



## Co-remediation of the lead-polluted garden soil by exogenous natural zeolite and humic acids

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### ABSTRACT

The current study reported the co-remediation effect on the lead-polluted garden soil by zeolite and humic acids (HA), which was from comparing with the remediation of single zeolite in term of the lead fraction of sequential extraction in the soil and the distribution of lead in different parts of rape. Mixed treatment (zeolite and HA) and single treatment (zeolite) were, respectively, applied to the artificially polluted garden soil to examine the difference of their remediation effects in pot experiment. Results indicated that the co-remediation led to significantly greater ( $p < 0.01$ ) reduction in the lead concentration in plants than by singly adding to zeolite. The co-application of zeolite and HA reduced the available fraction of lead compounds, but slightly increased ( $p < 0.01$ ) the water-soluble fraction of lead compounds in the garden soil, compared with the application of single zeolite, especially in the severe lead-polluted soil ( $\geq 1000 \text{ mg kg}^{-1}$ ). This method might be an efficient way to remediate the lead-polluted soils on a large scale, although zeolite is a kind of hazardous material.

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### 1. Introduction

The intensive use of wastewater irrigation, sewage sludge, pesticide and emissions from vehicle exhausts, mining, smelting and the rapid development of industries without effective control have resulted in a large accumulation of lead in garden soils [1–4]. The pollution by Pb in garden mould is severe, which seriously affects quality of edible vegetables growing in vegetable fields [5–8]. Methods for remediation of lead-contaminated soils have recently become a matter of increasing agricultural focus and concerns because the cultivation of lead-enriched soils is closely related to human health risk [8,9].

Both zeolite and humic acids (HA) are considered as important remediation agents for the immobilization of heavy metals in soils [10,11]. Any of the two remediation agents can effectively decrease plant availability of lead in soils [12–14].

Zeolite is a class of alkaline porous alumino-silicate [15], with a negative charge [16], neutralized by introducing exchanged cations in the structure sites of itself [17,18]. Zeolite serving as a kind of improvement modifier of soils is being developed, especially for

immobilization of heavy metals. Some studies indicate that zeolite favor the formation of oxides, metal-carbonate precipitates, complexes, which decrease metal solubility [11,12,13,19], and decrease in contents of heavy metals in vegetables [20].

Simultaneously, soil organic matter (OM) has been of particular interest in studies of heavy metal retention in soils due to the tendency of transition metals to form stable complex with organic ligands [21,22]. Because of this fact, HA, as the most abundant fraction of decomposed OM, have been the focus of much research. The researchers [2,14,23] found that organic amendments including Aldrich HA could lower the potential availability of metals by redistribution into less available forms.

Although many experiments have been carried out in order to study the effectiveness of the two materials for the immobilized soils [13,14,20,24], the co-application of the two materials has never been investigated together. The objective of this work is to evaluate the usefulness of exogenous zeolite and HA as amendments for co-remediation of the lead-contaminated garden soils.

### 2. Materials and methods

#### 2.1. The pot experiments I (no humic acids treated)

Uncontaminated garden soil was loess-derived incalcareous cinnamon soil. The soil properties are shown in Table 1. The soil

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<sup>1</sup> Shao Hong-Bo and Shi Wei-Yu contributed equally to this paper.

**Table 1**  
The properties of the tested soils.

Properties	Tested soil
pH (H <sub>2</sub> O)	8.2
Organic matter (%)	2.17
CEC (cmol kg <sup>-1</sup> )	10.43
Total N (%)	0.10
Fast available P (mg kg <sup>-1</sup> )	11.17
Fast available K (mg kg <sup>-1</sup> )	111.5
Bioavailable Pb (mg kg <sup>-1</sup> )	0.419
Particle size distribution (%)	
0.25–2 mm	28.7
0.05–0.25 mm	22.4
0.002–0.05 mm	29.2
<0.002 mm	17.7

