

## Article

# Neutralization of Industrial Alkali-Contaminated Soil by Different Agents: Effects and Environmental Impact

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**Abstract:** Industrial soil is susceptible to acid or alkali pollution, but studies focused on the remediation of such soil are still limited. This manuscript investigated the neutralization effect of five agents (hydrochloric acid, citric acid, ferrous sulfate, calcium superphosphate and raw gypsum) to alkali polluted soil. The results showed that regarding the initial pH after the neutralizing agent addition, it was better to set it lower than the target, as the pH would rebound. None of the five agents caused an obvious increase in the heavy metal contents of the leachates, but they all caused an increase in electrical conductivity, which indicated an increase in soil salinity. The leachates showed a luminous gain to *Vibrio fischeri*. However, remediation with hydrochloric acid would cause significant inhibition of germination and root elongation of pakchoi. In addition, the addition of neutralizing agents reshaped the soil microbial community structure in different patterns. Soils treated with hydrochloric acid and ferrous sulfate seemed to improve the microbial richness. The neutralization might be favorable for the biodegradation of polycyclic aromatic hydrocarbons (PAHs), which usually coexist in industrial contaminated soil. In general, the neutralization of alkaline industrial soils using ferrous sulfate, superphosphate and gypsum brought minimal environmental risk, among which ferrous sulfate was the first recommendation in industrial soil after a comprehensive comparison.

**Keywords:** soil pH neutralization; industrial soil remediation; heavy metal release; 16S rRNA sequencing



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## 1. Introduction

Industrial soil contamination has become a critical issue worldwide due to its potential hazards to public health and ecological environment [1,2]. Spills, leaks, or the illegal dumping of caustic chemicals often result in an abnormal soil pH, which poses acute toxicity to human health and a detrimental effect to the soil ecosystem [3,4]. Extreme soil pH also significantly affects the distribution and speciation of heavy metals, thus affecting their mobilization and availability, which exerts an important effect on plant growth [5–7]. In addition, alkalinity will influence the physico-mechanical properties of soil, such as the specific gravity, liquid limit, plastic limit, void ratio, and compression coefficient [8,9]. The mechanical integrity of building materials, such as steel and cement, can also be damaged under extreme soil pH conditions due to corrosion [10,11]. In general, under certain circumstances, industrial acid or alkali polluted soil may pose health, ecological and constructional risk for future use of the land; thus, adjusting the pH of the contaminated soil to relatively neutral range becomes necessary. As a result, although pH is not a routine indicator in site surveys and risk assessments, when extreme pH occurs, it often still requires attention and remediation.

Previous studies usually paid attention to the neutralization of agricultural soil, which suffered extreme pH from natural processes, such as exchanging the calcium and magnesium ions for sodium salt from groundwater or surface water [12,13]. The common chemical

amendments applied to agricultural alkali soils contain calcium chloride, superphosphate, gypsum, sulfur, ferrous sulfate, limestone, etc. [14,15] Among these substances, gypsum-like solid  $\text{Ca}^{2+}$  amendments are the most frequently used chemicals [16]. However, studies that focus on the alkali pollution to industrial soil are quite limited. In industrial soil, other heavy metals or organic pollution are often accompanied with the pH problem. For example, polycyclic aromatic hydrocarbons (PAHs) were detected in the subject soil, although the concentration is lower than the soil environmental risk control standard of China. During industrial soil remediation, not only the influence on plant growth should be considered, but that on human health and groundwater would also be taken into consideration.

In this work, the subject soil came from a caustic soda plant in China, and the strong soil alkalinity resulted from the improper disposal of the materials and products during caustic soda production. Five neutralizing agents were selected for use, among which hydrochloric acid and citric acid were often used in industrial site soil restoration as a pH adjuster, such as in Fenton oxidation technology [17]. Ferrous sulfate, calcium superphosphate and gypsum were usually used in amendments of agricultural alkali soils. This study aims to evaluate the chemical neutralizers based on their efficiency and persistency to treat the industrial alkali contaminated soil, while introducing minimal adverse effect to the soil environment by a series of ex situ experiments. The most suitable neutralizer will be recommended to be applied in the full-size soil remediation project.

## 2. Materials and Methods

### 2.1. Chemicals and Materials

Hydrochloric acid, citric acid, ferrous sulfate, calcium superphosphate and gypsum, which were used as the neutralizers, and potassium dichromate, phenanthroline, potassium chloride, which were used for the determination of soil physical and chemical properties, were of analytical grade, were all purchased from Nanjing Chemical Reagents Co., Ltd. The pakchoi cabbage seeds were purchased from the seed company of Nanjing Agricultural University. Reagents, such as triethanolamine, diethylenetriamine penta-acetic acid (DTPA) and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , which were used in the determination of heavy metals, were obtained from Aladdin Reagent Co., Ltd., Shanghai, P. R. China. Nitric acid used in the soil digestion was also analytical grade.

The test soil was collected from a closed caustic soda factory in Jiangsu Province, with an initial pH above 10. The basic physical and chemical properties are shown in Table 1. After the soil was air-dried, big stones and other debris were removed. Then the soil was ground up and passed through a 2.0 mm mesh screen for use.

