

Iron containing soil conditioner can effectively reduce cadmium and plumbum pollution in vegetable and soil

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Keywords: Zero-valent iron powder, Soil conditioner, Vegetable, Soil, Heavy metal, Contamination of Cadmium (Cd) and Plumbum (Pb).

Abstract. Some kinds of compound soil conditioners (i.e., Fe₁, Fe₂, Fe₃ and Fe₄) were made from materials including zero-valent iron, sulfur and calcium hydroxide according to a certain weight proportion of them. And a soil-pot trial was conducted to test effects of using those soil conditioners on vegetable yield, contents of cadmium and plumbum in vegetable, and the available contents of cadmium and plumbum in soils. Results indicated that, applying those soil conditioners could increase vegetable's yield, and decrease the contents of cadmium and plumbum in vegetables, enhance soil's pH, but reduce the available contents of Cd and Pb in soils to a certain extent. Among them, the effects of treatment "PS+CF+Fe₄" were relatively the best, it could increase vegetable's yield by 48.54%, decrease the contents of cadmium and plumbum in vegetables by 51.15%~71.31% and 10.63%~68.68%, respectively, and enhance soil's pH by 42.03%, but reduce the available contents of Cd and Pb in soils by 18.01% and 41.04%, respectively. Consequently, this kind of soil conditioner (Fe₄) has a good application prospect in the field of soils, which were suffered from the contaminated by heavy metals Cd or Pb.

Introduction

The heavy metal pollution of farmland soil in China is not optimistic. According to the "National soil pollution Survey Bulletin"^[1], the rate of soil spot pollution exceeding the standard in China is 19.4%, of which mild to moderate pollution points account for 94.3% of the total soil pollution levels, and the types of soil pollution throughout the country are cadmium, mercury, arsenic, copper, lead, chromium, zinc, eight kinds of heavy metals, such as nickel, account for 82.8% of the total. Due to the heavy metal pollution of farmland soil, the heavy metal pollution problem of agricultural products produced on the polluted farmland is becoming more and more serious. It has been reported that the heavy metals in Chinese vegetable soil are higher than those in the field^[2]. Therefore, the heavy metal pollution of vegetable soil is more concerned by the government and the general public.

The remediation techniques by changing the forms of heavy metals in soil, reducing their migration ability and bioavailability are easy to operate by environmental workers because of their low cost and simple operation^[3,4]. The effects of these techniques are fast and suitable for large area farmland pollution control, so it has been paid more and more attention

At present, the main passivator materials used for in situ passivation and remediation of soil heavy metals include: phosphorus containing materials, organic materials, calcium silicate, clay minerals, metal oxides, biochar and new materials. However, the activity of heavy metals passivated by reducing iron powder in situ is rarely reported. Due to the advantages of metal reductive iron, such as low cost, good reducibility and fast reaction rate^[5], since Gillllam and Hannesin proposed that iron scrap can be used for in situ remediation of groundwater contaminated by heavy metals, the

application of metal zero-valent iron to the reduction of heavy metal pollutants in water has become a very active research field. At present, the research on the application of zero-valent iron as a remediation agent for environmental pollution is mainly focused on the reaction of heavy metals in water, including degradation mechanism, reaction kinetics and influencing factors, etc. However, there are few studies on passivation and remediation of soils or sediments contaminated by heavy metals [6,7], especially in vegetable fields contaminated by heavy metals.

In this study, iron powder, sulfur and calcium hydroxide were used as the main materials to prepare several iron-containing heavy metal compound passivator products (i.e., soil conditioners), and were applied to the in situ passivation and remediation of farmland soil contaminated by heavy metals. The effects of using those soil conditioners on vegetables' yield, content of Cd and Pb in vegetables and the available content of Cd and Pb in soils were studied by a soil-pot trial. The aim of this paper is to provide new heavy metal passivator materials for the treatment of heavy metal polluted farmland.

Materials and Methods

The experiment was set up in the simulation room of the Institute of Soil and Fertilizers, Fujian Academy of Agricultural Sciences. The test soil was collected from the Fujian Science and Observation Station for Arable Land Conservation of Xitou Village, Baisha Town, Minhou County, Fujian Province. The soil was unpolluted paddy soil, and the parent material was hilly red soil, and the soil type was Huangnitian. In order to study the decontamination effect of heavy metal detergency agents, artificial addition of exogenous heavy metals were used to prepare experimental soils contaminated by heavy metals. The level of heavy metal pollution was designed to the level of "Soil Environmental Quality Standard" (GB15618-1995) (ie, $Cd \geq 1 \text{ mg} \cdot \text{kg}^{-1}$, $Pb \geq 500 \text{ mg} \cdot \text{kg}^{-1}$), among which Cd uses analytical reagent $Cd(NO_3)_2 \cdot 4H_2O$, Pb uses analytical reagent $Pb(NO_3)_2$.

