

## Article

# Efficient Inorganic/Organic Acid Leaching for the Remediation of Protogenetic Lead-Contaminated Soil

Longheng Xiao <sup>1</sup>, Xiang Cheng <sup>1</sup>, Tianhua Zhang <sup>1,2</sup>, Min Guo <sup>1</sup> and Mei Zhang <sup>1,\*</sup>

<sup>1</sup> State Key Laboratory of Advanced Metallurgy, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China; d202110123@xs.ustb.edu.cn (L.X.); b20190100@xs.ustb.edu.cn (X.C.); zhangtianhua@cribc.com (T.Z.); guomin@ustb.edu.cn (M.G.)

<sup>2</sup> MCC Group, Central Research Institute of Building and Construction Co., Ltd., Beijing 100088, China

\* Correspondence: zhangmei@ustb.edu.cn; Tel./Fax: +86-10-6233-4926

**Abstract:** In this study, inorganic acid and organic acid were used to leach and remediate superheavy, lead-contaminated protogenetic soil with a lead pollution level of 8043 mg·kg<sup>-1</sup>. Among the compounds studied, HCl and citric acid (CA) presented the best effects, respectively. Under the optimal experimental conditions, the remediation efficiency of 0.05 mol·L<sup>-1</sup> CA reached 53.6%, while that of 0.2 mol·L<sup>-1</sup> HCl was 70.3%. According to the lead morphology analysis, CA and HCl have certain removal ability to different fractions of lead. Among them, the removal rates of acid-soluble lead in soil by HCl and CA are 93% and 83%, and the soil mobility factor ( $M_F$ ) value decreased from 34.4% to 7.74 % and 12.3%, respectively, indicating that the harm of lead in soil was greatly reduced. Meanwhile, the leaching mechanisms of CA and HCl were studied. The pH values of the soil after leaching with HCl and CA were 3.88 and 6.97, respectively, showing that HCl leaching has caused serious acidification of the soil, while the process of CA leaching is more mild. CA has a relatively high remediation efficiency at such a low concentration, especially for the highly active acid-soluble fraction lead when maintaining the neutrality of the leached soil. Hence, CA is more suitable for the remediation of lead-contaminated soil.

**Keywords:** lead; protogenetic contaminated soil; acid leaching; citric acid; HCl



**Citation:** Xiao, L.; Cheng, X.; Zhang, T.; Guo, M.; Zhang, M. Efficient Inorganic/Organic Acid Leaching for the Remediation of Protogenetic Lead-Contaminated Soil. *Appl. Sci.* **2022**, *12*, 3995. <https://doi.org/10.3390/app12083995>

Academic Editors: Ramaraj Boopathy, Eldon R. Rene and Mark Zappi

Received: 13 March 2022

Accepted: 13 April 2022

Published: 14 April 2022

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## 1. Introduction

Soil contaminated by heavy metals, due to both natural sources and human activities such as mining industry, waste water irrigation, and sewage sludge applications, can influence animals' ground water and human health via the biological chain [1–3]. Lead (Pb) exposure has been of major public concern due to its well-established adverse effects on human health (e.g., affecting nervous, skeletal, and enzymatic systems) [4,5]. In Pb-contaminated sites such as mining and smelting areas, childhood Pb poisoning is also worthy of concern; research indicates that the average soil intake rate for children ranges from 1.2 to 23 mg per day via hand-to-mouth behaviors and inhalation of resuspended soil particles [6,7]. Therefore, remediation of lead-contaminated soil is an urgent need.

Various remediation technologies have been developed over the past few decades, such as physical remediation, chemical remediation, bioremediation, and combined repair, which could be applied to the remediation of lead-contaminated soil [8–12]. Among them, soil leaching is a quite effective remediation technology that can be widely used in the field of the remediation for heavy-metal-contaminated soils because of its advantages such as stable remediation efficiency, permanent remediation, ease of operation, and short repair cycle [13,14]. In particular, the key factor of remediation efficiency is the choice of eluting agent, and the repair mechanism and repair capacity vary according to the eluting agent. There are four main kinds of eluting agent, namely inorganic eluting agents, low-molecular-weight organic acids, artificial chelating agents, and biosurfactants [15–17].

Recently, many studies have researched the leaching remediation of contaminated soil using different eluting agents. As a typical artificial chelating agent, EDTA can form stable complexes with most heavy metals in a higher pH range. The equilibrium constant of the Pb-EDTA complex is 19.0, which could further promote the dissolution of Pb from the soil and inhibit re-adsorption into the soil [18]. A  $0.05 \text{ mol}\cdot\text{L}^{-1}$  concentration of EDTA was used to extract lead from the waste residue of a lead smelter, and the leaching efficiency reached 72% when the leaching time was 1 h [19]. Although EDTA has a high remediation efficiency for lead-contaminated soils, its application prospect is limited due to its poor biodegradability. Due to the high cost and low remediation efficiency, biosurfactants are rarely used solely for remediation of lead-contaminated soil, but is normally used combined with other eluting agents [20,21]. Inorganic eluting agents are the most frequent eluents used in the leaching remediation of heavy-metal-contaminated soil. Among them, inorganic acid has a strong acid-dissolving effect; moreover, some inorganic acids have complexing ability, so they could effectively and quickly remove heavy metals from soil at a low cost. Yang used HCl to repair soil with a lead-pollution intensity of  $105.38 \text{ mg}\cdot\text{kg}^{-1}$  and found that the remediation effect of low-concentration HCl was poor. When the concentration of HCl was  $0.8 \text{ mol}\cdot\text{L}^{-1}$ , a remediation efficiency of Pb of 90.46% was achieved [22]. HCl always had a good remediation effect on soil contaminated with heavy metal. For soil with a lead pollution intensity of  $64,195 \text{ mg}\cdot\text{kg}^{-1}$ , the remediation efficiency could reach 83% under  $6 \text{ mol}\cdot\text{L}^{-1}$  HCl, but when the concentration of HCl was  $1 \text{ mol}\cdot\text{L}^{-1}$ , the remediation efficiency was only 35% [23]. Although increasing the concentration of HCl will have a better remediation effect on heavy-lead-contaminated soil, it also might destroy the physical, chemical, or biological properties of the soil due to its acidity and corrosive property.