**Table 1.** Physiochemical properties of the soil.

Organic Carbon Content (g/kg)	Electrical Conductivity ( $\mu\text{s}/\text{cm}$ )	pH	Field Capacity (g/kg)
$6.77 \pm 0.65$	$266.00 \pm 5.66$	$10.05 \pm 0.06$	$253.22 \pm 10.02$

### 2.2. Experimental Method

The 200.0 g/L solution of hydrochloric acid, citric acid, and ferrous sulfate were prepared for use, and superphosphate and gypsum were used in powder directly due to their low solubility. A series of beakers, each holding 300.0 g of alkaline contaminated soil, were prepared. The neutralizing solution or powder was added into the soil gradually and fully stirred to ensure the homogeneity. The 10.0 g soil was taken out from the beaker, and extra water was supplemented to reach the ultimate soil–water ratio of 1:2.5 to determine the pH, until it reached 6.5 or 8.0. Then deionized water was added to each beaker to keep the soil water content of 45.0 mL/300.0 g, which was about 60% of its water holding capacity. After mixing thoroughly, the beaker was wrapped in aluminum foil and stored in a biochemical incubator at 20 °C in the dark. On the 0, 1st, 3rd, 8th, 15th and 28th days, 10.0 g of soil was sampled, respectively, to measure the soil pH. After 28 days, 60.0 g of soil was

taken to evaluate the growth inhibition to the pakchoi cabbage. Then, 10.0 g soil was taken and freeze-dried for DNA extraction and 16S rRNA amplification and sequencing. Another 30.0 g soil in the reactors was used to prepare the leachate. A vessel containing 30.0 g soil and 300.0 mL deionized water was tightly capped and shaken on a horizontal oscillator for 8 h before standing for 16 h. After the leachate was filtered, its pH, conductivity, heavy metal content, and luminescence inhibition were measured. Only deionized water was added to the alkaline soil in the control group. Other treatments were the same as the experimental groups. All treatments were carried out in triplicate.

### 2.3. Analysis Method

The organic carbon content of soil was determined by the potassium dichromate oxidation spectrophotometric method. Briefly, ground soil samples were oxidized using a  $K_2Cr_2O_7-H_2SO_4$  solution at 180 °C, and the organic content was determined by the titration method with  $FeSO_4$  standard solution. The soil was oscillated sufficiently with deionized water (m/V = 1:5), and the electrical conductivity was measured using a conductivity meter (DDSJ 308A, Leici instrument Co., Shanghai, China) after the water was filtrated. The soil pH was determined using a pH meter and probe (PB-10, Sartorius Ltd., Göttingen, Germany) after sufficient oscillation of the soil and deionized water. Considering the water volume in the neutralizing solution or cultivation system, the ultimate soil–water ratio reached 1:2.5 for pH determination. The field water-holding capacity was obtained from periodical measurements of soil water content, after 8 h of continued infiltration [18].

The 60.0 g of soil was put in a glass petri dish and equilibrated for 48 h before 10 equal-sized cabbage seeds were selected for planting. The incubation was held in a constant temperature incubator at  $25\text{ °C} \pm 1\text{ °C}$  in the dark. Soil used in the control groups was collected from the vicinity of the soda plant, which had a neutral pH and was free of other contaminations. When the seed in control groups had a germination rate of no less than 65% and the root elongation reached 20 mm, the tests were terminated. The germination ratio and average root length for each treatment were determined as a result.

The pH and conductivity of the leachate was measured after filtration. The Cr, Ni, Cu, Zn, Cd, Pb and As concentrations of the leachates were analyzed on an inductively coupled plasma mass spectrometer (iCAP TQ ICP-MS, Thermo Fisher Scientific, Bremen, Germany) after digestion by 2:1 nitric acid to hydrochloric acid.

The toxicity test was performed by Microtox assay with a DeltaTox<sup>®</sup> II water toxicity detector (SDIX, Newark, NJ, USA) in terms of bioluminescence inhibition of the marine bacteria *Vibrio fischeri* (*V. fischeri*) after 15 min of exposure.

### 2.4. Characterization of Bacterial Communities

We investigated the patterns of bacterial communities in different soil samples using high-throughput sequencing. Total genome DNA from samples was extracted using the CTAB/SDS method. The V4–V5 region of bacterial 16S rRNA gene was amplified, quantified, and purified. Sequencing libraries were generated using TruSeq<sup>®</sup> DNA PCR-Free Sample Preparation Kit (Illumina, San Diego, CA, USA). The library quality was assessed on the Qubit<sup>®</sup> 2.0 Fluorometer (Thermo Scientific, Waltham, MA, USA) and Agilent Bioanalyzer 2100 system. At last, the library was sequenced on an Illumina NovaSeq 6000 platform and 250 bp paired-end reads were generated. Using usearch software (11.0.667), sequences with more than 97% similarity level were clustered as the same open-reference operational taxonomic unit (OUT). The alpha diversity, as evaluated by Shannon and Chao1 index, was used to characterize soil bacterial richness [19]. Principal coordinate analysis (PCoA, beta diversity) was carried out using the weighted UniFrac distance matrices, and then generated in R using the “ade4” package. To identify the bacterial taxa that tend to colonize specific soil, the LEfSe tool was applied. Bacterial taxa with linear discriminant analysis (LDA) scores > 4.0 were deemed as biomarkers. The functional genes prediction was conducted by Phylogenetic Investigation of Communities by Reconstruction of Unobserved States (PICRUSt).