was treated by the following methods: The soil (5 kg) was put in polyethylene pots and mixed well with Pb(NO<sub>3</sub>)<sub>2</sub> of different strengths (0, 125, 500, 1000, and 2000 mg kg<sup>-1</sup>). Then, zeolite was blended into the treated soils at various proportions (0, 5, 10, and 20 g kg<sup>-1</sup>). Each treatment was performed in triplicates and incubated for 30 days at room temperature (25 °C). The water content of pot experiment was controlled by weighing the pot every 3 days. After incubation for 30 days, six seeds of rapes were planted in each pot. Plants were grown for 2 months under control conditions (temperature 15–25 °C, relative humidity 30–50%). The pots were laid out by a random complete block design (RCBD) under glasshouse conditions. For 2 months, all the plants were harvested and the shoot (leaves plus stem) separated from the roots; no plant mortality was recorded and there were no other symptoms of toxicity. The roots and aerial parts were rapidly and profusely washed with water under pressure and serially rinsed in recipients containing distilled water. They were then dried in an oven at 80 °C for 24 h. One gram of plant materials was digested with a 10 ml of HNO<sub>3</sub>:HClO<sub>4</sub> mixture (4:1, v/v) for 12 h and the digested solution was heated till it became clear. The digestion solutions were filtered with a Whatman No. 42 filter paper and diluted to 50 ml. The concentration of lead in the solution obtained was analyzed with atomic adsorption spectrophotometer (Varian-AA240).

## 2.2. Sequential extraction of lead in soils

The soil samples were air dried for 5–6 days and sieved to <2 mm for analysis. Sequential extraction scheme was developed from Tessier et al. [25], and retains the same terminology. The extraction was carried out progressively on an initial weight of 2.000 g of material. Concentrations of Pb in these sequential frac-

tions were determined by atomic absorption spectrophotometry (Varian-AA240)

## 2.3. The pot experiments II (humic acids treated)

The soils, which were left (4.5 kg) in the polyethylene pots after completing 2.1 and 2.2 steps, were evenly blended with 60 g ammonium humate in every pot. After incubation for 30 days, six seeds of rapes were planted in each pot again. Plants were grown for 2 months under control conditions (temperature 15–25 °C, relative humidity 30–50%). For 2 months, all the plants were harvested. Then, the next method of the determination of the lead in plants and soil was the same as 2.1 and 2.2 steps.

## 2.4. Statistical analysis

The variance and significant differences of concentrations of Pb in plants and soils, which were between pot experiments I and pot experiments II, were analyzed by independent samples *t* test. The statistical significance in this analysis was defined at  $p < 0.05$ ,  $p < 0.01$ , and  $p < 0.001$ . Moreover, the data were subjected to one-way variance analysis (ANOVA) and differences of concentrations of Pb in different zeolite-treated plants and soils were determined using the Duncan test. The statistical significance in this analysis was defined at  $p < 0.05$ .

## 3. Results

### 3.1. Lead concentration in plants

Results from Tables 2 and 3 show the concentration of Pb in the roots and shoots (leaves plus stems) of the rape grown in the soil samples. The Pb concentration in shoots decreased progressively in all four zeolite doses, irrespective of the data in pot experiment I or pot experiment II. The changing trend of Pb concentration in roots was the same as that in shoots, but the difference was that Pb concentration in roots at 2000 mg kg<sup>-1</sup> Pb treatment was much more than above other Pb treatments. The difference of data between no-humic acid (NHA) and HA was that the lead concentration in grape roots and shoots by HA treatment declined more. For some plant samples, especially shoots at low Pb treatment ( $\leq 125$  mg kg<sup>-1</sup>), ammonium humate addition led to significantly greater ( $p < 0.01$ ) reductions in lead concentration in plants than just adding zeolite. Furthermore, according to ANOVA test, concentration of lead in plants was more significantly decreased in HA than in NHA with increasing zeolite addition dose at the same level of Pb treatment.

