The leaching research of environmental materials on Pb and Cd contaminated soil

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***Abstract*—In this paper, the leaching experiments are conducted with four kinds of environmental materials, polymer material (SAP), coal-based nutrient (HA), mineral adsorption material (FS) and mineral chemical material (SS), to explore the remediation effects of environmental materials on lead (Pb) and cadmium (Cd) contaminated soil. Electric conductivity (EC), pH value and Pb and Cd concentrations of leachates are measured to indicate the effects. The results show that the EC values of leachates reduce gradually in the four time leaching, and the pH values of leachates are insignificantly influenced by the environmental materials, meaning these environmental materials are suitable in farmland restoration. Environmental materials are effective in Pb and Cd contaminated soil remediation and could reduce heavy metal pollution of underground water. Among these materials, SS is the best material for Pb remediation, and the total content of Pb in leachates is 57.3% of CK after treated by SS; FS is the best for Cd, and compared with CK, the total Cd content is 66.4% after adding FS.**

***Index Terms*—leaching, environmental materials, lead, cadmium, soil remediation**

I. INTRODUCTION

In recent years, the growing heavy metal pollution in soil causes expanding damage and soil environmental quality deterioration [1]. The heavy metals could not only gather in crops, agricultural products, and groundwater, but enter human body through the food chain, causing various hazards to human health. Among all the heavy metal elements, both lead (Pb) and cadmium (Cd) are two serious soil pollutants. They could lead to significant toxic effects on plants and human, such as affecting plant cell metabolism and human intelligence development [2-3]. Therefore, the treatment of heavy metals Pb and Cd contaminated soil has become an urgent environmental problem around the world [4].

Heavy metal pollution management could be classified broadly into three methods, physical repair, chemical restoration and bioremediation [5]. Among these three methods, the ameliorant remediation of contaminated soil in chemical restoration method has advantages of cost-saving and quick response, developing more and more rapidly. Its mechanism of remediation includes precipitation, adsorption, ion exchange, chelation or other reactions between ameliorants and heavy metals [6].

Professor Ryoichi Yamamoto from the University of Tokyo proposes the concept of environmental material first in his material research, which mainly means the materials with performance both in usability and environmental coordination [7]. From that time on, environmental material has grasped scientists' attention. Now, the argument on environmental material's categories, including environment purification materials, environment repair material, and alternative materials, is reached by the whole world [8].

The soil column leaching simulation test with heavy metals Pb and Cd contaminated soil is conducted in this study, by adding different environment materials as ameliorants, polymer materials (SAP), coal-based nutrient (HA), mineral adsorption material (FS) and mineral chemical material (SS). The electric conductivity (EC), pH values and Pb and Cd concentrations of leachates would explain the effects of environmental materials on Pb and Cd contaminated soil improvement, directing groundwater quality after restoration. The main purpose of this research is obtaining effective ameliorants for Pb and Cd contaminated soil, relieving heavy metal hazards to ecological environmental and human health.

II. MATERIALS AND METHODS

A. Materials

Tested soil is the shallow farmland soil (0-20cm) taken from southern suburb of Beijing, China. Its properties are tested as follow, pH 7.35, EC 0.16ms/cm, Pb background value 17.27mg/kg, Cd background value 0.012mg/kg. After dried naturally and sieved by griddle (2mm), 1 kg soil is put in each column. Then, $Pb(NO_3)_2$ and $CdCl_2$ solutions are added to the soil. The concentrations of Pb and Cd in soil are 500 mg/kg and 20 mg/kg, separately.

Four kinds of environmental materials are used in the research. Environmental materials SAP, HA, FS and SS are provided by Tianjin Sannongjin Technology Company, Neimenggu Huolinhe Coal Industry Group, Sinopharm Chemical Reagent and Qinghai Hongfu Jewelery Company, respectively.

B. Experimental Design

The experiment contains one control group and nine experimental groups. All groups are filled with contaminated soils, while only experimental groups are mixed with environmental materials, as is shown in TABLE I. During the leaching, three repetitions are done in each treatment to ensure the authenticity.

TABLE I. EXPERMENTAL DESIGN

Added materials	Treatments									
	CK	A	B	C	D	E	F	G	H	I
SAP(3g)		√				√	√	√		√
HA(1g)			√			√	√		√	
FS(5g)				√		√	√	√	√	√
SS(5g)					√	√		√	√	

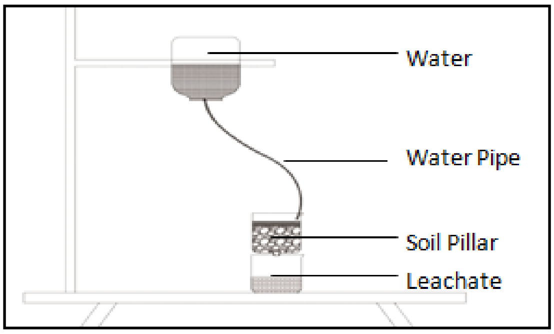

Fig.1. Leaching equipment

C. Experimental Equipment and Procedure

Soil leaching simulator is shown in Fig.1. Before utilizing, all the equipment should be soaked in HNO_3 (5%) more than 24 hours to remove the attached heavy metals.