Numerous studies have shown that low-molecular-weight organic acids could remove heavy metal ions in contaminated soil via chelation reactions. At the same time, they have good biodegradability and are a relatively green and mild eluting agent [24,25]. Árpád's [26] research shows that AA can effectively leach lead, and the leaching efficiency is related to the concentration. When the concentration of AA is  $1 \text{ mol}\cdot\text{L}^{-1}$ , the final leaching efficiency exceeds 80%. Hong [27] used three kinds of organic acids (CA, MA, and TA) to leach and remediate artificial simulated contaminated soil with a pollution intensity of  $1520 \text{ mg}\cdot\text{kg}^{-1}$  and found that the remediation efficiency of lead was 46.13%, 51.67%, and 52.86%, respectively. Ke [28] used CA to carry out ultrasonic enhanced leaching for artificial simulated contaminated soil. When the concentration of CA was  $0.05 \text{ mg}\cdot\text{L}^{-1}$ , the Pb concentration of soil decreased from  $947.62 \text{ mg}\cdot\text{kg}^{-1}$  to  $447.66 \text{ mg}\cdot\text{kg}^{-1}$ . Most of the studies on the remediation of lead contaminated soil by organic acids are artificially simulated contaminated soil or lower Pb-contaminated protogenetic soil. However, due to long-term pollution and natural weathering, there are more contaminated protogenetic soils with extremely high lead content in nature, and their complexity and toxicity are relatively high, inhibiting the leaching of Pb. Therefore, it is necessary to reconsider the lead leaching ability of inorganic acid and organic acid eluents. Additionally, the lead-leaching mechanism of acid eluents has not been uniformly determined, which is worthy of discussion. In addition, acid leaching agents may cause soil acidification, so the soil quality after leaching should also be investigated.

Therefore, in this paper, commonly used inorganic acids and low-molecular-weight organic acids with a good application prospect were carried out on the remediation of heavy Pb-contaminated protogenetic soil with oscillating leaching experiments. The optimal eluting agent and leaching conditions were determined. The redistribution of the existing fraction of Pb in the soil before and after leaching was investigated, and the mechanism of HCl and CA leaching was explored. The pH value of soil was measured before and after leaching, and the applicability, advantages, and disadvantages of CA and HCl and their effects on soil were compared.

## 2. Materials and Methods

### 2.1. Soil Sampling

Soil samples were collected from the surface layer soil (0–100 cm) in a lead alloy smelting plant in Northwest China. Impurities such as stones and plant roots were removed from soil samples, and the samples were air-dried naturally in the absence of light. After crushing, the whole sample was pulverized and mixed for homogenization. Part of the separated sample was transferred to 150 mesh after fine grinding for measurement of physical and chemical properties of the soil, and other separated samples were passed through 100 mesh after a fine grinding experiment for the oscillating leaching experiments.

Physicochemical characteristics of the contaminated soil are shown in Table 1. The content of lead-contaminated in soil is 8043 mg·kg<sup>-1</sup>, which seriously exceeds the control value standard (2500 mg·kg<sup>-1</sup>) for the national construction land (the second type of land, GB36600-2018), indicating that the soil is heavily contaminated with lead. The pH value of the contaminated soil is 7.98, namely, neutral. The soil has high OM and OC content, 40.4 and 23.5 g·kg<sup>-1</sup>, respectively. The surface charge of the soil is −10.3 mv when the pH value is 8.0. The composition and content of main compounds in soil are shown in Table 2.

**Table 1.** Chemical and physical properties of the contaminated soil.

	Total Pb Content (mg·kg <sup>-1</sup> )	pH	CEC (cmol(+)-kg <sup>-1</sup> )	OM (g·kg <sup>-1</sup> )	OC (g·kg <sup>-1</sup> )	Zeta Potential (mv)
Soil sample	8043	7.98	8.72	40.4	23.5	−10.3

**Table 2.** Main chemical composition of the contaminated soil.

Composition (%)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	PbO	P <sub>2</sub> O <sub>5</sub>	MnO
Soil Sample	58.4	12.3	11.5	6.54	3.74	3.09	1.60	0.84	0.71	0.26	0.14

### 2.2. Soil Leaching

#### 2.2.1. Inorganic Acid Leaching

A single factor experimental study with different inorganic acids (HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>) was firstly carried out to compare their effects on the remediation efficiency, and deionized water was used as a comparison. All eluents, including organic and inorganic acids, are AR-grade, purchased from Sinopharm Chemical Reagents Co., Ltd (Beijing, China). Firstly, a batch of 1.0 g soil was mixed with 20 mL different acid at a same concentration (0.5 mol·L<sup>-1</sup>) in a 50 mL glass bottle, stirring at 180 ± 10 rpm for 24 h. Then, the mixtures were separated by centrifuging at 6000 rpm for 15 min, and the supernatant was filtered with a 0.45 μm filter membrane. The contents of Pb were determined by Inductively Coupled Plasma Massspectrometry (ICP-MS). The remediation efficiency,  $\eta$ , was defined by the ratio of leaching amount to total lead, as shown in Equation (1)

$$\eta = \frac{m_1}{m_0} \times 100\% \quad (1)$$

where  $m_0$  (mg) is the amount of Pb in the primary soil, and  $m_1$  (mg) is the amount of Pb in the leaching solution.

Subsequently, an orthogonal experiment was carried out for exploring the importance of factors, and the specific experimental conditions are shown in Table S1. Afterward, single-factor experimental studies with different concentrations of HCl (0.1, 0.2, 0.3, 0.5 and 0.7 mol·L<sup>-1</sup>) and stirring times (0.5, 1, 2, 4, 8, 12, 24, 24 and 48 h) were carried out under the solid-to-liquid ratio of 20:1.

#### 2.2.2. Low-Molecular-Weight Organic Acid Leaching

Similarly, leaching experiments with a low-molecular-weight organic acid system as the inorganic acid leaching system were carried out, and CA, OA, TA, AA, and MA

were selected as eluting agent. Firstly, the single factor soil leaching experiments with different low-molecular-weight organic acids were conducted for 1.0 g protogenetic soil in a 50 mL glass bottle at the concentration of eluting agent of  $0.5 \text{ mol}\cdot\text{L}^{-1}$ . The orthogonal experimental of CA were then carried out to seek the optimal experimental combination, and the orthogonal experiment conditions are shown in Table S2. In order to find the best repair concentration of CA, single-factor experimental studies were subsequently carried out under the solid-to-liquid ratio of 20:1 and stirring time of 8 h, while the concentration of CA was set to 0.01, 0.03, 0.05, 0.07, 0.1, and  $0.3 \text{ mol}\cdot\text{L}^{-1}$ , respectively.

