 mL/g);
- F3: Fe–Mn oxides (extracted by 0.04 mol/L  $\text{NH}_4\text{OH} \cdot \text{HCl}$  at L/S of 20 mL/g);
- F4: Organic (extracted by 0.02 mol/L  $\text{HNO}_3 + 30\% \text{H}_2\text{O}_2$  at L/S of 11 mL/g);
- F5: Residual (digested by concentrated  $\text{HNO}_3$  and  $\text{HClO}_4$ ).

## 2.4. Characterization tests

The chemical compositions of the samples were determined by XRF. Pb concentration in the leachate was determined by using an inductively coupled plasma/optical emission spectroscopy (ICP-OES, FMX 36, SPECTROBLUE) after digesting the samples by

concentrated nitric acid. The crystalline phases in the samples were analysed by X-ray diffraction (XRD, Rigaku Smartlab) with  $2\theta$  ranging from  $5^\circ$  to  $60^\circ$  at  $0.02^\circ$  intervals. The morphology of the samples were observed by using a scanning electron microscope (SEM, Tescan VEGA3) with energy dispersive X-ray spectroscopy which could indicate the elemental distribution on the sample surface. The functional groups in the samples were checked by a Fourier Transformation Infrared microscopy (FTIR, PerkinElmer, Spectrum Two) in the range of  $4000\text{--}400 \text{ cm}^{-1}$ .

## 3. Results and discussion

### 3.1. Adsorption experiment

Batch adsorption experiments were conducted to evaluate the effectiveness of different ISSAs in stabilizing Pb in contaminated soil. The influence of pH and time on the removal of Pb from the aqueous solutions is shown in Fig. S1. It can be seen from Fig. S1a that both the Coarse and Fine ISSA could achieve over 94% removal rates within the pH range of 3.0–9.0. This performance could be ascribed to the alkali nature of ISSA and the precipitation of Pb with sulfate and phosphate when the solution pH value is less than 4.0 (Wang et al., 2019a, 2019b). Although the Pb removal rate of Residual ISSA increased with the initial pH value, the Pb removal performance was poor (<30%) in acidic solutions. Fig. S1b presents the adsorption of Pb by different ISSAs as time lapsed. The adsorption trends of the three materials are similar. Pb was removed rapidly within the initial 5 min and very slowly thereafter reaching maximum values of 6.2, 38.5 and 39.5 mg/g with Residual, coarse and fine ISSAs, respectively. At the beginning, adsorption sites of ISSAs were abundant and the concentration gradients between the aqueous solution and the ISSAs were high, allowing fast removal of Pb from the solution. The Residual ISSA exhibited a weaker adsorption capacity compared with the coarse and fine ashes due to the removal of active components like phosphate from the ISSA during the treatment process (Li et al., 2018a).

The experimental data were further fitted into the commonly applied adsorption kinetic models, namely, the pseudo-first and -second order kinetic models, to check the possible mechanism controlling the adsorption rate. The corresponding parameters derived from the two adsorption kinetic models are shown in Table S1. The results revealed that the pseudo-second order kinetic model could better fit the experimental data because of the higher  $R^2$  and the lower  $\chi^2$  values compared with the pseudo-first order kinetic model. Chemisorption might therefore play an important role during the Pb adsorption process with ISSAs.

To acquire the potential adsorption mechanisms as well as the maximum adsorption capacities towards Pb(II) by different ISSA samples, adsorption isotherm reflecting the interaction between the adsorbate and adsorbent were conducted as shown in Fig. 1. As can be seen from the figure, with both Fine and Coarse ISSA