### 3. Results and Conclusions

#### 3.1. Remediation Agent Dosage

The pH of the soil was neutralized to pH 6.5 and 8.0, respectively. The amount of the five remediation agents added and the actually achieved pH are shown in Table 2. Among them, the gypsum reduced the soil to about pH 8.2 at most; the reason may be the pH limitation of gypsum itself. In addition, it should be noticed that the additive dose of calcium superphosphate and gypsum was obviously higher than the soluble neutralizers. The excess addition may disturb the earthwork balance during the remediation engineering and result in increased costs, which was not considered a scientific problem, but a practical one. The increased earthwork was hardly needed to be considered in the agricultural soil reclamation.

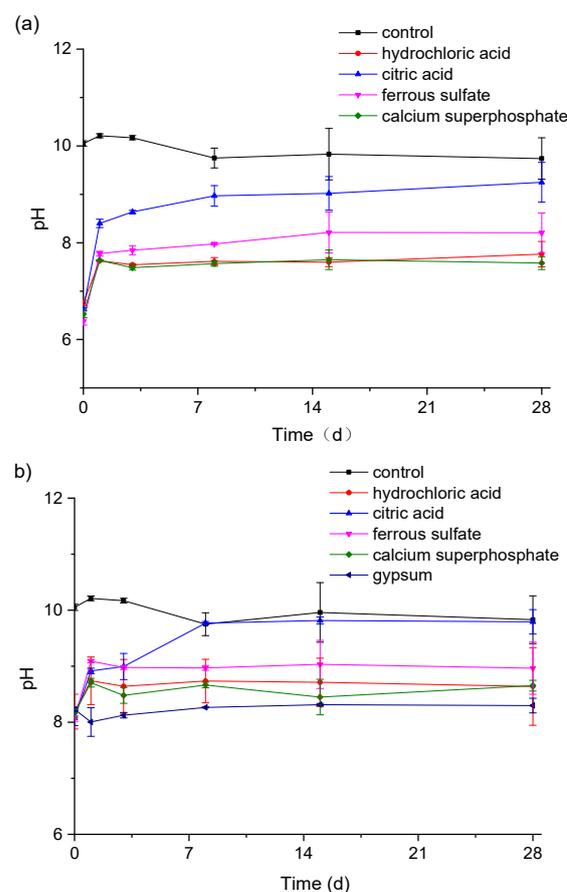
**Table 2.** Remediation agent dosage <sup>(a)</sup> and the actually achieved soil pH.

Remediation Agent	Dosage <sup>(b)</sup> (g)	pH	Dosage (g)	pH
hydrochloric acid	1.07 ± 0.03	6.56 ± 0.14	0.09 ± 0.01	8.19 ± 0.31
citric acid	2.24 ± 0.05	6.54 ± 0.09	0.45 ± 0.03	8.08 ± 0.13
ferrous sulfate	3.02 ± 0.08	6.41 ± 0.09	0.29 ± 0.01	8.07 ± 0.05
calcium superphosphate	10.69 ± 0.13	6.52 ± 0.06	1.11 ± 0.11	8.16 ± 0.07
gypsum	-	-	45.00 ± 1.20	8.22 ± 0.03

<sup>(a)</sup> The original soil is 100.0 g with pH 10.05 ± 0.06. <sup>(b)</sup> The dosage is solute weight as in aqueous solution.

#### 3.2. Persistency of Neutralization Effect

The change in soil pH after the neutralizer addition is shown in Figure 1.



**Figure 1.** The soil pH change after the agent addition when (a) pH was adjusted to 6.5 and (b) adjusted to 8.0.

The pH rose again after the neutralizer addition in a short time, except for the gypsum, and then became stable gradually. As the soil alkalization might result from both sodium and hydroxyl ion, the rebound of pH might be caused by the release of both ions from soil grain. After the soil pH was reduced to 6.5, hydrochloric acid and calcium superphosphate demonstrated the strongest capacity to prevent pH from rebounding. The soils did not exceed pH 8.0 after 28 days. Soil amended with ferrous sulfate achieved a pH of about 8.2 after 15 days and remained stable ever since. Soil amended with citric acid rebounded rapidly in a short time and continued to rise gradually even after 28 days. When the soil was remediated to pH 8.0, none of hydrochloric acid, citric acid, ferrous sulfate and calcium superphosphate showed long term pH retention abilities. Among five additives, although gypsum reduced the soil pH to 8.2 at most, it could inhibit the rebound of the soil pH quite well. One possible reason was the high additive dosage. It is recommended that the soil be adjusted to initial pH 6.5 or below except gypsum to ensure the long-term neutralizing effects.

### 3.3. pH and Conductivity of the Leachate

The pH and conductivity of the soil leachate reflect the potential of releasing hydroxide and salinity from the contaminated soil to the surrounding environment, which may adversely affect the soil ecosystem and groundwater quality. In this study, soil leachates in groups where soil was amended to pH 6.5 with hydrochloric acid, citric acid, ferrous sulfate and calcium superphosphate, and that where it was amended to pH 8.2 with gypsum were prepared after 28 days after the neutralization agent addition. The pH and conductivity of the soil leachates are shown in Table 3.