### 2.3. Characterization and Measurement

The soil pH was measured using a pH meter with a triple complex electrode (201T-M, Shanghai, China) at a soil-to-water ratio of 1:2.5 ( $\text{g}\cdot\text{mL}^{-1}$ ) (NY/T 1377-2007) [29]. The CEC was determined using the Hexammincobalt trichloride solution-Spectrophotometric method (HJ 889-2017) on ultraviolet spectrophotometer (UV5100, Shanghai, China) [30]. The OM and OC contents were determined by the determination method of organic matter in forest soil and carbon-nitrogen ratio (LY/T 1237-1999) [31]. The surface charge of the soil was measured by electrophoresis using Zetasizer Nano (ZS90, Malvern, UK). The total Pb content and chemical composition in soil samples was measured by X-ray fluorescence (XRF-1800, Shimadzu, Japan). The concentration of lead in the leach solution was measured by ICP-MS (iCAP-RQ, Thermo Scientifi, Germany).

Different lead speciation distribution in the soil before and after leaching were determined. Heavy metals in soil were divided into 4 fractions ( $F_1$ ,  $F_2$ ,  $F_3$ , and  $F_4$ ) by the Bureau Community of Reference (BCR) and measured by modified BCR three-step sequential extraction procedure [32]. In order to evaluate the relative mobility and bio-availability of lead in soil, the  $M_F$  developed by Gusiatin and Klimiuk [33] was used to describe the mobility of Pb in soil samples. The  $M_F$  was calculated as a ratio of metal concentration in the mobile fraction to the sum of all fractions:

$$M_F = \frac{F_1}{F_1 + F_2 + F_3 + F_4} \times 100\% \quad (2)$$

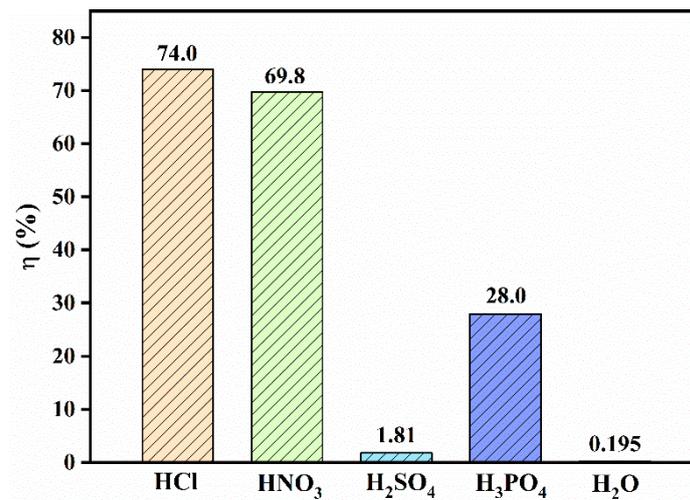
where  $M_F$  is the mobility factor of Pb,  $F_1$  ( $\text{mg}\cdot\text{kg}^{-1}$ ) is the content of acid-soluble fraction lead,  $F_2$  ( $\text{mg}\cdot\text{kg}^{-1}$ ) is the content of reducible fraction lead,  $F_3$  ( $\text{mg}\cdot\text{kg}^{-1}$ ) is the content of oxidizable fraction lead, and  $F_4$  ( $\text{mg}\cdot\text{kg}^{-1}$ ) is the content of residual fraction lead. The sum of  $F_1 + F_2 + F_3 + F_4$  is the total lead amount of soil.

## 3. Results and Discussion

### 3.1. Soil Leaching by Inorganic Acids

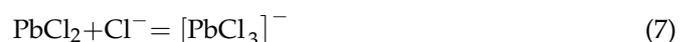
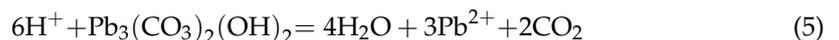
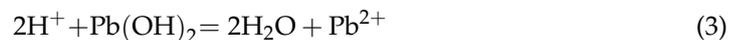
#### 3.1.1. Effects of Inorganic Acids on the Lead Removal from Protogenetic Soil

Four kinds of inorganic acids (HCl,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_3\text{PO}_4$ ) and deionized water were used for leaching remediation of lead-contaminated soil, and the results are shown in Figure 1. It is indicated that the remediation efficiency of deionized water was 0.195%, which was similar to that reported by Moutsatsou [23]. The soil pH value had a great influence on the form of lead in the soil. Generally, the content of soluble lead is higher in the acidic soil, in which the pH was 7.89 (Table 1), resulting in lead ions that were very tightly bound to the soil particles. The inorganic compounds of lead in the alkaline contaminated soil are rarely tetravalent and mainly exist in the insoluble divalent state, such as  $\text{Pb}(\text{OH})_2$ ,  $\text{PbS}$ ,  $\text{PbCO}_3$ , and  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ; thus, it was difficult to obtain a higher remediation efficiency using only deionized water.



**Figure 1.** Remediation efficiency ( $\eta$ ) of four inorganic acids and deionized water.

In the case of Pb removal, soil leaching using HCl and HNO<sub>3</sub> showed a significant effect. After leaching with HCl and HNO<sub>3</sub>, the lead concentration in the contaminated soil was reduced from 8043 mg·kg<sup>-1</sup> to 2091.2 and 2429 mg·kg<sup>-1</sup>, respectively, which satisfied the control value standard of national construction land (the second type of land). When HCl and HNO<sub>3</sub> were used as eluents, a large amount of H<sup>+</sup> entered the solution and reacted with the inorganic compounds of lead in the soil, as shown in Equations (3)–(5), making the insoluble lead ions in the soil transform into soluble lead ions. Additionally, the other reason was that the amphoteric properties of functional groups such as hydroxyl groups in soil particles tend to absorb protons under highly acidic conditions [34], resulting in the decrease in the available anion concentration in the surface layer of soil and weakening the soil adsorption capacity for Pb<sup>2+</sup>. Compared with HNO<sub>3</sub>, Cl<sup>-</sup> can form soluble lead ion complexes ([PbCl<sub>4</sub>]<sup>2-</sup>) with Pb<sup>2+</sup>, as shown in Equations (6)–(8), and the strong oxidation of HNO<sub>3</sub> may lead to the formation of insoluble metal compounds [23]; therefore, the remediation efficiency of HCl was slightly higher than that of HNO<sub>3</sub>. The remediation efficiencies of H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> were only 1.81% and 28.0%, respectively. Though they could also produce a lot of H<sup>+</sup>, promoting the dissolution of Pb<sup>2+</sup> from soil, their anions could react with lead ions to form precipitates, as shown in Equations (9) and (10). Both PbSO<sub>4</sub> and Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> could be precipitated as insoluble salts, which have a very small solubility product constant, making them remain in the soil. Moon [35] studied the removal efficiencies of Zn by various inorganic acids, and they exhibited efficiencies in the order of HCl > HNO<sub>3</sub> > H<sub>2</sub>SO<sub>4</sub> > H<sub>3</sub>PO<sub>4</sub>, which is similar to our result. Hence, HCl is the most suitable eluent for the remediation of lead-contaminated soil.