Seven treatments were designed, namely: (1) Clean soil (without addition of exogenous heavy metals Cd and Pb); (2) Contaminated soil (addition of exogenous heavy metals Cd $1 \text{ mg} \cdot \text{kg}^{-1}$ soil, Pb $500 \text{ mg} \cdot \text{kg}^{-1}$ soil, the same below); (3) Contaminated soil + Chemical fertilizer (N $180 \text{ kg} \cdot \text{hm}^{-2}$ for each vegetable, and P_2O_5 $72 \text{ kg} \cdot \text{hm}^{-2}$, K_2O $90 \text{ kg} \cdot \text{hm}^{-2}$, the same applies hereinafter); (4) Contaminated soil + Chemical fertilizer + Iron-containing soil conditioner 1 ($450 \text{ kg} \cdot \text{hm}^{-2}$ per stubble vegetable); (5) Chemical fertilizer + Iron-containing soil conditioner 2 ($480 \text{ kg} \cdot \text{hm}^{-2}$ per stubble vegetable); (6) Contaminated soil + Chemical fertilizer + Iron-containing soil conditioner 3 (each vegetable $1950 \text{ kg} \cdot \text{hm}^{-2}$); (7) Chemical fertilizer + Iron-containing soil conditioner 4 ($1980 \text{ kg} \cdot \text{hm}^{-2}$ per stubble vegetable). They are represented by seven codes, i.e.: CS, PS, PS+CF, PS+CF+Fe₁, PS+CF+Fe₂, PS+CF+Fe₃ and PS+CF+Fe₄. Each treatment was repeated 3 times. The chemical fertilizers and iron-containing soil conditioners used for each treatment were mixed well with the soil samples before sowing. The first vegetable was Chinese cabbage (*Brassica campestris* L. *ssp.*, Qingjiang cabbage), and the second crop was a spinach (*Ipomoea aquatica* Forsk, Thailand double axe).

The basic physicochemical properties of soil were determined by routine analysis of soil agrochemical methods [8] and the available heavy metals Cd and Pb in soil were determined by DTPA extraction-atomic absorption spectrophotometry [9]. Test data processing using Microsoft Excel-2003 office software, statistical analysis using SPSS11.0 statistical software.

Results and Analysis

Effects of applying iron-containing compound soil conditioners on the biological productivity of vegetables.

Results (Table 1) showed that on the basis of conventional chemical fertilizer treatment of polluted soil, adding soil conditioners (i.e., PS+CF+Fe₁, PS+CF+Fe₂, PS+CF+Fe₃ and PS+CF+Fe₄) could increase the yield of vegetables to a certain extent. Compared with the PS+CF treatment, the yield of the first stubble and second stubble vegetables increased by 3.43%~33.54% and

4.39%~187.19% respectively. The average increase of the total yield of the two vegetables was 3.56%~54.72%. And the yields of vegetables produced by PS+CF+Fe₃ and PS+CF+Fe₄ were higher, and the total yield of the 2 stubbles of vegetable reached at 631.28 g·pot⁻¹ and 606.07g·pot⁻¹, respectively. The results of variance analysis showed that the effects of PS+CF+Fe₃ treatment on the increase of total yield of two crops of vegetables were very significantly ($P<0.01$) better than those treatments of PS+CF+Fe₂, PS+CF+Fe₁, PS+CF, PS and CS, etc. But there was no significant ($P>0.05$) difference between PS+CF+Fe₄. PS+CF+Fe₄ treatment was also significantly superior ($P<0.01$) to the treatments of PS+CF+Fe₁, PS+CF, PS and CS, and superior ($P<0.05$) to PS+CF+Fe₂. And PS+CF+Fe₂ was significantly ($P<0.05$) better than PS, but it was no significant difference between treatments of PS+CF+Fe₁, PS+CF and CS.