**Table 3.** The leachate pH and conductivity after the neutralization for 28 days.

Group	pH	Conductivity ( $\mu\text{s}/\text{cm}$ )
control	$9.825 \pm 0.021$	$266.0 \pm 5.66$
hydrochloric acid	$8.395 \pm 0.049$	$2780.0 \pm 70.71$
citric acid	$8.200 \pm 0.099$	$1598.5 \pm 51.62$
ferrous sulfate	$8.515 \pm 0.035$	$383.0 \pm 4.24$
calcium superphosphate	$7.505 \pm 0.049$	$743.5 \pm 10.61$
gypsum	$8.085 \pm 0.021$	$2570.0 \pm 14.14$

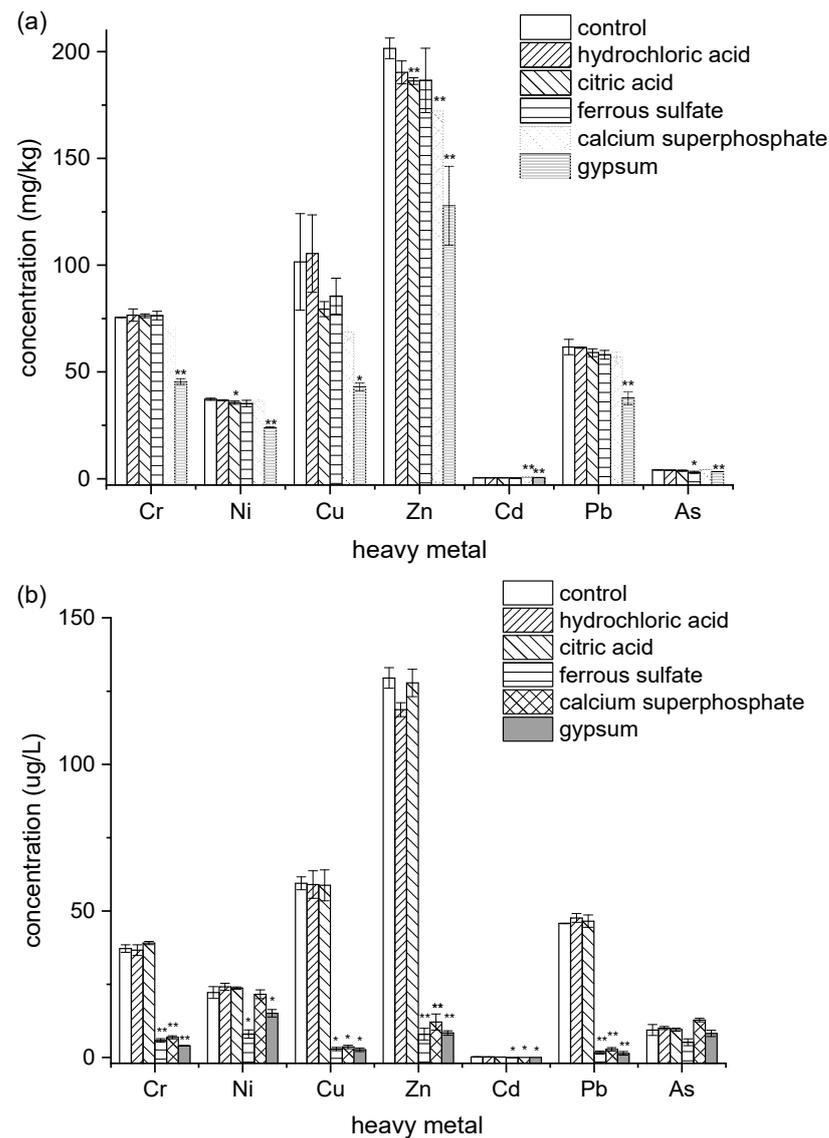
As is shown in Table 3, the pH values of the soil leachates amended with three soluble neutralizing agents of hydrochloric acid, citric acid and ferrous sulfate were all close to 8.5. The pH of citric acid neutralized soil leachate was the lowest, followed by hydrochloric acid and ferrous sulfate. It is a little different from the soil pH after 28 days of incubation, especially for citric acid. It seems that citric acid was more inclined to decrease the pH of the leachate compared to the soil. The reason might be that the organic acid had so big a volume that it was difficult for it to enter the soil pores. In general, when the soil pH was restored to about 6.5 (gypsum to 8.2), hydrochloric acid, ferrous sulfate, calcium superphosphate and gypsum not only had good stabilization effects on the soil pH, but also brought acceptable change to the pH of soil leachates. The calcium superphosphate and gypsum had the best stabilizing effects of all. The reason may be that the application of superphosphate or gypsum could increase the concentration of  $\text{Ca}^{2+}$  in the soil and reduce the concentration ratio of  $\text{Na}^+/\text{Ca}^{2+}$ . The  $\text{Ca}^{2+}$  entered soil colloids to amend the soil alkalinity [20,21].