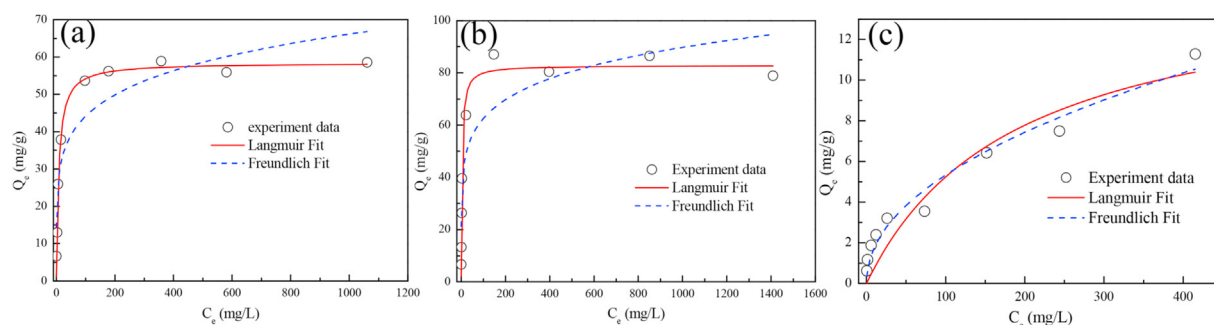


Fig. 1. Adsorption isotherm of Pb onto a) Fine ISSA; b) Coarse ISSA and c) Residue.

samples, an increase in  $C_e$  at low level resulted in an increase in  $Q_e$  due to the presence of sufficient adsorption sites for capturing Pb ions. When the initial Pb concentration was over 100 mg/L,  $Q_e$  remained constant and the isotherm curve became flattened due to the exhaustion of adsorption sites on the ISSAs. However, with the Residual ISSA,  $Q_e$  continuously increased with increase in  $C_e$  within the studied concentration range and the isotherm exhibited a rising curve.

The experimental data were then fitted into Langmuir and Freundlich isotherm models, and the associated parameters are shown in Table 3. Both the statistical factors including  $R^2$  and reduced  $\chi^2$  were used to assess the suitability of the model fitting. For the Coarse and Fine ISSA samples, the experiment data could be better fitted into Langmuir isotherm models because the higher  $R^2$  and lower  $\chi^2$  values than those estimated by Freundlich model. The adsorption data of the Residual ISSA, however, could be better predicted by Freundlich isotherm model revealing the adsorption of Pb(II) by Residual ISSA was a heterogeneous multi-layer sorption process (Wang and Guo, 2020). The increased adsorption capacity by ball milled ISSA could be largely due to the increased surface area which provided more active sites for the attachment of Pb(II). The reduced Pb(II) removal performance however could be largely related to its acidic properties due to the presence of residual sulfate and the removal of phosphate (as shown in Table 1).

In summary, the above finding shows that the ISSA possessed quite good capacity in adsorbing Pb. XRD tests showed that in both Coarse and Fine ISSAs, new precipitates containing Pb including anglesite and lead phosphate hydroxide were detected after mixing with Pb solution (Fig. S2). Milling of the ISSA could increase the BET surface area of the ISSA particles, generating more active adsorption sites for the adsorption of Pb. Considering the high consumption of ISSA for treating large contaminated sites in real applications and the high cost of ball milling, Coarse ISSA was thus selected as the agent for stabilizing Pb contaminated soil in this study.

### 3.2. Stabilization of Pb contaminated soil by combination of OA and ISSA

As discussed above, the Coarse ISSA had quite good capacity in

removing Pb from aqueous solutions. It was reported that ISSA was by its own an effective stabilizer for Pb(II) contaminated soil (Li and Poon, 2017). Knowing that ISSA is rich in phosphate which could be released by washing with acid like OA (Fang et al., 2018a), there is good potential for the released phosphate to combine with Pb in soil to form stable lead phosphate precipitates with low leachability. The following sections describe the results of experiments on the stabilization of Pb contaminated soil by a combination of ISSA and OA and discuss the effectiveness of this method.

#### 3.2.1. Soil characterization before and after treatment

Fig. 2 presents the SEM images of the soil particles before and after the Pb immobilization treatment. As shown in Fig. 2(a), the soil mainly composed irregular plate-like particles, a typical appearance of clay minerals such as kaolinite which was consisted of assembled silica tetrahedral and aluminium octahedral sheets. In addition, some needle-like crystals were found intermixed together. After treatment by OA, the morphology of the soil (Fig. 2(b)) did not significantly change. After mixing the soil with 20% ISSA alone, many smaller plate-like particles/(flocules) appeared as shown in Fig. 2(c). After treatment with the ISSA and OA together the morphology of the soil changed significantly (Fig. 3(d)). Further increasing the amount of ISSA from 10% to 30%, denser needle-like crystals were observed (Fig. 2(f)). The EDX analysis was applied to identify the element components of treated soil samples, and the results are shown in Fig. S3.