### 3.1.2. Effect of HCl Leaching Conditions in Orthogonal Experiment

The effects of HCl concentration, solid-to-liquid ratio, and stirring time on the remediation efficiency were investigated by an orthogonal experiment according to Table S1. The results and analysis are shown in Table S3. The influence of each factor on the remediation efficiency of contaminated soil was determined by the range ( $R$ ), as shown in Equation (11):

$$R_i = k_{i(\max)} - k_{i(\min)} \quad (11)$$

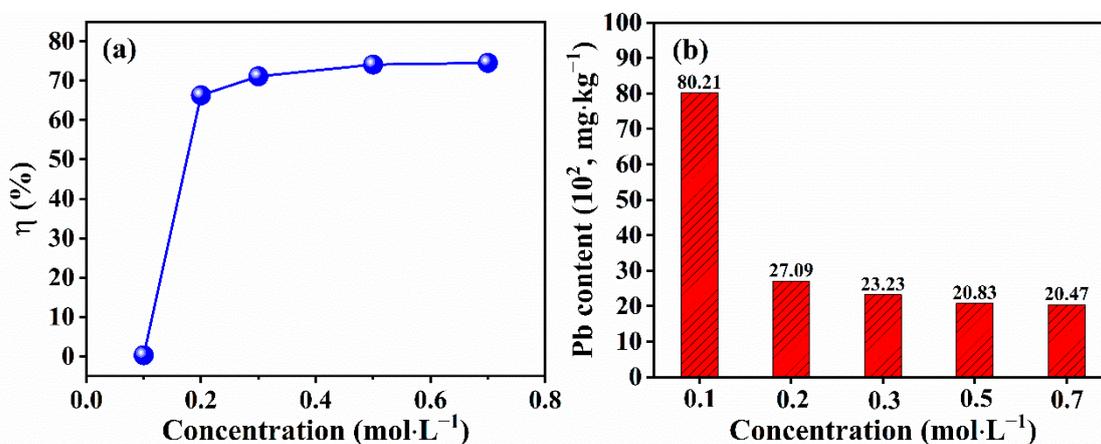
where  $k_i$  is the average value of  $K_i$ , and  $K$  values ( $K_1, K_2, K_3, K_4$ ) are the sum of the results of each level and represent different levels of each factor between the minimum and the maximum in the orthogonal experiments.

According to the  $R$  value of various factors, the order of factors on remediation efficiency was as follows: acid concentration > solid-to-liquid ratio  $\approx$  stirring time, and their  $R$  values are 71.9%, 19.8%, and 14.5%, respectively. The HCl concentration is the key factor, and its  $k$  value changed noticeably from 0.314% to 72.2%. The larger the concentration of HCl, the higher the removal efficiency of Pb from soil, with the highest remediation efficiency of 74.0%. The concentration of lead in the soil was reduced from 8043 to 2091.2 mg·kg<sup>-1</sup>. However, excessively high HCl concentration could cause severe soil acidification and damage the soil structure. It is necessary to further find an optimal HCl concentration with a higher remediation efficiency. The  $k$  value of the solid-to-liquid ratio increased from 17.7% to 37.5% when it was decreased from 1:10 to 1:25. When the solid-liquid ratio is relatively large, reducing the solid-to-liquid ratio can significantly improve the repair efficiency. When the solid-to-liquid ratio decreased from 1:10 to 1:15, the  $k$  value increased from 17.7% to 31.5%. However, there were no significant changes in the remediation efficiency when the solid-to-liquid ratio exceeded 1:20, which may mean that the total amount of HCl had reached relative saturation and that continuously decreasing the solid-to-liquid ratio will increase the cost of soil remediation. Based on the average remediation efficiency and remediation cost, the optimal solid-to-liquid ratio is selected as 1:20. It can be seen from Table S3 that with the increase in stirring time from 8 h to 48 h, the  $k$  value decreased from 34.5% to 30.7%. This shows that the stirring time also has a certain influence on the remediation efficiency. Although the change is not obvious, it is worth further exploring the optimal stirring time to shorten the experimental process.

### 3.1.3. Effect of HCl Concentration

A concentration experiment was carried out to investigate the relationship between the removal efficiency of Pb and HCl concentration; five concentration gradients of 0.1, 0.2, 0.3, 0.5 and 0.7 mol·L<sup>-1</sup> were set. As can be seen from Figure 2a, when the concentration of HCl increased from 0.1 to 0.7 mol·L<sup>-1</sup>, the removal efficiency of Pb sharply increased from 0.29% to 74.6%, and the content of Pb in the leaching soil decreased from 8021 to 2047 mg·kg<sup>-1</sup> (Figure 2b). Low concentration of HCl was proved to be inefficient for the removal of lead in the contaminated soil, which was closer to that of deionized water; however, a high concentration of HCl was shown to be more effective. As already mentioned, the pH value of protogenetic soil was 7.89, which caused Pb<sup>2+</sup> to exist in an insoluble form. When the concentration of HCl was low, it was difficult to change the alkalinity of the soil, and the concentration was also easily affected by other heavy metal ions and complexes in the soil, which do not help the desorption of lead ions from soil particles, so the leaching concentration of Pb was lower. Kuo [36] reported that the concentration of HCl used for soil leaching should exceed 0.1 mol·L<sup>-1</sup>. Otherwise, it is was found to be difficult to remove the heavy metal elements in the soil, which was consistent with our results. When the concentration of HCl continued to increase, the remediation efficiency increased significantly and tended to be stable when it reached 0.2 mol·L<sup>-1</sup>. There was no significant increase when the leaching concentration continued to increase. It may be that excessive Cl<sup>-</sup> may form a protective layer around the solid particles, thereby inhibiting further dissolution of lead. Moreover, increasing the concentration of HCl will damage soil