Soil electrical conductivity reflects the state of soil salinity. The salt content of soil solution is positively correlated with the electrical conductivity in a specific range, which will affect the transformation, speciation and availability of soil nutrients and pollutants [22,23]. The electrical conductivity of the soil leachates is also shown in Table 3. It can be seen that when the pH was reduced to 6.5 (gypsum to pH 8.2), five remediation agents all caused increases in electrical conductivity. Among them, the degree of increase caused by hydrochloric acid, gypsum, and citric acid was quite obvious. The probable causes are that hydrochloric acid brought a large amount of  $\text{Cl}^-$  into the soil, and gypsum introduced  $\text{SO}_4^{2-}$  and exchanged

$\text{Ca}^{2+}$  for  $\text{Na}^+$  in the soil colloid [24,25]. The citric acid has metal ion complexing actions [26,27]. All of these led to a significant increase in electrical conductivity.

### 3.4. Heavy Metal Content in Soil and Leachate

Since pH is an important factor affecting the migration and transformation of heavy metals [28], this study investigated the concentrations of seven common heavy metals (Cr, Ni, Cu, Zn, Cd, Pb, and As) in the soil and leachates. The results are shown in Figure 2 when the soil was neutralized to pH 6.5 with hydrochloric acid, citric acid, ferrous sulfate, and superphosphate, and to pH 8.2 with gypsum.



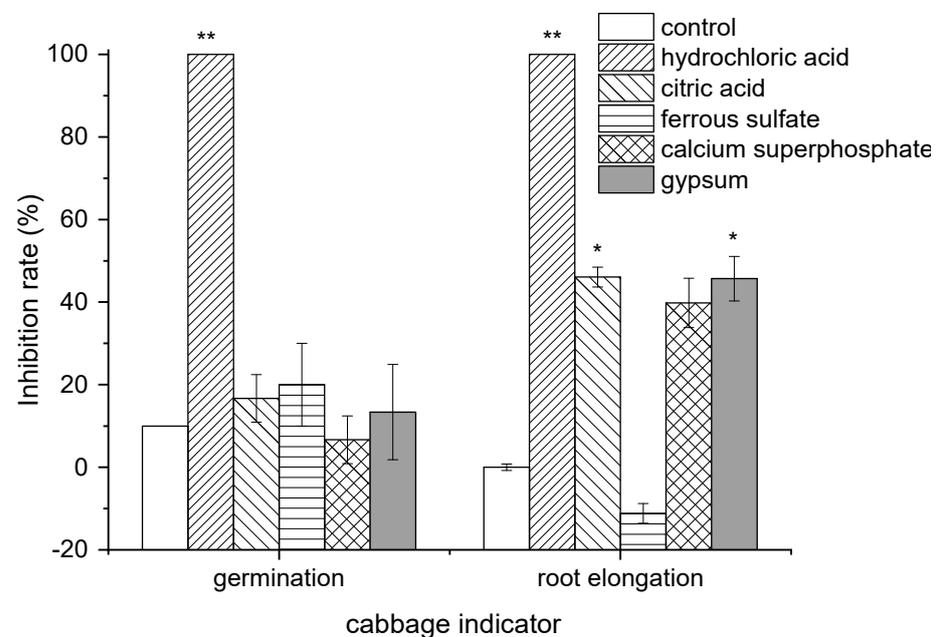
**Figure 2.** Heavy metal concentrations in (a) soil and (b) leachate after neutralization, in which \*, \*\* mean the difference compared with the control at the 0.05 and 0.01 level, respectively.

It can be seen from Figure 2a that hydrochloric acid, citric acid and ferrous sulfate had little significant effect on the content of seven heavy metals in soil. Calcium superphosphate reduced the content of Cu and Zn in soil. Gypsum reduced the content of seven heavy metals in the soil significantly ( $p < 0.05$  or  $p < 0.01$ ). The reason might be the high additive amount of neutralizer, which diluted the heavy metal content in the soil. It is worth noting that calcium superphosphate and gypsum increased the Cd content in the soil, which reminded us of the impurities introduced by neutralizers. Although the neutralization led to

a decrease in soil pH, the heavy metal contents in the leachates did not increase significantly. Conversely, the contents of some heavy metals in the leachates were reduced, especially by ferrous sulfate, calcium superphosphate, and gypsum. The possible reason for the decrease in heavy metal concentration by ferrous sulfate is the  $\text{Fe}(\text{OH})_2/\text{Fe}(\text{OH})_3$  coprecipitation [29]. The reason why superphosphate and gypsum reduced the concentrations of heavy metals in the leachates is their stabilizing effects [30]. It is noteworthy that the commonly used industrial grade calcium superphosphate often contained arsenic [31], thus had a risk of increasing arsenic levels in the soil and leachate, although no significant differences were observed in this study. In general, the neutralization processes did not cause an increase in the metal contents of the leachate, and conversely demonstrated a positive effect on the stabilization of heavy metals.

### 3.5. Soil and Leachate Toxicity after Neutralization

The inhibition effect on the seed germination and root elongation of pakchoi is shown in Figure 3 when the soil is restored to pH 6.5 with hydrochloric acid, citric acid, ferrous sulfate, and superphosphate, and to pH 8.2 with gypsum, respectively.



**Figure 3.** Inhibition of germination and root elongation of pakchoi after neutralization, in which \*, \*\* mean the difference compared with the control at the 0.05 and 0.01 level, respectively.

It can be seen from the figure that when the soil pH is reduced to 6.5 with hydrochloric acid, the soil germination inhibition rate is 100%. The possible reason is that hydrochloric acid brought lots of inorganic salt ions, which led to a significant increase in soil salinity and water loss of seed cells. It could be verified by the conductivity result. The inhibition of seed germination rate by citric acid, ferrous sulfate, superphosphate and gypsum was not significantly different from that of the control.