The changes in mineral phases of the samples before and after treatment were analysed by XRD and the patterns of typical samples are shown in Fig. 3. The mineral phases identified in the raw soil samples included quartz, muscovite, albite and kaolinite, which were common minerals in soils (Rinklebe et al., 2016). A Pb related mineral, i.e., cerussite with a solubility of  $10^{-12.8}$  was also observed (Ruby et al., 1994). After treatment by OA alone, a new Pb compound, i.e., lead oxalate, was detected. This product was found to be critical in the bio-immobilization of Pb contaminated soil by fungus *A. niger* SANRU (Jalili et al., 2020). The leaching risk of Pb from the soil depends significantly on the solubility of the Pb-bearing compounds, nevertheless, both cerussite and lead oxalate are far more soluble than Pb–P minerals, and can be risky under a changeable soil environment such as the reduction in soil pH (Beiyuan et al.,

Table 3  
Parameters corresponding to the Langmuir and Freundlich isotherm models.

Material	Langmuir				Freundlich			
	$Q_m$ (mg/g)	$K_L$ (L/mg)	$R^2$	Reduced $\chi^2$	$K_F$ (mg/g)/(mg/L <sup>1/n</sup> )	n	$R^2$	Reduced $\chi^2$
Coarse ISSA	58.2	0.127	0.984	6.886	19.7	5.7	0.850	64.650
Fine ISSA	82.8	0.275	0.973	28.104	30.4	6.4	0.820	190.183
Residue	15.1	0.005	0.883	1.429	0.588	2.1	0.964	0.438