Tab.1 Effect of applying iron-containing soil conditioners on vegetable fresh yield

Treatment	<i>Brassica campestris</i> L. ssp.			<i>Ipomoea aquatica</i> Forsk			Total		
	Yield /(g·pot ⁻¹)	Comparison / %	Comparison / %	Yield /(g·pot ⁻¹)	Comparison / %	Comparison / %	Yield /(g·pot ⁻¹)	Comparison / %	Comparison / %
CS	296.67Bde	8.74	-15.16	81.41Bbcd	59.45	39.53	378.08Dcd	16.74	-7.34
PS	272.82Be	\	-21.98	51.06Be	\	-12.49	323.88Dd	\	-20.62
PS+CF	349.66ABcde	28.17	\	58.35Bde	14.28	\	408.01CDcd	25.98	\
PS+CF+Fe ₁	361.66ABcde	32.56	3.43	60.91Bcde	19.29	4.39	422.56CDcd	30.47	3.56
PS+CF+Fe ₂	380.91ABabcd	39.62	8.94	90.34Bb	76.93	54.82	471.25BCDbc	45.5	15.5
PS+CF+Fe ₃	466.95Aab	71.16	33.54	164.33Aa	221.84	181.63	631.28Aa	94.91	54.72
PS+CF+Fe ₄	438.49Aabc	60.73	25.4	167.57Aa	228.19	187.19	606.07ABa	87.13	48.54

Note: Different capital or small letters after data in the same column stand for very significant difference ($P<0.01$) or significant difference ($P<0.05$) in above table, the same below.

Effect of applying iron-containing soil conditioners on the contents of Cd and Pb in vegetables

Results (Table 2) showed that, on the basis of conventional chemical fertilizer treatment of contaminated soil(PS+CF), the application of iron-containing soil conditioners (i.e., PS+CF+Fe₁,PS+CF+Fe₂,PS+CF+Fe₃ and PS+CF+Fe₄) could reduce the heavy metal Cd and Pb contents in vegetables to a certain extent.Compared with PS+CF treatment, the content of Cd in the first and second stubble vegetable was decreased by 6.92%~71.31% and 18.75%~57.6%, respectively, and the Pb decreased by 0.1%~10.63% and 3.81%~68.68%, respectively.The effects of PS+CF+Fe₄ and PS+CF+Fe₃ on the reduction of Cd content in vegetable were better than other treatments. The contents of Cd in the first and second vegetables were decreased by 71.31% and 51.15%, 57.6% and 46.31%, respectively. While the effects of PS+CF+Fe₄ on the reduction of Pb content in vegetable were relatively the best,and the contents of Pb in the first and second stubble vegetables were decreased by 10.63% and 68.68%, respectively. However, the contents of Cd and Pb in vegetable were the highest in polluted soil without fertilization treatment(PS), and the lowest in clean soil without fertilization treatment(CS).

Tab.2 Effect of applying iron-containing soil conditioners on contents of cadmium and plumbum in vegetable

Treatment	<i>Brassica campestris</i> L. ssp.				<i>Ipomoea aquatica</i> Forsk			
	Cd		Pb		Cd		Pb	
	Mass fraction /(mg·kg ⁻¹)	Comparison / %						
CS	0.17Ee	-92.11	0.08B	-95.65	0.07Gf	-93.50	0.24De	-95.76
PS	2.13Aa	0.20	2.12Aa	13.94	1.09Aa	8.14	6.14Aa	6.73
PS+CF	2.13Aa	\	1.86Aa	\	1.01ABa	\	5.75Aab	\
PS+CF+Fe ₁	1.86ABCa	-12.49	1.74Aa	-6.18	0.82BCb	-18.75	5.53ABab	-3.81
PS+CF+Fe ₂	1.98ABa	-6.92	1.83Aa	-1.59	0.62CDEc	-38.71	4.88Bc	-15.14
PS+CF+Fe ₃	1.04CDcd	-51.15	1.86Aa	-0.10	0.54Ecd	-46.31	1.80Cd	-68.68
PS+CF+Fe ₄	0.61DEde	-71.31	1.66Aa	-10.63	0.43EFd	-57.60	1.82Cd	-68.37

The results of variance analysis showed that PS+CF+Fe₄ had the best effect on the reduction of Cd content of Brassica chinensis, which was very significantly ($P<0.01$) better than PS,PS+CF,

PS+CF+Fe₁ and PS+CF+Fe₂, but there was no significant difference between PS+CF+Fe₃. And PS+CF+Fe₃ treatment was also very significantly better than PS and PS+CF, and significantly superior ($P<0.05$) to PS+CF+Fe₁ and PS+CF+Fe₂ treatment. In addition to the Clean soil treatment(CS), there was no significant difference between other treatments except for the reduction of heavy metal Pb content in pakchoi (*Brassica campestris* L.).The effects of PS+CF+Fe₄ treatment on reducing Cd content of water spinach were very significantly better than PS,PS+CF and PS+CF+Fe₁ treatments, and significantly better than PS+CF+Fe₂ treatment, but there was no significant difference between PS+CF+Fe₃ treatment.The effects of PS+CF+Fe₃ and PS+CF+Fe₄ on the reduction of heavy metal Pb content were better than PS,PS+CF,PS+CF+Fe₁ and PS+CF+Fe₂ treatments, but there was no significant difference between them. PS+CF+Fe₂ treatment was also very significantly better than PS and PS+CF, and significantly better than PS+CF+Fe₁.