Similarly, when the soil pH was reduced to 6.5 with hydrochloric acid, the root elongation inhibition rate was 100%. The root length was also inhibited when the soil was neutralized with citric acid, superphosphate and gypsum, and the inhibition rate was around 50%. The inhibition effect of soil remediated with ferrous sulfate was not significantly different from that of the control. In general, there were some correlations between the inhibition and soil leachate conductivity.

The soil leaching solution was subjected to the *V. fischeri* luminescence inhibition test, and the results are shown in Table 4. It can be seen that there was no obvious photoinhibition effect in the control leachate, while the leachates showed an obvious luminous gain in the

treatment groups. One possible reason was that the change in pH reduced the toxicity to luminescent bacteria. The other was that the highly saline conditions favored the growth of *V. fischeri*.

**Table 4.** Luminescence inhibition rate to *V. fischeri*.

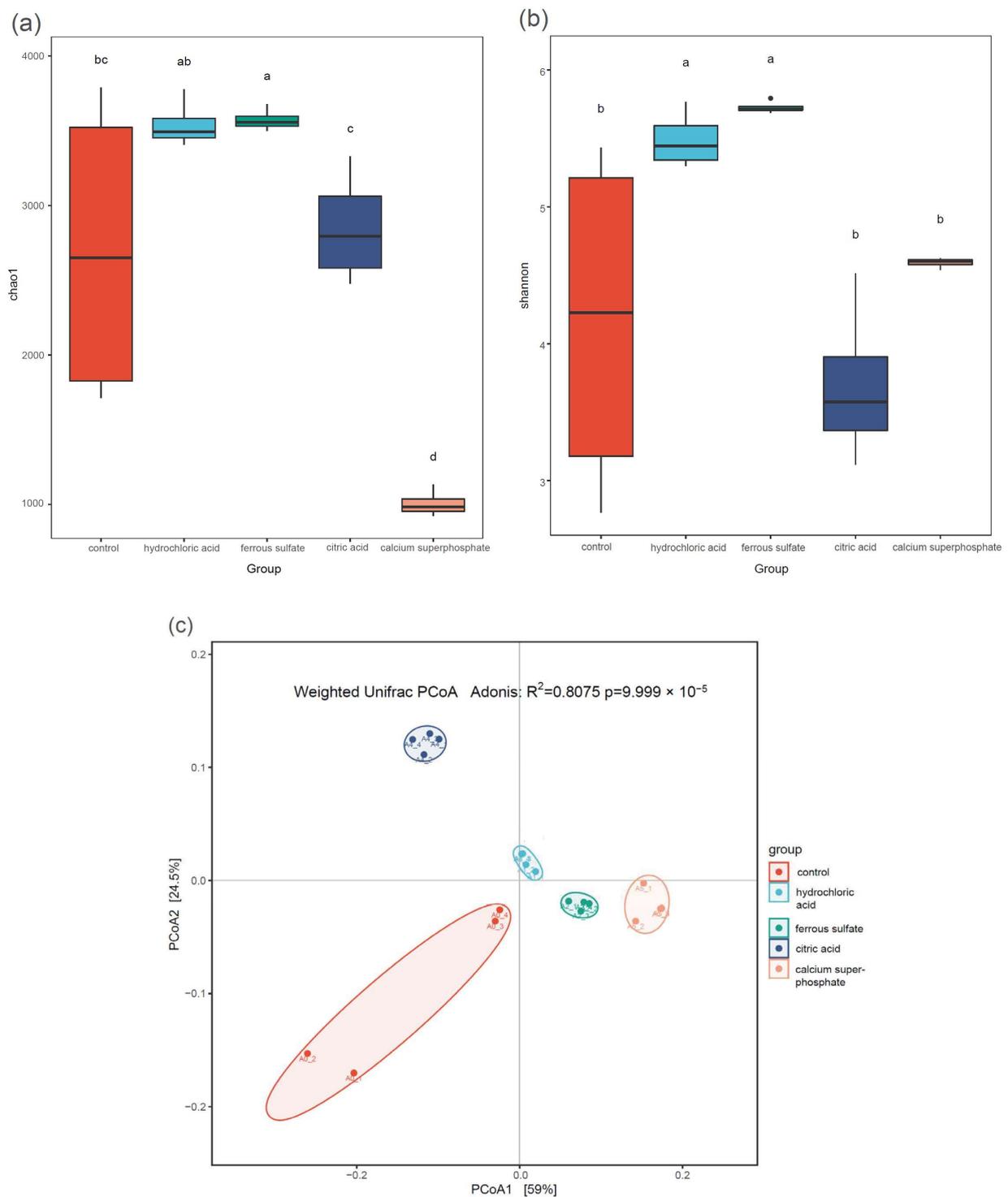
Group	Luminescence Inhibition Rate/% (Average $\pm$ Standard Deviation)
control	$-7.69 \pm 2.58$
hydrochloric acid	$-92.38 \pm 21.14$
citric acid	$-73.77 \pm 5.62$
ferrous sulfate	$-63.62 \pm 6.53$
calcium superphosphate	$-82.71 \pm 7.82$
gypsum	$-71.29 \pm 7.36$