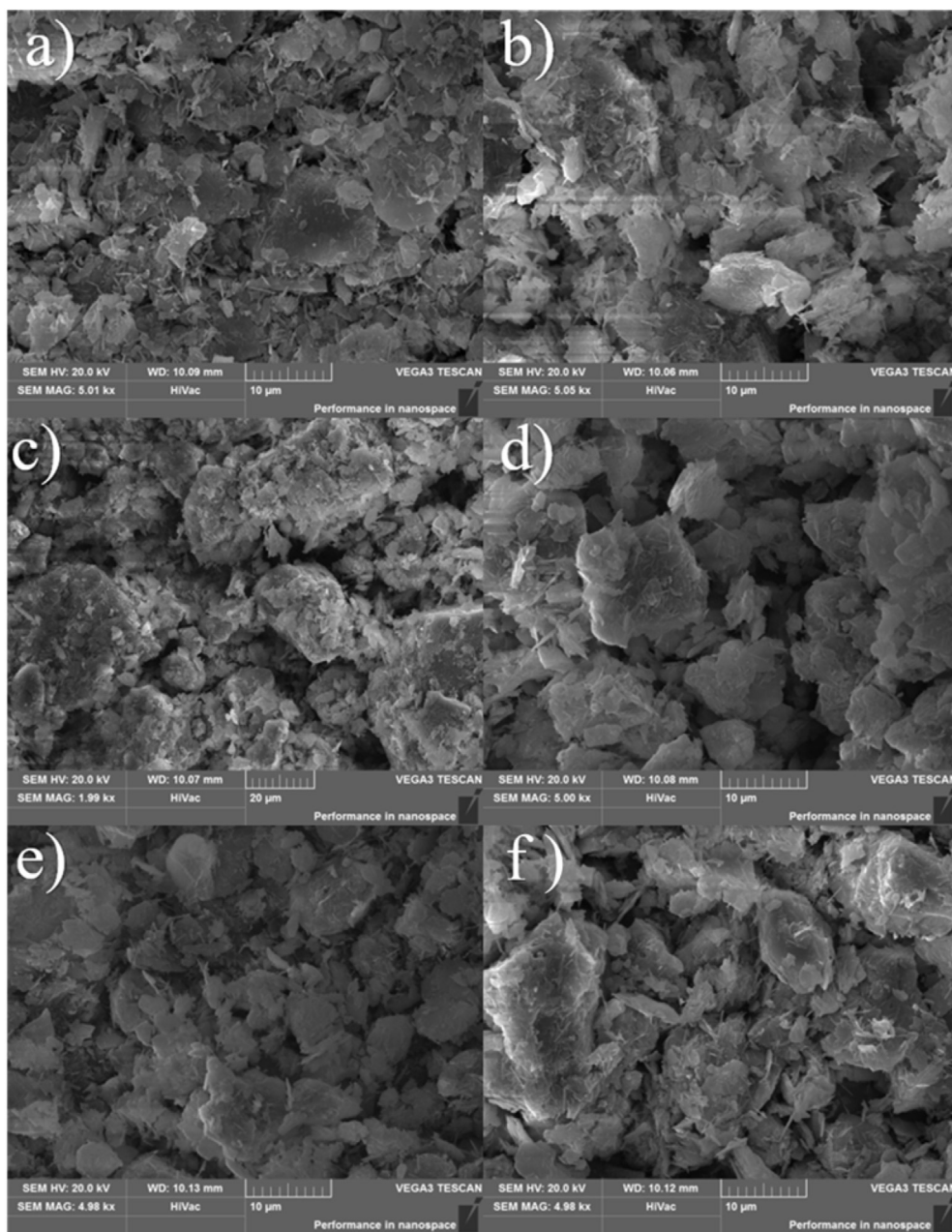


Fig. 2. SEM images of soil after different treatment: (a) CK; (b) 0.20; (c) 20I; (d) 10I0.50; (e) 20I0.50; (f) 30I0.50.

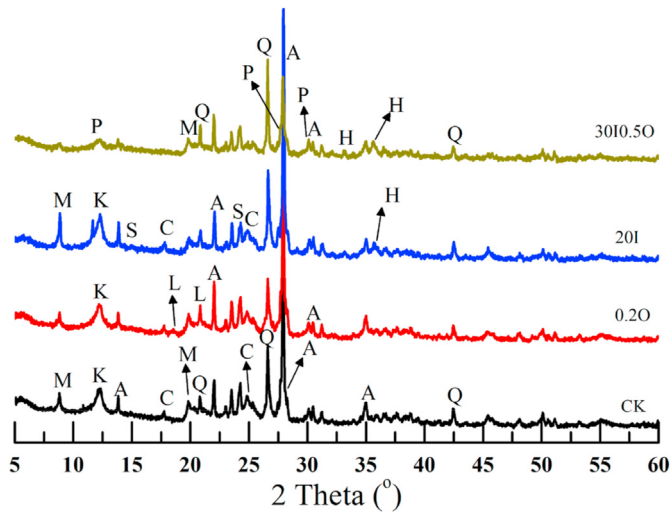
2020; Ruby et al., 1994; Shen et al., 2019). On the other hand, after treatment with the ISSA alone, the XRD pattern showed hematite which was widely found in ISSA (Fang et al., 2018b; Wang et al., 2019a) and lead oxide sulfate which was likely formed from the reaction between the ISSA and the soil. The combined use of ISSA and OA to stabilize Pb contaminated soil however resulted in the formation of lead phosphate hydroxide instead of lead oxalate and lead oxide sulfate. Particularly, lead phosphate hydroxide (hydroxypyromorphite) with a log  $K_{sp}$  of  $-76.8$  was considered quite stable under earth-surface environments (Ruby et al., 1994). It was believed that OA released phosphate from the ISSA, which then combined with Pb to form more stable lead phosphate hydroxide, which was conducive for S/S of the Pb contaminated soil.

The components of typical samples were further investigated by FTIR spectroscopy as shown in Fig. S4. All the selected samples

exhibited a peak centered at around  $1656\text{ cm}^{-1}$  which was likely associated with  $-\text{OH}$  due to the presence of water (Jalili et al., 2020), and a peak centered at around  $1400\text{ cm}^{-1}$  due to the vibration of carbonates (Jalili et al., 2020). The broad peak centered at around  $1000\text{ cm}^{-1}$  might be due to the Si–O vibration of soil, and P–O vibration of  $\text{PO}_4^{3-}$  originating from the application of ISSA (Jalili et al., 2020). With 30I0.50 treatment, a new peak centered at  $1316.14\text{ cm}^{-1}$  peak appeared indicating the presence of oxalate minerals (Jalili et al., 2020).