**Table 2**  
Pb concentration in aerial part of rape<sup>a</sup>.

Pb treatment (mg kg <sup>-1</sup> )	Zeolite dose (g kg <sup>-1</sup> )			
	0	5	10	20
<b>NHA<sup>b</sup></b>				
0	0.963 ± 0.099a	0.715 ± 0.062b	0.588 ± 0.034c	0.506 ± 0.021d
125	4.067 ± 0.204a	3.384 ± 0.352a	2.827 ± 0.238b	2.813 ± 0.249b
500	10.685 ± 0.334a	8.687 ± 0.108b	6.620 ± 0.433c	5.786 ± 0.111c
1000	17.304 ± 0.904a	16.075 ± 0.218a	14.093 ± 0.558b	12.678 ± 0.381b
2000	23.228 ± 0.217a	19.223 ± 0.0245b	19.058 ± 0.319b	16.324 ± 1.422c
<b>HA</b>				
0	0.933 ± 0.051a*	0.533 ± 0.101b**	0.441 ± 0.041b ns	0.225 ± 0.075c**
125	3.725 ± 0.066a**	2.658 ± 0.164b**	1.900 ± 0.301c*	1.894 ± 0.076c
500	10.008 ± 0.498a ns	6.975 ± 0.371b ns	5.167 ± 0.085c ns	5.533 ± 0.222c ns
1000	15.883 ± 0.864a ns	15.600 ± 0.088a ns	14.458 ± 0.196a*	12.250 ± 0.189b ns
2000	22.858 ± 169a ns	19.017 ± 0.147b ns	17.925 ± 0.214b ns	14.525 ± 0.760c ns

<sup>a</sup> The different among treats tested by one-way ANOVA, the number of which on the same row followed by different letters was significantly different at  $p < 0.05$  (Duncan method); mean values between NHA and HA denoted by ns ( $p \geq 0.05$ ), \* ( $p < 0.05$ ), \*\* ( $p < 0.01$ ) differ significantly, according to independent samples *t* test.

<sup>b</sup> NHA: sample is not treated by humic acids and just treated by zeolite in pot experiment I; HA: sample is treated by humic acids and zeolite in pot experiment II.

**Table 3**  
Pb concentration in roots of rape<sup>a</sup>.

Pb treatment (mg kg <sup>-1</sup> )	Zeolite dose (g kg <sup>-1</sup> )			
	0	5	10	20
<b>NHA<sup>b</sup></b>				
0	1.395 ± 0.015a	1.256 ± 0.029b	1.231 ± 0.011b	1.036 ± 0.090c
125	34.623 ± 0.362a	34.589 ± 0.420a	32.757 ± 0.350b	32.035 ± 0.174b
500	51.146 ± 0.594a	46.796 ± 0.219b	44.776 ± 0.143b	38.744 ± 1.295c
1000	137.217 ± 4.711a	123.213 ± 2.741b	86.697 ± 1.285c	72.414 ± 3.808d
2000	905.582 ± 23.567a	828.268 ± 17.878b	532.877 ± 16.321c	459.498 ± 8.723d
<b>HA</b>				
0	1.348 ± 0.040a ns	1.193 ± 0.024b ns	1.093 ± 0.025b**	1.023 ± 0.039c ns
125	13.808 ± 0.399a ns	12.683 ± 0.353b*	12.683 ± 0.017b ns	10.208 ± 0.074c*
500	30.508 ± 0.379a ns	25.958 ± 0.354b ns	24.108 ± 0.842c ns	16.283 ± 0.272d**
1000	133.692 ± 1.171a ns	110.875 ± 2.343b*	81.425 ± 2.745c ns	64.517 ± 2.223d ns
2000	882.192 ± 5.798a**	829.350 ± 10.770b ns	306.367 ± 18.757c ns	235.157 ± 14.048d ns

<sup>a</sup> The different among treats tested by one-way AVONA, the number of which on the same row followed by different letters was significantly different at  $p < 0.05$  (Duncan method); mean values between NHA and HA denoted by ns ( $p \geq 0.05$ ), \* ( $p < 0.05$ ), \*\* ( $p < 0.01$ ) differ significantly, according to independent samples *t* test.