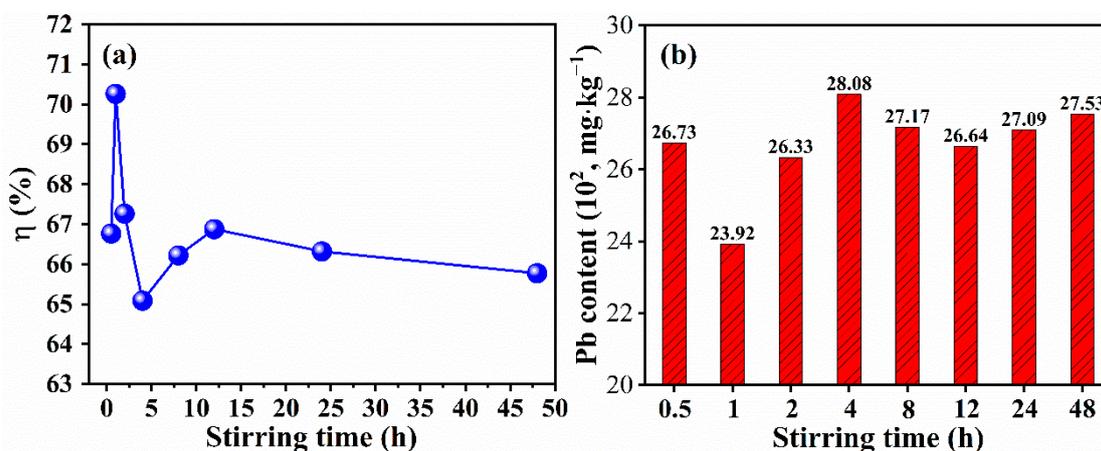
physical and chemical properties, resulting in serious soil acidification, and also increase the remediation cost. Therefore,  $0.2 \text{ mol}\cdot\text{L}^{-1}$  HCl solution is the suitable concentration for leaching remediation of heavy Pb-contaminated soil. Herein, the removal efficiency of Pb reached 66.3%, and the lead content in soil after leaching was  $2709 \text{ mg}\cdot\text{kg}^{-1}$  (Figure 2b).



**Figure 2.** Lead-contaminated soil is remediated by HCl: (a) remediation efficiency, (b) Pb content in soil after leaching.

#### 3.1.4. Effect of Stirring Time

According to the results of the orthogonal experiment, stirring time also has effect on the remediation efficiency by HCl, but appropriate leaching time could shorten the period of soil remediation as well as reduce costs. Therefore, we had made a stirring time experiment in order to find a suitable stirring time, and the results are shown in Figure 3. When the stirring time was 0.5 h, the remediation efficiency was 66%, and it reached 70.3% at 1 h. When the stirring time exceeded 1 h, the repair efficiency decreased slightly and then stabilized, indicating that HCl reacted with the lead in the soil and reached equilibrium quickly. With further prolonged stirring time, there was no significant improvement in remediation efficiency. Thus, 1 h of stirring is usually enough for the extraction of pollutants.



**Figure 3.** Lead-contaminated soil is remediated by  $0.2 \text{ mol}\cdot\text{L}^{-1}$  HCl: (a) remediation efficiency, (b) Pb content in soil after leaching.

Therefore, considering various factors for remediating the heavy Pb-contaminated soil, such as leaching cost, soil property after leaching, remediation period, etc., for the inorganic acid leaching system, HCl performed better in terms of its removal effect of lead, and the optimum concentration was  $0.2 \text{ mol}\cdot\text{L}^{-1}$ , the optimal solid-to-liquid ratio was 1:20,

and the optimal stirring time was 1 h. Herein, the remediation efficiency of Pb was 70.3%, and the content of lead in soil after leaching was  $2388 \text{ mg}\cdot\text{kg}^{-1}$ ; however, the pH value of detoxifying soil was 3.88.

### 3.2. Soil Leaching by Low-Molecular-Weight Organic Acids

Although HCl can effectively remove lead in contaminated soil, it will cause serious soil acidification due to its strong acidity, and the pH of the soil after leaching is 3.88. It has been found that organic acids, such as CA and MA, can effectively remove soil lead pollutants. The leaching process is mild and has good biodegradability [37,38]; therefore, we used organic acids to conduct the leaching experiments.

#### 3.2.1. Effects of Organic Acids on the Lead Removal from Protogenetic Soil

Five kinds of inorganic acids (CA, OA, TA, AA, and MA) were used for leaching remediation of lead-contaminated soil. The remediation results are shown in Figure 4. It can be seen that under the same leaching conditions, CA showed the highest leaching efficiency of  $\text{Pb}^{2+}$  in contaminated soil, reaching 61.4%, which is slightly higher than that of MA, i.e., 58.5%, followed by AA, while TA and OA had a weak ability to leach  $\text{Pb}^{2+}$  from soil. Compared with inorganic acids such as HCl, the remediation efficiency of organic acids was not much lower. Generally speaking, the remediation ability of organic acids to heavy metals is related to the number of functional groups such as hydroxyl and carboxyl groups. CA is a tribasic acid, which can provide more reaction sites and more  $\text{H}^+$  at the same time, so it has a strong acid dissolving effect and can dissolve lead ions adsorbed in the soil; in addition, it is also a natural chelate agent, with a certain complexing ability; that is, it can couple with  $\text{Pb}^{2+}$  in the soil to form soluble complexes, enhancing the activity and mobility of the  $\text{Pb}^{2+}$  so as to be leached out. TA and OA are both dicarboxylic acids and have fewer reaction sites, which could provide limited acidity and acid radical ions. In addition, their acid radical ions, such as oxalic acid ions, could further react with  $\text{Pb}^{2+}$ , as shown in Equation (12) and form insoluble compounds  $\text{PbC}_2\text{O}_4$  ( $K_{\text{sp}} = 4.8 \times 10^{-10}$ ) [39], thereby inhibiting the leaching of  $\text{Pb}^{2+}$ , leading to the lower remediation efficiency. Hence, CA presents the best repair effect.

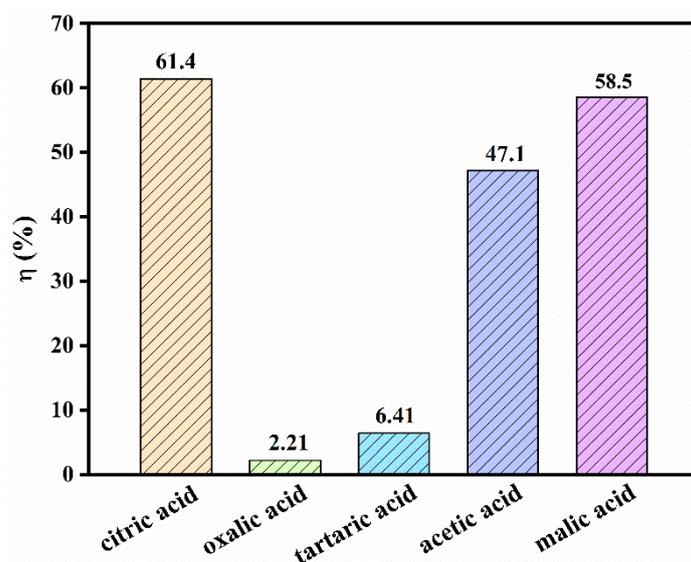


Figure 4. Remediation efficiency of five organic acids.