### 3.2.2. Leaching characteristics

The efficacy of stabilizing Pb contaminated soil by a combination of the ISSA and OA was assessed by the standard DI leaching test (BS EN 12457–2) and TCLP. The variations of soil pH were measured since it was one of the most important geochemistry factors



**Fig. 3.** XRD patterns of the soil before and after different treatments (Q: quartz (00-005-0490); M: muscovite (01-082-0576); A: albite (00-009-0466); K: kaolinite (00-001-0527); L: lead oxalate; C: cerussite; H: hematite (01-089-0597); P: lead phosphate hydroxide (00-024-0586); S: lead oxide sulfate (00-006-0275)).

affecting the solubility of Pb-precipitates in soil. As shown in Fig. 4, the application of OA alone caused a reduction of soil pH from 5.37 to 4.13. Such a reduction of soil pH had been widely reported when acids like H<sub>3</sub>PO<sub>4</sub> were applied to stabilize Pb in soil (Jalili et al., 2020; Yang et al., 2001). However, the combined application of the ISSA and OA resulted in light increase of soil pH to a range of 5.46–6.76. This increase in soil pH could be attributed to the alkalinity of ISSA (Wang et al., 2018b) which overtook the acidity of OA applied in this study. The increase in soil pH was reported to be conducive to the retention of cationic heavy metals including Pb on soil surface since higher pH could promote processes like adsorption, inner sphere complexation and/or precipitation and multinuclear-type reactions resulting reduced leachability and mobility of Pb in soil (Palansooriya et al., 2020; Su et al., 2015).

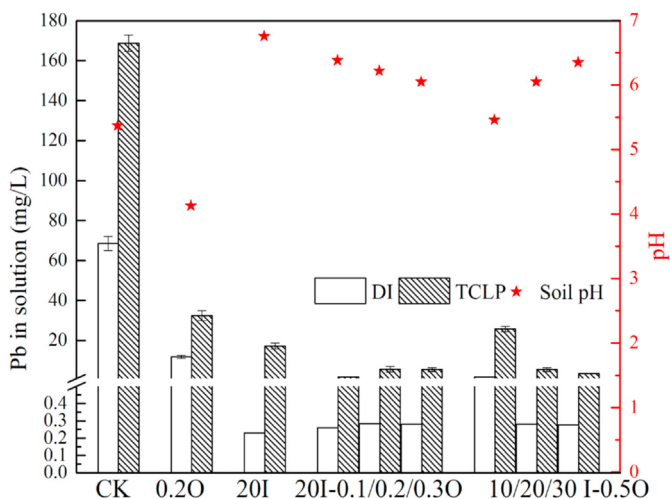
The concentration of Pb leached from the untreated soil as measured by the standard DI leaching test was 68.50 mg/L. As can be seen from Fig. 4, all treatment groups could reduce the Pb concentration in the leachate. The application of OA reduced the

concentration of Pb to 11.76 mg/L, by about 83% compared to the untreated soil. This reduction was achieved due to the formation of lead oxalates as revealed by XRD analysis. The application of ISSA alone or together with OA achieved a much better Pb immobilization efficiency (over 97% reduction) than OA alone. The application of 20%ISSA reduced the concentration of Pb leachate to 0.23 mg/L because the alkaline components in the ISSA made soil Pb resistant to DI washing. The combination of OA and ISSA, in most cases, reduced the concentration of Pb in the leachate to below 0.5 mg/L. However, the less effective combination (10I0.5OA) gave slightly inferior S/S efficacy. It was found that the concentration of Pb in the leachate correlated inversely with soil pH. Su et al. (2015) also reported that the water-soluble Pb in soil increased with decrease in soil pH after treatment with OA alone or a combination of OA and phosphates. The decrease in soil pH could adversely affect the stabilization of cationic heavy metals because a) low soil pH favoured the dissolution of Pb-bearing minerals, vice versus; and b) H<sup>+</sup> could change the surface charge of the soil, and compete for the active sorption sites on soil components responsible for the retention of heavy metals such as clays (Palansooriya et al., 2020; Rinklebe et al., 2016). In addition, under acidic soil environment the potential dissolution of Fe/Mn oxides would further enhance the leaching risk of Pb as a large fraction of Pb existed in Fe–Mn oxide fraction (Rinklebe et al., 2016).