<sup>b</sup> NHA: sample is not treated by humic acids and just treated by zeolite in pot experiment I; HA: sample is treated by humic acids and zeolite in pot experiment II.

### 3.2. Sequential extraction of lead in soils

Tables 4 and 5 indicate the general sequence of portion of lead fraction in NHA and HA soil samples: Fe-Mn oxide-bound > carbonate-bound > organic-bound > exchangeable > water-soluble. However, the sequence was changed a little: the carbonate-bound was more than Fe-Mn oxide-bound in HA-lead-contaminated soil samples. The portion of the available lead (water-soluble and exchangeable) was the smallest, but its content was up to 37.25 mg kg<sup>-1</sup> (NHA) and 33.69 mg kg<sup>-1</sup> (HA) in the seriously polluted soil (2000 mg kg<sup>-1</sup> Pb). And the data also indicated a significant decrease in water-soluble, exchangeable, carbonate-bound and Fe-Mn oxide-bound concentration in soils following treatment with increasing doses of zeolite at same level of Pb concentration. Conversely, organic-bound concentration increased for HA soil samples.

The concentration of available Pb in NHA and HA soil samples with different doses of zeolite treatment is shown in Table 4. Addition of HA resulted in increasing of lead in water-soluble

fraction and decreasing of exchangeable fraction, but the major data of content of water-soluble lead did not vary significantly. Although the decreasing of water-soluble fraction was significant ( $p < 0.01$ ) at 2000 mg kg<sup>-1</sup> Pb and 20 g kg<sup>-1</sup> zeolite treatment, the variety was not marked by comparing with exchangeable lead ( $p < 0.001$ ). Besides, according to ANOVA test, the changing trend of the available lead in NHA and HA, respectively, was the same as concentration of lead in plants with increasing of doses of zeolite at the same level of Pb treatment.

The data from Table 5 show the concentration of less-available Pb (carbonate-bound, Fe-Mn oxide-bound and organic-bound) in NHA and HA soil samples with different doses of zeolite at different levels of Pb concentration. Almost, the concentration of carbonate-bound and Fe-Mn oxide-bound lead decreased significantly in soil samples ( $p < 0.01$ ) after adding HA. Especially, HA addition induced markedly greater ( $p < 0.001$ ) abatement of Fe-Mn oxide-bound fraction of lead than that of carbonate-bound fraction. On the contrary, HA addition enhanced the content of organic-bound fraction and the trend was not significant when compared with carbonate-

**Table 4**  
Effect of different addition of zeolite doses and humic acids between NHA and HA on available fractions of lead in different Pb treated garden soil (mg kg<sup>-1</sup>)<sup>a</sup>.