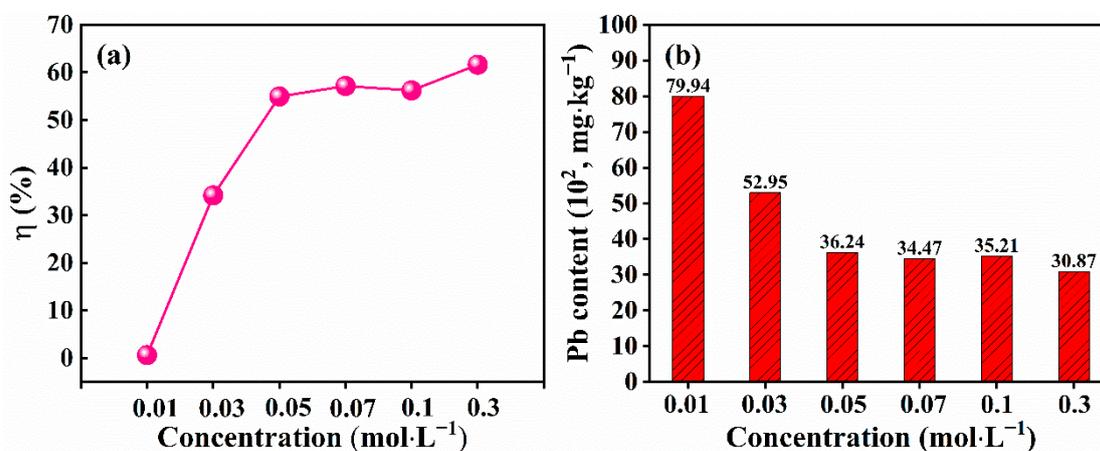
### 3.2.2. Effect of CA Leaching Conditions in Orthogonal Experiment

Three important parameters of the leaching process, i.e., the concentration of CA, stirring time, and solid-to-liquid ratio, were investigated through the orthogonal experiment, and the results are shown in Table S4. The  $R$  values of three factors were 50.4%, 20.32%, and 38.97%, respectively, indicating that the CA concentration is the most important factor, followed by the solid-to-liquid ratio, and finally the stirring time. For the CA concentration, as it changed from 0.01 to 0.2 mol·L<sup>-1</sup>, the  $k$  value increased significantly, from 0.81% to 51.21%. The remediation efficiency of Pb increases linearly with the increase in the concentration, indicating that the higher the concentration of CA, the more the chelating reaction of lead ions is directly promoted, and the more lead ions it can bind to.

As the solid-liquid ratio decreases from 1:10 to 1:25, the  $R$  value increases from 8.28% to 47.25%, meaning that the leaching effect was inversely proportional to the solid-to-liquid ratio, probably because the essence of reducing the solid-to-liquid ratio is to increase the amount of eluent. Since decreasing the solid-to-liquid ratio will greatly increase the cost, the appropriate solid-to-liquid ratio was set to 1:20 in the following experiment, because there was only a slight improvement from 1:20 to 1:25. The stirring time also had a certain effect on the repair effect. In the orthogonal experiment, the remediation efficiency was inversely proportional to the stirring time. The  $R$  value decreased from 33.19% to 12.87% when the stirring time was lengthened from 8 h to 48 h. Therefore, 8 h was chosen as the stirring time for the subsequent leaching experiment of CA.

### 3.2.3. Effect of CA Concentration

Consequently, a concentration experiment was carried out, and the concentration gradient was designed to be 0.01, 0.03, 0.05, 0.07, 0.1, and 0.3 mol·L<sup>-1</sup>. The results are shown in Figure 5. With the increase in CA concentration from 0.01 to 0.3 mol·L<sup>-1</sup>, the remediation efficiency of Pb increased from 0.61% to 61.6% (Figure 5a), and the content of Pb decreased from 7994 to 3087 mg·kg<sup>-1</sup> (Figure 5b), which is slightly lower than that of HCl. When the concentration of CA was too low, such as 0.01 mol·L<sup>-1</sup>, the remediation efficiency was very poor. This may be because the CA content was too low to dissolve lead ions. The remediation efficiency was significantly increased and reached 54.9%, while the concentration of CA increased from 0.01 to 0.05 mol·L<sup>-1</sup>. Herein, CA had strong acid dissolving effect and complexing ability. Generally speaking, the higher the concentration of CA is, the more lead ions are complexed. However, when the concentration exceeded 0.05 mol·L<sup>-1</sup>, there was little increase in the remediation efficiency, which may be that the complexing capacity of CA had reached its limit. Lead in contaminated soil, such as residual lead, is usually difficult to leach using CA. Hence, 0.05 mol·L<sup>-1</sup> was chosen as the optimum reaction concentration for the leaching experiments.



**Figure 5.** Lead-contaminated soil is remediated by CA: (a) remediation efficiency, (b) Pb content in soil after leaching.

Not only is the removal effect of CA on lead related to acid dissolution effect, but it also depends on the complexation ability of the anion acid group to a certain extent. In order to further understand the removal mechanism of metal ions by CA, it is necessary to consider the interaction between lead ions and anionic ligands, and the complex characteristic of CA and lead ions forming a variety of 1:1 stable soluble complexes. As reported in [40], CA can be dissociated into four forms ( $H_3A$ ,  $H_2A^-$ ,  $HA^{2-}$ ,  $A^{3-}$ ) in solution if it is expressed as  $H_3A$ , so the reaction between the lead ion and the anion of CA under different pH conditions can be interpreted as follows:



The order of the complexation equilibrium constant of CA and lead ions is as follows:  $(PbA)^- > (PbH_2A)^+ > PbHA$  [40]. When the temperature is fixed, the existing forms of CA are only related to pH. When  $pH < 4$ , strong acidic conditions are conducive to the dissociation of  $Pb^{2+}$  from soil colloids, and the complexation is strong at the same time. Therefore, CA has a higher remediation efficiency of lead at low pH ( $< 4$ ), and the existing form of lead complexes is mainly  $(PbH_2A)^+$ .  $H_2A^-$  gradually transforms into  $HA^{2-}$  and a small amount of  $A^{3-}$  when pH is between 4 and 6. At present, the acid dissolution effect of CA is weak, and the complexing ability plays a leading role. The main existing form of lead complexes is  $(PbHA)$ . A further increase in pH will lead to the complete failure of acid dissolution effect, and only complex Pb is produced. Although the complexation ability of CA is strong at this time, the remediation efficiency is low due to the hydrolysis of  $Pb^{2+}$ . As a result, the acid dissolution's effect and complexation ability play different roles at different pH values, and the pH value is affected by CA concentration, which is the essence of changing the CA concentration and thus affecting the remediation efficiency.