The effect of applying iron-containing soil conditioners on soil pH and available Cd, Pb after harvest

The results of potted soil sampling and analysis after planting two crops of vegetables (Table 3) showed that: on the basis of conventional application of chemical fertilizer to polluted soil (PS+CF), adding soil conditioners could improve the soil pH to a certain extent and increase the soil pH by 3.78%~41.28%, and decrease the contents of available Cd and Pb by 3.77%~18.01% and 7.57%~41.04%, respectively. PS+CF+Fe₄ treatment had the best effect on increasing soil pH and reducing soil available Cd and Pb contents.The results of variance analysis showed that the effect of PS+CF+Fe₄ was very significantly ($P<0.01$) better than that of CS,PS,PS+CF,PS+CF+Fe₁ and PS+CF+Fe₂, but the difference with PS+CF+Fe₃ treatment was not significant. PS+CF+Fe₃ treatment was also very significantly ($P<0.01$) better than that of CS,PS,PS+CF,PS+CF+Fe₁ and PS+CF+Fe₂.The effect of clean soil treatment(CS) on the reduction of available Cd content in soil was significantly better than that of other treatments.The available Cd content in polluted soil (PS)was significantly higher than that in other treatments.Compared with PS+CF treatment, PS+CF+Fe₄ treatment could very significantly reduce soil available Cd content, and PS+CF+Fe₂ treatment could also significantly reduce that.The decrease of available Pb content in soil was the best in PS+CF+Fe₄ treatment, which was very significantly ($P<0.01$) better than that in PS+CF+Fe₁,PS+CF and PS treatment, but there was no significant difference between PS+CF+Fe₂ and PS+CF+Fe₃. The content of available Pb in clean soil (CS) was very significantly ($P<0.01$) lower than that in other treatments.

Tab.3 Effect of applying iron-containing soil conditioners on pH, contents of available cadmium and plumbum in soil after harvest of vegetables

Treatment	pH			Available Cd		Available Pb			
	Value	Comparison /%	Comparison /%	Mass fraction / (mg·kg ⁻¹)	Comparison /%	Comparison /%	Mass fraction / (mg·kg ⁻¹)	Comparison /%	Comparison /%
CS	4.14Cc	-6.54	-6.05	0.01De	-99.42	-99.29	1.63Ee	-99.47	-99.45
PS	4.43BCc	\	0.53	0.95Aa	\	22.59	307.55Aa	\	3.65
PS+CF	4.41Cc	-0.53	\	0.77Bb	-18.43	\	296.71ABa	-3.52	\
PS+CF+Fe ₁	4.58BCc	3.23	3.78	0.74BCbc	-21.50	-3.77	274.25ABCab	-10.83	-7.57
PS+CF+Fe ₂	4.75BCc	7.07	7.63	0.68BCcd	-28.02	-11.76	213.81CDcd	-30.48	-27.94
PS+CF+Fe ₃	6.10Aab	37.67	38.40	0.71BCbcd	-24.99	-8.05	208.58CDcd	-32.18	-29.70
PS+CF+Fe ₄	6.26Aa	41.28	42.03	0.63Cd	-33.12	-18.01	174.94Dd	-43.12	-41.04

Discussions

Effect of using iron-containing soil conditioners on vegetable yield

At present, there is no report on the application of iron-containing soil conditioner to the yield of vegetables grown on heavy metal contaminated vegetable fields. Our experimental results showed that: on the basis of conventional chemical fertilizer treatment of polluted soil, adding

several iron-containing soil conditioners could increase the total yield of two crops of vegetables by 3.56%~54.72%, and the yields of vegetables treated with PS+CF+Fe₃ and PS+CF+Fe₄ were higher than other treatments. The vegetable yield of polluted soil without fertilization treatment was the lowest, and that of clean soil without fertilization treatment was lower. The addition of several iron-containing soil conditioners (i.e., PS+CF+Fe₁, PS+CF+Fe₂, PS+CF+Fe₃ and PS+CF+Fe₄) could increase the biological yield of vegetables to a certain extent, which was due to the fact that several soil conditioners could be used to form insoluble compounds with active cadmium and lead ions in soil, which to some extent reduce the content of available cadmium lead in the soil (see Table 3), thus alleviating to some extent the inhibition of excessive heavy metals in the soil on vegetable growth. It is beneficial to the increase of vegetable yield.