Fraction	Treatment (mg kg <sup>-1</sup> )	Zeolite dose (g kg <sup>-1</sup> )			
		0	5	10	20
<b>Water soluble</b>					
<b>NHA<sup>b</sup></b>					
	0	0.051 ± 0.003a	0.041 ± 0.002b	0.019 ± 0.001c	0.005 ± 0.001d
	125	0.989 ± 0.057a	0.849 ± 0.049b	0.775 ± 0.045b	0.401 ± 0.023c
	500	2.049 ± 0.066a	1.828 ± 0.079b	1.297 ± 0.106c	1.147 ± 0.118d
	1000	2.173 ± 0.088a	1.922 ± 0.103a	1.314 ± 0.114a	1.249 ± 0.134b
	2000	2.829 ± 0.104a	2.518 ± 0.116a	2.249 ± 0.121b	1.772 ± 0.140b
<b>HA</b>					
	0	0.053 ± 0.001a ns	0.047 ± 0.002b ns	0.025 ± 0.001c*	0.006 ± 0.001d ns
	125	1.200 ± 0.127a ns	0.842 ± 0.019b ns	0.770 ± 0.013b ns	0.390 ± 0.012c ns
	500	2.015 ± 0.108a ns	1.783 ± 0.002b ns	1.560 ± 0.110b ns	1.448 ± 0.192b ns
	1000	2.443 ± 0.004a ns	2.093 ± 0.020b*	1.893 ± 0.111c ns	1.778 ± 0.003c*
	2000	3.228 ± 0.292a ns	3.113 ± 0.003a**	2.448 ± 0.186b ns	2.108 ± 0.002b**
<b>Exchangeable</b>					
<b>NHA<sup>b</sup></b>					
	0	0.368 ± 0.031a	0.354 ± 0.062a	0.340 ± 0.071a	0.285 ± 0.095b
	125	3.86 ± 0.10a	3.35 ± 0.31a	3.18 ± 0.08a	2.85 ± 0.29b
	500	6.31 ± 0.13a	5.17 ± 0.23b	4.43 ± 0.17c	4.23 ± 0.16c
	1000	11.37 ± 0.09a	11.36 ± 0.36a	11.26 ± 0.14a	9.71 ± 0.25b
	2000	34.43 ± 0.51a	33.69 ± 1.43a	27.79 ± 1.72b	26.68 ± 1.16c
<b>HA</b>					
	0	0.365 ± 0.041a ns	0.330 ± 0.063b ns	0.286 ± 0.109b ns	0.256 ± 0.061c ns
	125	3.77 ± 0.08a ns	3.28 ± 0.04a ns	2.97 ± 0.23b ns	2.74 ± 0.21c ns
	500	5.63 ± 0.18a*	4.75 ± 0.11b ns	3.93 ± 0.29c ns	3.37 ± 0.11c**
	1000	11.69 ± 0.67a*	10.55 ± 0.31a ns	9.74 ± 0.41b*	8.17 ± 0.32c*
	2000	30.47 ± 0.75a*	27.78 ± 2.58a ns	24.07 ± 2.18b ns	16.42 ± 0.54c***

<sup>a</sup> The different among treats tested by one-way AVONA, the number of which on the same row followed by different letters was significantly different at  $p < 0.05$  (Duncan method); mean values between NHA and HA denoted by ns ( $p \geq 0.05$ ), \* ( $p < 0.05$ ), \*\* ( $p < 0.01$ ), \*\*\* ( $p < 0.001$ ) differ significantly, according to independent samples *t* test.

<sup>b</sup> NHA: sample is not treated by humic acids and just treated by zeolite in pot experiment I; HA: sample is treated by humic acids and zeolite in pot experiment II.

**Table 5**Effect of different addition of zeolite doses and humic acids between NHA and HA on less-available fractions of lead in different Pb treated garden soil ( $\text{mg kg}^{-1}$ )<sup>a</sup>.