The concentration of Pb leached from the untreated soil as measured by TCLP was 162.85 mg/L, which was much higher than the legal limit (5 mg/L) set by the Ministry of Ecology and Environment of China and the United States Environmental Protection Agency. Treatment with OA reduced the Pb concentration in leachate by 80% to 32.43 mg/L. Treatment with 20% ISSA alone, achieved a greater reduction to 89%. The Pb stabilization performance of the ISSA and OA mixes varied. 10I0.5O was the most inferior treatment group, while 20I0.1O achieved the best stabilization effect as it could reduce the Pb concentration in leachate by 99% to 1.74 mg/L. In case of deviation from the optimal OA concentration of 0.1 mol/L, 20I0.2O and 20I0.5O could still reduce the Pb concentrations in leachate to 5.51 and 5.40 mg/L respectively, nearly complying with the limit. The addition of a higher amount of the ISSA (30%) had a negligible effect on Pb stabilization. However, a significant adverse effect was observed when a lower amount of the ISSA was used. Compared with 20I0.5O (20% ISSA) which could reduce Pb concentration in leachate to 5.4 mg/L, 10I0.5O (10% ISSA) only reduced Pb concentration in leachate to 25.7 mg/L far above threshold. These results demonstrate that a proper mix of the ISSA and OA can effectively stabilize highly contaminated soil by Pb.

The toxicity of Pb in the soil was further evaluated by the sequential extraction procedure. In general, exchangeable Pb (F1) has the highest toxicity due to its easy leachability with changes of soil pore solutions. Pb in carbon-bound (F2) and Fe/Mn oxide-bound (F3) forms are also potentially toxic as they can be released with changing environment conditions such as soil pH and redox conditions (Palansooriya et al., 2020). Pb in F5 is the most stable form with negligible migration in soil (Zhang et al., 2020).

The results of fractionation of Pb in the soil before and after different immobilization treatments are shown in Fig. 5. The dominant species of Pb in the contaminated soil were F2 (52%), F1 (26%) and F3 (19%) which accounted for around 97% of the total Pb, this fractionation results were similar to a previous study, in which Pb dominantly presented in forms of F2 and F1 in urban park soil and dust soils collected in Hong Kong (Li et al., 2001). Different treatment groups resulted in re-speciation of the soil Pb. Overall, all the treatment groups except OA and 10I0.5O reduced the most labile fraction F1 and increased the most stable fraction F5, reflecting the efficacy of the treatment methods. After treatment by OA alone, F1 increased to 39% and F2 remained at the original level



**Fig. 4.** Pb concentration measured by DI method and TCLP, and changes in soil pH after different treatments.

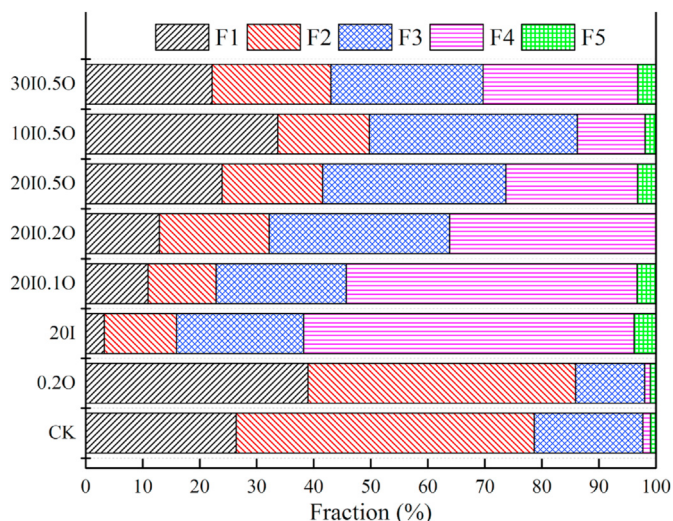


Fig. 5. Fraction of Pb species in soils before and after stabilization treatment (F1: Exchangeable; F2: Carbonate; F3: Fe–Mn oxides; F4: Organic; F5: Residual).