Effect of using iron-containing soil conditioners on heavy metal content in vegetable-soil system

At present, there are few reports on the treatment of heavy metal pollution in farmland soil by using iron-containing soil conditioner. The results showed that ferrous sulfate has obvious fixation effect in arsenic-contaminated soil. However, the soil acidification caused by it can not be ignored, it can release the fixed Cd、Cu、Zn in soil, and the pH change of soil must be controlled by the application of lime. Compared with FeSO₄, the process of conversion of zero-valent Fe into oxide in soil is slower than that of FeSO₄. However, the amount of oxides produced is relatively large, so the zero-valent Fe is preferable in the long-term stability of remediation effect, and it will not cause soil acidification^[10,11]. This is also verified by the results of this trial (see Table 3). In the study of using zero-valent iron to degrade the soil contaminated by Cr-VI, Franco and others^[12] used nano-iron particles to repair the contaminated soil. Through batch and semi-batch experiments, they were reduced and removed by using different kinds of metal iron with different treatment methods. Including Fe²⁺ (sulphate solution), zero-valent iron (metal scrap iron, non-stabilized zero-valence iron, colloidal zero-valence iron [through carboxymethyl cellulose) stabilization and ultrasonic action]. The results showed that the modified dispersed colloidal zero-valence iron was the best. Under the condition that the average mass concentration of Cr(VI) in soil was (456±35)mg·kg⁻¹, 1 g colloidal zero-valent iron could reduce 280mg Cr(VI). This study indicates that the zero-valent iron technique is an effective method for remediation of Cr(VI) contaminated soil and sediment. Li Tianran, *et al's* results^[13] showed that the immobilization efficiency of iron powder on V and Cr in vanadium smelting slag contaminated soil was 99.6% and 78.5%, respectively. In addition, some studies have shown that zero-valent iron can immobilize heavy metals in soils and sediments^[14,15]. At present, the application of soil conditioner containing iron on vegetable ground has not been reported. Our results showed that on the basis of conventional chemical fertilizer treatment in polluted soil, the contents of Cd and Pb in vegetables could be reduced by adding soil conditioners (i.e., PS+CF+Fe₁, PS+CF+Fe₂, PS+CF+Fe₃ and PS+CF+Fe₄). And the contents of available Cd and Pb in soil were reduced, and the effects of PS+CF+Fe₄ treatment on reducing the contents of heavy metal Cd and Pb in vegetables and the available Cd and Pb contents in soil were relatively best.

Conclusion

The results of this study showed that: on the basis of conventional chemical fertilizer treatment of polluted soil, the application of iron-containing soil conditioners could increase the yield of vegetables (pakchoi and water spinach) by 3.56%~54.72%, reduce the heavy metal Cd content of vegetables by 6.92 %~71.31%, Pb 0.10%~68.68%, and increase soil pH by 3.78 ~ 41.28, decrease soil available Cd 3.77%~18.01% and available Pb 7.57%~41.04%. Among them, the PS+CF+Fe₄ treatment increased vegetable yield by 48.54%, decreased vegetable's Cd by 51.15%~71.31% and Pb by 10.63%~68.68%, increased soil pH value by 42.03%, and decreased soil available Cd content in soil by 18.01% and Pb by 41.04%, and the relative optimum passivation effect was obtained.

To sum up, the addition of "iron-containing soil conditioner 4" to soils polluted by heavy metal Cd and Pb, not only increased the yield of vegetables, decreased the content of Cd and Pb in

vegetables, but also significantly reduced the content of available Cd and Pb in soil. Therefore, this iron-containing soil conditioner has a certain prospect of popularization and application in farmland where the content of heavy metal Cd and Pb in soil exceeds the standard. However, the results of this experiment are only obtained from the greenhouse pot experiment and need to be further verified by field experiments.

Acknowledgements

This research was financially supported by National science and technology support program (2015BAD05B01-05), Fujian province belongs to the basic scientific research project of public welfare (2017R1022-1, 2018R1022-4); The scientific and technological innovation team of the Fujian Academy of Agricultural Sciences (STIT2017-2-10); and The research center of Fujian provincial land cultivation engineering technology.

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