Fraction	Treatment ( $\text{mg kg}^{-1}$ )	Zeolite dose ( $\text{g kg}^{-1}$ )			
		0	5	10	20
<b>Carbonate-bound</b>					
NHA <sup>b</sup>	0	16.1 ± 0.07a	15.80 ± 0.85a	14.63 ± 0.68a	14.05 ± 0.55a
	125	64.0 ± 0.40a	61.33 ± 1.39a	36.60 ± 1.26b	32.82 ± 0.99c
	500	304.99 ± 5.60a	189.70 ± 9.98b	183.97 ± 1.14b	154.32 ± 2.04c
	1000	421.60 ± 4.63a	409.12 ± 9.23a	226.94 ± 11.90b	221.65 ± 17.13b
	2000	674.85 ± 27.05a	587.6 ± 20.52a	538.92 ± 7.41b	450.16 ± 16.64c
HA	0	8.62 ± 0.16a**	6.88 ± 0.07b**	6.19 ± 0.15c***	5.00 ± 0.26d***
	125	48.51 ± 0.58a***	47.63 ± 2.12a**	33.29 ± 1.57b ns	26.43 ± 1.17c**
	500	218.79 ± 15.67a**	184.54 ± 0.83a ns	163.31 ± 2.23b**	130.34 ± 14.81c ns
	1000	246.48 ± 0.40a**	239.73 ± 5.79a***	220.07 ± 16.45a ns	190.39 ± 15.17b ns
	2000	507.62 ± 22.93a**	464.38 ± 8.14b***	364.55 ± 2.55c**	324.05 ± 3.09d**
<b>Fe-Mn oxide-bound</b>					
NHA	0	59.42 ± 1.07a	57.52 ± 3.79a	55.62 ± 2.91a	45.18 ± 3.98b
	125	564.3 ± 23.20a	497. ± 21.53b	427.23 ± 5.58c	426.68 ± 2.18c
	500	421.87 ± 8.26a	330. ± 27.01b	323.28 ± 3.59b	288.92 ± 15.49b
	1000	689.17 ± 5.66a	640.9 ± 7.87b	487.93 ± 12.32c	471.22 ± 7.96c
	2000	1155.6 ± 7.12a	1080 ± 13.79b	1048.5 ± 4.83b	1036.83 ± 16.12c
HA	0	17.17 ± 0.99a***	13.04 ± 0.51b**	11.23 ± 0.59b**	9.94 ± 0.24c*
	125	87.60 ± 4.64a**	69.99 ± 1.49b***	67.15 ± 1.52b***	59.30 ± 2.49c***
	500	243.27 ± 6.52a***	227.05 ± 21.71a*	200.91 ± 16.98a**	178.92 ± 10.79b**
	1000	443.74 ± 11.20a***	441.20 ± 11.81a***	434.87 ± 2.15a*	358.73 ± 3.21b***
	2000	737.21 ± 14.81a***	674.28 ± 49.17a**	620.30 ± 28.82b***	422.05 ± 10.68c***
<b>Organic-bound</b>					
NHA	0	6.70 ± 0.94c	6.75 ± 0.31c	8.99 ± 0.41b	17.11 ± 0.27a
	125	17.30 ± 0.71a	17.63 ± 0.37a	17.81 ± 2.18a	21.10 ± 0.40a
	500	18.20 ± 0.52c	18.93 ± 0.38c	20.29 ± 0.28b	30.56 ± 1.57a
	1000	43.65 ± 0.61b	45.57 ± 1.65b	47.16 ± 4.69b	66.50 ± 2.56a
	2000	44.54 ± 4.75c	51.13 ± 1.03c	67.14 ± 3.19b	77.94 ± 2.38a
HA	0	7.10 ± 0.07c ns	8.11 ± 0.21c*	12.93 ± 0.52b**	19.63 ± 0.61a ns
	125	15.89 ± 0.42c ns	17.39 ± 0.44b ns	18.38 ± 0.81b ns	25.19 ± 0.23a ns
	500	20.87 ± 1.40b**	21.01 ± 2.67b*	25.02 ± 1.55a*	30.82 ± 1.10a ns
	1000	46.02 ± 2.19b	48.20 ± 0.53b	55.70 ± 1.42a*	59.30 ± 0.08a ns
	2000	71.40 ± 0.60b***	77.04 ± 2.96b**	90.82 ± 1.02a**	98.55 ± 5.81a ns

<sup>a</sup> The different among treats tested by one-way ANOVA, number which on the same row followed by different letters was significantly different at  $p < 0.05$  (Duncan method); mean values between NHA and HA denoted by ns ( $p \geq 0.05$ ), \* ( $p < 0.05$ ), \*\* ( $p < 0.01$ ), \*\*\* ( $p < 0.001$ ) differ significantly, according to independent samples  $t$  test.

<sup>b</sup> NHA: sample is not treated by humic acids and just treated by zeolite in pot experiment I; HA: sample is treated by humic acids and zeolite in pot experiment II.

bound and Fe-Mn oxide-bound fractions. Similarly, according to ANOVA test again, the changing trend of carbonate-bound and Fe-Mn oxide-bound lead in NHA and HA was also the same as the concentration of lead in plants with increasing dose of zeolite at the same level of Pb treatment. Nevertheless, the content of organic-bound was more significantly increased in NHA than in HA at the same level of Pb treatment with increasing doses of zeolite.