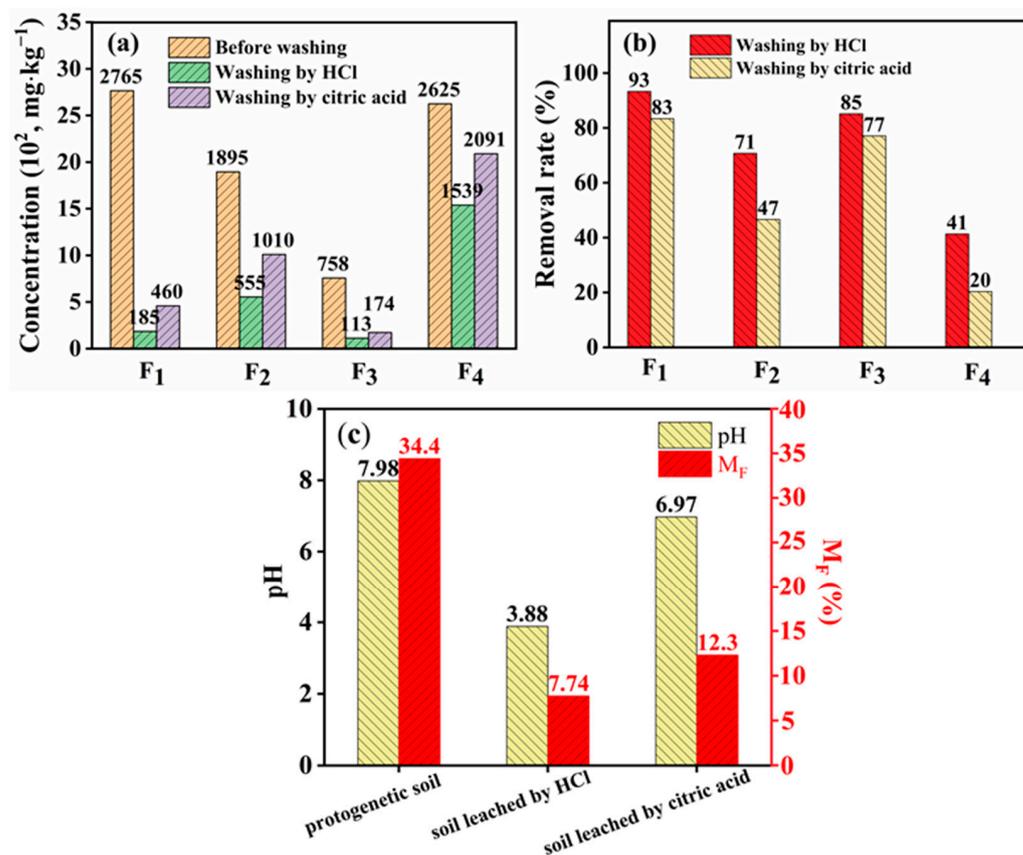
Combined with Table S4 and Figure 5 and factors such as the cost of soil remediation, the harm of the eluent to the soil, and the efficiency of remediation are considered. The best remediation efficiency of CA achieved is 53.6% under the optimal conditions, that is, when the concentration of CA is  $0.05 \text{ mol}\cdot\text{L}^{-1}$ , the solid–liquid ratio is 1:20, the stirring time is 8 h, the content of lead in soil after leaching is  $3732.0 \text{ mg}\cdot\text{kg}^{-1}$ , and the pH value is 6.97. Compared with  $0.2 \text{ mol}\cdot\text{L}^{-1}$  HCl leaching, the remediation efficiency of CA is slightly lower, but the leaching concentration is much lower than HCl, only one quarter of that of HCl. At the same time, the pH of the soil after leaching is neutral and closer to the protogenetic soil, while HCl leaching causes serious acidification of the soil. Therefore, CA is more suitable for lead-contaminated soil remediation than HCl.

### 3.3. Effects of Leaching on Lead Speciation and Soil Quality

The biological toxicity of heavy metals in soil is not only determined by its total amount; it is more dependent on the existing forms. Hence, the speciation analysis of heavy metals in soil will help to further explore the effectiveness of the repair technology, degrading the bioavailability of heavy metals. For this reason, this study further compared the speciation evolution of lead in contaminated soil before and after leaching with HCl and CA, respectively. Under optimal conditions, lead was separately leached by HCl and CA from the contaminated soil. The lead speciation in soil after leaching was divided into four fractions and measured by a modified three-step sequential extraction BCR procedure.

The speciation concentration distribution of lead in soil before and after leaching with  $0.02 \text{ mol}\cdot\text{L}^{-1}$  HCl and  $0.05 \text{ mol}\cdot\text{L}^{-1}$  CA are shown in Figure 6a, respectively. In the protogenetic soil, the existing forms of lead are mainly acid-soluble and residual fractions. The content of acid-soluble lead is as high as  $2765 \text{ mg}\cdot\text{kg}^{-1}$ , accounting for 34.4% of the total lead, indicating that much of the lead in the contaminated soil has a high mobility and bioavailability. The content of residual lead is  $2625 \text{ mg}\cdot\text{kg}^{-1}$ , accounting for 32.6% of the total lead, and it mainly exists in soil crystal lattices such as silicate and primary

and secondary minerals, which is the result of natural geological weathering processes. Compared with other forms lead, it is not easily released under normal conditions and can be stable in the sediment for a long time. The  $M_F$  value of protogenetic soil, as shown in Figure 6c, is 34.4%; that is, such higher mobility of Pb will lead to the great soil toxicity and harmfulness.



**Figure 6.** Speciation distribution of Pb in soils before and after leaching: (a) concentration of different forms of Pb, (b) removal rates of different forms of Pb, (c) the  $M_F$  value and pH of soil before and after leaching. F<sub>1</sub>: Acid-soluble fraction. F<sub>2</sub>: Reducible fraction. F<sub>3</sub>: Oxidizable fraction. F<sub>4</sub>: Residual fraction.