(47%). The sum of F1 and F2 increased from 78% to 84% indicating a higher leaching potential of Pb in the soil after such a treatment. When 20% of the ISSA was added to treat the soil, the total Pb content was reduced due to the dilution effect brought by the incorporation of the ISSA. Both F1 and F2 were significantly reduced (the F1 exchangeable Pb only comprising 3% for the total Pb), while the F4 (barely soluble species) was greatly increased to around 58%. This result confirmed the effectiveness of the ISSA in stabilizing Pb in the contaminated soil since it turned mobile Pb to more stable species (Li and Poon, 2017). The combined treatment with ISSA and OA reduced F1 and F2 and increased F3 and F4 in most cases, which demonstrated the effectiveness of such a combination in treating Pb contaminated soil. When 20% ISSA was used together with 0.1, 0.2 and 0.5 mol/L OA respectively, F1 (>10%) increased with the concentration of OA. Both F2 and F3 also increased when a higher concentration (0.2 or 0.5 mol/L) of OA was used together with the ISSA. F4, however, dropped with increase in the concentration of OA. When 0.5 OA was used with different amount of the ISSA. In general, F1 and F3 reduced while F2 and F4 increased when more ISSA was added. From this perspective, all the treatments except OA alone could stabilize Pb in the soil.

### 3.3. Environmental considerations

Despite the proven effectiveness of P-based compounds in the stabilization of Pb contaminated soil, concerns about side effects including leaching of phosphate and heavy metals deserve attention (Zeng et al., 2017). In this study, phosphate was not detected in the DI leachate of CK, 0.20 and 20I treatments, but was found with treatment using the ISSA and OA together. Moreover, phosphate was found in the TCLP leachate in almost all groups using the ISSA. When a lesser amount of the ISSA was used with a large amount of OA, even notable water-soluble phosphate could be found in the soil after the immobilization treatment. Besides, Zn (4.26 mg/L) was also detected in the TCLP leachate, which could come from the ISSA used for treatment. Reutilization of waste materials could mitigate some environmental problems but might generate new problems such as introducing other contaminants from the waste materials (Zhou and Haynes, 2010). With appropriate mix proportion, the combined use of OA and the ISSA could effectively stabilize Pb contaminated soil. Unfortunately, inappropriate combination of the ISSA and OA could result in the leaching of both phosphate and Zn

due to the co-dissolution of phosphate and Zn from the ISSA under the effect of OA. Special attention should be paid when phosphate compounds are used together with acid to stabilize heavy metal contaminated soil (Palansooriya et al., 2020). What's more, the artificially contaminated soils cannot represent real contaminated soil. Further onsite research work should therefore be conducted on the long-term effect of this technology before wide application of ISSA and OA together for the immobilization of real Pb contaminated soil.

## 4. Conclusions

The ISSA possessed quite good capacity in adsorbing Pb and achieve over 94% removal rates within the pH range of 3.0–9.0. Soil artificially contaminated by Pb was treated by different combinations of ISSA obtained from an incinerator and OA. The results demonstrated that the ISSA, alone and appropriate combinations of the ISSA and OA could effectively stabilize Pb in the soil. The combined use of the materials was more effective because OA could activate ISSA to release phosphate which combined with Pb to form lead phosphate hydroxide. 20% ISSA together with 30% OA (0.2 mol/L) reduced leached Pb concentration by 99%. However, improper combinations especially for mixes with large amount of OA could cause some contamination problems including the leaching of excessive phosphate and Zn existing in the ISSA. Overall, this study shows that the combined use of the ISSA and OA with appropriate mix proportion can be a low-cost and effective remediation method for the stabilization of Pb contaminated soil.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2021.117120>.

## Author statement

Jiang-shan Li: Conceptualization, Methodology, Writing – review & editing. Qiming Wang: Methodology, Data curation, Writing – original draft, Visualization. Zhen Chen: Writing – review & editing. Qiang Xue: Supervision, Funding acquisition. Xin Chen: Writing – review & editing. Yanhu Mu: Funding acquisition, Project administration. Chi Sun Poon: Conceptualization, Project administration.



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