#### 4. Discussion

Many studies have indicated that the potential environmental availability of metals from contaminated soil may be controlled by soil amendments with exogenous zeolite or humic substances [2,12,13,14]. However, in most cases, remediation of contaminated soils only by a kind of amendment cannot reach the requirement [26], especially, for polluted soils. The effect of HA for restoring lead-contaminated garden soils by zeolite has been investigated by co-remediation in our study.

Sequential extraction scheme, which was established by Tessier et al. [25], almost is the standard method of comparing and evaluating lead in soil, so the extracted concentration of lead in the polluted soil samples can be compared and evaluated by sequential extraction of lead in soil, such as water-soluble, exchangeable, carbonate-bound, Fe-Mn oxide-bound, organic-bound. The residual (no extracted) lead is not measured and considered because the bioavailability of residual lead is the weakest in comparison with other fraction. It almost is not up-taken by plants [27,28].

Currently, there are two opposite opinions about function of HA for remediation of heavy-contaminated soils. Tordoff and Baker

[29] found organic amendment could decrease the bioavailability of heavy metals in soil, thus permitting the re-establishment of vegetation at contaminated sites. This relies on the ability of the humic substance to re-distribute heavy metals from available form to non-available ones [23,30,31]. The opinion is supported by more researches. The opposite opinion is White and Chaney's [32], who reported that OM was more effective in remediating the effects of toxic metals through plant uptake. However, results from Table 4 indicate that HA addition caused the increase of water-soluble fraction and decrease of exchangeable fraction. And the variety of water-soluble fraction was not markedly significant compared with that of exchangeable fraction. Outwardly, the result seemed to be not related with the above two opinions, because exchangeable fraction was investigated as available form and the water-soluble fraction was not considered in previous studies. Nevertheless, the controversy can be settled when water-soluble and exchangeable fractions were investigated. It can be concluded that OM can promote bioremediation action for lead due to the slight increase of water-soluble fraction, and because transformation of exchangeable fraction into less-available form consequently decreases bioavailability of lead. Besides, exchangeable lead is major part of available lead. Maybe the above could explain why HA just caused significant reduction of lead concentration in plants, especially aerial parts at low Pb treatment. Otherwise, the reduced trend of lead concentration in plants and available form with increasing zeolite addition doses at the same level of Pb treatment after HA addition proved that HA improve remediation by adding zeolite to lead-contaminated garden soil.

HA lead to highly remarkable reduction of carbonate-bound and Fe-Mn oxide-bound fractions, but content of the organic-bound fraction does not increase significantly. It suggests that a great lot of less-available lead was transformed into non-available lead (residual fraction). Likewise, the trend of the two fractions in HA and NHA with increasing zeolite addition doses at the same level of Pb treatment also indicates that HA enhance and promote lead immobilization in garden soil to assist zeolite. Differently, the change of the organic-bound fraction is more significant in NHA than in HA with increasing zeolite addition doses at the same level of Pb. That is because HA is a dominant factor for forming the organic-bound fraction compared with zeolite, and HA addition dose is not different in each sample.

## 5. Conclusions

The exogenous zeolite and HA appear effective as co-amendment to remediate garden soil polluted by lead. HA not only promote lead immobilization in garden soil to assist zeolite but also slightly increase water-soluble lead. So HA not only restrain availability of lead in contaminated garden soil, but also enhance validity of phytoremediation [33–37].

The co-application of exogenous zeolite and humic effectively decrease lead concentration in edible parts of rape (aerial parts) at low lead-contaminated garden soil. In other words, the co-remediation of exogenous zeolite and HA can control lead toxicity, therefore, ascending the safety for edible vegetables at low lead-contaminated garden soil and opening a better way for co-remediating the lead-polluted soils.

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