### 3.6. Effect on Soil Microorganisms Using Different Neutralizing Agents

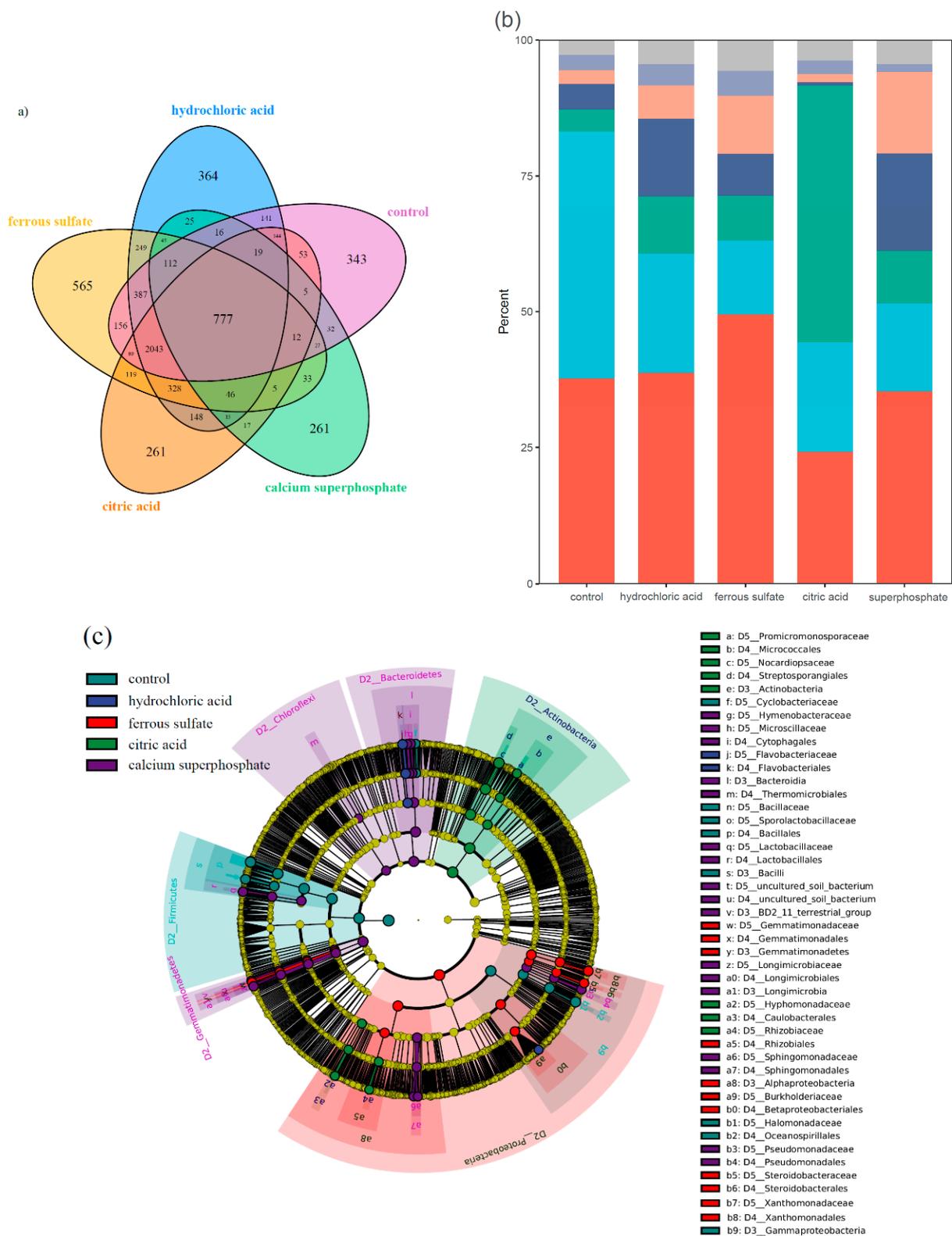
The analysis of soil microbial diversity was performed. The group treated with gypsum obtained insufficient sample abundance, indicating the soil contained limited microorganisms, and hence this group was not used for further microbiological analysis. Bacterial communities in soils treated with ferrous sulfate seemed had the highest  $\alpha$ -diversity, and that treated with hydrochloric acid also had a higher  $\alpha$ -diversity than the control, although the differences were not always statistically significant (Figure 4a,b). PCoA results revealed that the microbial communities of five groups can be clearly separated, suggesting that the neutralizers reshaped the soil microbiomes in variable patterns (Figure 4c, Adonis  $R^2 = 0.8075$ ,  $p = 9.999 \times 10^{-5}$ ).

The analysis of microbial community composition between the treated groups was further carried out. The Venn diagram of Figure 5a shows unique and shared bacterial OTUs of different treated soils. Here, the control group contained 343 unique OTUs, and samples treated with hydrochloric acid, citric acid, ferrous sulfate, calcium superphosphate contained 364, 261, 565, and 261 unique OTUs, respectively. The five samples had 777 OTUs in common. The hydrochloric acid and control shared a minimum of 3639 OTUs, citric acid and control shared 3152 OTUs, ferrous sulfate and control shared 3613 OTUs, while the OTUs shared by calcium superphosphate and control was 1000.