It can be seen from Figure 6a,b that, after leaching, the form distribution of lead in the soil changed greatly, and the contents of the acid-soluble fraction, reducible fraction, oxidizable fraction, and residual fraction decreased, and the acid-soluble state decreased the most. Ke [40] indicated that CA can mainly remove exchangeable, carbonate-bound, oxide-bound forms of the four heavy metals after leaching, which is similar to our results. The acid-soluble lead is mainly composed of two parts: one is the clay minerals adsorbed on the sediment and other components; the other part is the lead combined with the carbonate precipitation. The acid-soluble fraction is a very unstable form because it is sensitive to environmental changes and easily migrates and transforms. Especially at a low pH, it can easily be washed out. The results showed that, after leaching by HCl and CA, the content of acid-soluble lead in the soil decreased from  $2765 \text{ mg}\cdot\text{kg}^{-1}$  to 185 and  $460 \text{ mg}\cdot\text{kg}^{-1}$ , a decrease of 93% and 83%, respectively, indicating that the removal capacity of CA to the active lead fraction is comparable to that of HCl. Furthermore, the  $M_F$  values of the soil were 7.74% and 12.3%, and the pH values of the soil were 3.88 and 6.97, respectively. Both of them can obviously reduce the mobility of lead ions in the soil and its biological toxicity, but the high-concentration HCl leaching will make the soil severely acidified, destroying its structure.

The removal ability of HCl for other less active lead fractions is stronger than CA, which is why HCl acid has a higher remediation efficiency for lead-contaminated soil. The reducible fraction mainly refers to the part combined with oxides such as Fe and Mn in the soil. The pH value fluctuation of soil and redox conditions has important effects on the reducible fraction. After leaching with HCl, a large amount of iron and manganese was extracted during the leaching process, resulting in a reduction in the reducible lead content from 1895 mg·kg<sup>-1</sup> to 555 mg·kg<sup>-1</sup>, a decrease of 71%. Compared with HCl, the remediation efficiency of CA for the reducible lead was only 47% because of its weak acidity and oxidation reduction. The oxidizable fraction usually refers to lead binding with OM and sulfide in soil. Since the soil used in this study contains high OM (Table 1), the oxidizable lead could be easily removed by the chelation of Cl<sup>-</sup> and CA. The residue fraction is usually relatively stable, but the residual lead in soil after leaching by HCl and CA also decreased by 41% and 20%, respectively. This may be due to the dynamic equilibrium of lead forms in the soil. When the other forms of lead (acid-soluble fraction, reducible fraction, and oxidizable fraction) are consumed, part of the residual lead will be converted into them [41].

A 0.05 mol·L<sup>-1</sup> concentration of CA has a high removal rate of 83% for the highly active, acid-soluble lead in contaminated soil, and the removal rate of the oxidizable lead is as high as 77%, which was comparable to 0.2 mol·L<sup>-1</sup> HCl. CA can reduce the total lead content from 8043 to 3732 mg·kg<sup>-1</sup>, and the remediation efficiency reaches 53.7%. The  $M_F$  value of the soil after leaching by CA is 12.3%, meaning that the mobility of lead is greatly reduced. The pH of the soil after leaching by CA is 6.97, and that of the protogenetic soil is 7.89, indicating that CA is a mild eluent that is biodegradable and causes no secondary pollution, which is very suitable for the remediation of lead-contaminated soil. In the future, compound leaching will be used to further solve the problem that the total lead content in the residue soil after single CA leaching still slightly exceeded the standard.

#### 4. Conclusions

The experiment results show that it is feasible to repair superheavy lead-contaminated protogenetic soil by leaching with inorganic acids and low-molecular-weight organic acids. Among them, HCl and CA had the best leaching effects, respectively. Under optimal conditions, the remediation efficiency of 0.2 mol·L<sup>-1</sup> HCl could reach 70.3%, the Pb content in the leaching soil was 2388 mg·kg<sup>-1</sup>, and 0.05 mol·L<sup>-1</sup> CA leaching could reduce the total amount of soil from 8043 to 3732 mg·kg<sup>-1</sup>, accounting for 53.7%. The remediation efficiency of CA is slightly lower than that of HCl, but the leaching concentration is only a quarter of that of HCl. Most importantly, the pH value of the soil after leaching with CA is 6.97, while that of HCl is 3.88, indicating that leaching by CA causes less damage to the soil.

The results of lead speciation change before and after leaching indicate that the leaching mechanism of HCl can be speculated as being that HCl removes acid-soluble lead and reducible lead through the effect of acid dissolution and oxidizable lead by the complexation of Cl<sup>-</sup>. CA mainly removes acid-soluble lead via its acid dissolution effect and oxidizable lead through its strong complexing ability. The removal rates of acid-soluble lead in soil by HCl and CA are 93% and 83%, and the soil  $M_F$  values are 7.74 % and 12.3%, respectively, meaning that removal capacity of active lead fraction in soil by low-concentration CA is equivalent to that of high-concentration HCl.

As a result, CA is more suitable for leaching remediation of protogenetic lead-contaminated soil with high lead content than HCl. Due to the higher complexity and higher lead content of the protogenetic soil, it is difficult to achieve good results using a single CA for leaching. Therefore, in the future, we may try to use several leaching agents for compound leaching. At the same time, the waste solution generated after washing should be extracted and treated to avoid water pollution.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app12083995/s1>, Table S1. Orthogonal experiment design of HCl leaching.

Table S2. Orthogonal experiment design of CA leaching. Table S3. Orthogonal experiment results and analysis of HCl leaching. Table S4. Orthogonal experiment results and analysis of CA leaching.

**Author Contributions:** L.X.: execution of the experiments and initial draft of the manuscript. X.C.: experiments and analysis. T.Z.: methodology and analysis. M.G.: review and editing of the manuscript. M.Z.: conceptualization, methodology, investigation, writing the original draft of manuscript. All authors have read and agreed to the published version of the manuscript.

**Funding:** National Natural Science Foundation of China (No.U1810205,51972019), and National Key Research and Development Program of China (No. 2019YFC1905702).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** All data generated from this study are available within the text of this manuscript.

**Conflicts of Interest:** The authors declare no conflict of interests.

## Abbreviations

$\eta$	Remediation efficiency
AA	Acetic acid
$F_1$	Acid-soluble fraction lead
CEC	Cation exchange capacity
CA	Citric acid
EDTA	Ethylenediaminetetraacetic acid
MA	Malic acid
$M_F$	Mobility factor
OC	Organic carbon
OM	Organic matter
OA	Oxalic acid
$F_3$	Oxidizable fraction lead
$F_2$	Reducible fraction lead
$F_4$	Residual fraction lead
TA	Tartaric acid

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