In addition, the composition of the bacterial structure from the soil samples had an apparent difference. As shown in Figure 5b,c, the order of *Bacillales* and *Oceanospirillales*, which belonged to *Firmicutes* and *Proteobacteria* respectively, accounted for a large proportion of the control but was significantly reduced in all the treated groups. It is consistent with the previous study reporting that the abundance of *Proteobacteria* and *Firmicutes* could be altered by soil texture, organic carbon and heavy metal contents easily [32]. In hydrochloric acid group, the order of *Flavobacteriales* was abundant. In ferrous sulfate group, the order of *Rhizobiales*, *Betaproteobacteriales*, *Steroidobacteriales* and *Xanthomonadales* were significantly abundant, most of which belong to *Proteobacteria*. Increased abundance of *Proteobacteria* is often beneficial to soil health or indicates a strong resistance of soil microorganisms to toxic substances [33]. *Proteobacteria* also contains a variety of metalophilic bacteria, which are predominant in metal-rich environments and has the ability to biomineralize metal elements [34]. The order of *Micrococcales*, *Streptosporangiales* and *Caulobacteriales* has higher abundance in citric acid group. It has been revealed that the phylum of *Actinobacteria*, which was significantly abundant in citric acid group, had a great potential for biodegradation of organic and inorganic toxic compounds [35,36]. The order of *Cytophagales*, *Thermomicrobiales*, *Lactobacillales*, *Longimicrobiales*, *Sphingomonadales* and *Pseudomonadales* were significantly abundant in calcium superphosphate treated groups, in which *Thermomicrobiales*, belonging to *Chloroflexi*, have been previously described as soil oligotrophs [37]. In addition, the PICRUSt showed that the neutralized soil, whatever the agents, would favor the biodegradation of PAHs, which coexisted in the subject soil at a low level and were widely distributed in industrial contaminated soil [38].



**Figure 4.** Boxplots showing the microbial diversity indices. **(a)** The chao1 index; **(b)** the Shannon index; **(c)** PCoA analysis showing the weighted-UniFrac distance of the communities' beta diversities. In **(a,b)**, the boxes indicate estimates of frequency densities. The upper/lower hinges of boxes represent the 75th/25th quantiles, and the lines inside boxes indicate the median value. The whiskers above/below boxes extend to the maximum/minimum values within  $\leq 1.5$  inter-quantile-range, whereas data points outside the range are plotted separately. a, b, c and d indicate significance at  $p \leq 0.05$ . In **(c)**, samples with high community structure similarity tend to be clustered together, while samples with large community differences will be farther apart.



**Figure 5.** Composition and abundance of different genera from the soils. (a) Venn diagram of the soil samples. (b) Comparison of the bacterial structure from soil samples at the phylum level. (c) LefSe analysis of soil microorganism species under different treatments (LDA > 4).

#### 4. Concluding Remarks

The strong alkali contaminated soils with pH  $10.05 \pm 0.06$  were neutralized by hydrochloric acid, citric acid, ferrous sulfate, calcium superphosphate and gypsum, respectively. The pH of the soils increased rapidly after adding the agents before the pH change became stable, in which the citric acid-remediate soil showed the most obvious rebound. To ensure the long-term neutralizing effect, the agent amounts should be added until a soil pH of 6.5 or below. However, the soil pH could be reduced to about 8.2 at most using raw gypsum, and the amount added reached about 45.0 g/100 g dry soil. None of the five agents caused a significant change in the leachate pH, in which calcium superphosphate and gypsum showed the best stabilizing effect. The agents all caused an increase in electrical conductivity, among which the increase caused by hydrochloric acid, gypsum, and citric acid were quite obvious. After the neutralization, the heavy metal contents of leachates were not significantly increased. On the contrary, ferrous sulfate, superphosphate and gypsum had fair stabilization effects on various metals, but attention should be paid to the fact that industrial grade agents might bring heavy metal impurities in practical use. Remediation with hydrochloric acid would cause a significant inhibition of germination and root elongation of pakchoi. Furthermore, the addition of hydrochloric acid and ferrous sulfate seemed to improve the microbial diversity. The neutralization might be favorable for the biodegradation of PAHs, which usually coexisted in the industrial contaminated soil.

In general, the neutralization of alkaline industrial soils using ferrous sulfate, superphosphate and gypsum caused minimal environmental effects, but it should be noticed that excessive agent addition might disturb the earthwork balance during the remediation engineering. In addition, ferrous ion was a common activator in advanced oxidation, and could reduce Cr(VI) in the soil [39]. This indicates that its addition was also favorable for the removal of other pollutants in the soil, except for alkalinity. As a result, ferrous sulfate is recommended preferentially in this manuscript. In addition, the price of ferrous sulfate was about CNY 1200 per ton in China; considering the additive amount, the engineering price was acceptable. However, it is suggested that an on-site pilot test be carried out before the practical project, as differences usually exist between results in the laboratory and in the field.

**Author Contributions:** T.L. contributed to the original conception and design of the study, and all other authors commented on it. Material preparation, data collection and analysis were performed by J.S., L.Z., S.G. and L.W. The first draft of the manuscript was written by J.S., and other authors, especially T.L., commented on previous versions of the manuscript and helped revise it. All authors have read and agreed to the published version of the manuscript.

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