Firstly, add water to the max field moisture capacity of soil, weigh and stand for 4 weeks. Secondly, after 4 weeks' evaporation, extra water is replenished to soil to the initial weight. Thirdly, 300ml water is put in the column to obtain leachate 24 hours later. Then EC values, pH values, and Pb and Cd concentrations of the leachates are measured. The other three times follow the same steps in the first leaching.

D. Measuring Items and Methods

Leachate EC is measured by conductometer (DDS-11A Yoke China). pH value is measured by acidometer (PHS-3C Zhiguang China). Pb and Cd concentrations are measured by ICP-MS (iCAP6000 Thermo U.S.A.). All the experimental data is analyzed by ANOVA (LSD, α=0.05) in SPSS19.0.

III. RESULTS AND DISCUSSION

A. EC values of leachates

As can be seen from Fig. 2, the different treatments show similar trend in the four time leaching, the EC values of leachates in different treatments reducing gradually with the leaching time increasing. In each leaching, the EC values of treatments B, C, D and H are lower than that of CK, while EC values of E, F, G and I are higher than that of CK. Treatment A shows a lower EC value than CK in the first leaching, and a higher one in the following three times. The results indicate environmental material SAP could promote EC value's increase of leachates, while HA, FS and SS show reduction.

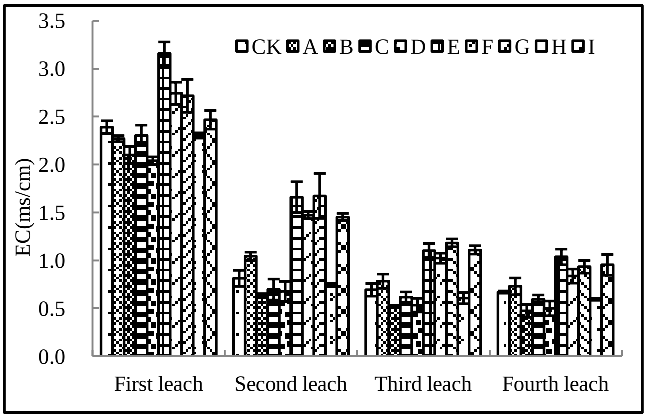

Fig.2. EC values of leachates

The EC value is an important chemical property of soil. EC value could indicate the dissolution of water-soluble ions in the contaminated soil [9], show electrical current capacity of substance, and reflect the extent of the electrolyte in the solution. Therefore, the higher EC value of leachate means higher levels of water-soluble ions and the lower EC value illustrates less water-soluable ions. This result is consistent with the heavy metal content trend in the leachate measured later. Pb and Cd concentrations of treatment B, C, D and H leachates are lower than CK, while concentrations of A, E, F, G and I are higher than CK.

B. pH values of leachates

Figure 3 illustrates that the leachates are all alkalescent. The pH values rise first, then fall, and go up at the end in the four leaching after treated by different environmental materials. But the changes are insignificant, between 0.01 and 0.38, indicating the four kinds of environmental materials could hardly change the soil acidity and alkalinity, which makes them suitable in farmland soil without damaging the normal growth of crops. Among all nine experimental groups, the pH value of treatment B is slightly less than that of CK, while other treatments are similar to CK. This might due to the nature of the environmental material HA. Specifically, HA molecule contains functional group -COOH and displays the character of weakly acidic after dissolved in water, leading lower pH value of B than CK.

Soil pH is a reflection of the soil chemical property. The pH value change can lead to chemical existing status change of heavy metals in the soil, and pH value affects the contents of dissolved metal ions in the soil [10]. Usually, with the rise of pH value, the absorption amount of heavy metals by the soil increases, the concentration of heavy metals in solution decreases, and the bioavailability of heavy metals drops [11].

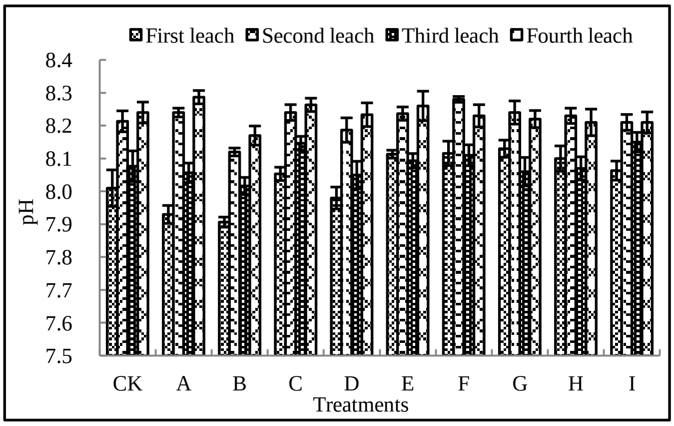

Fig.3. pH values of leachates

C. Pb and Cd concentrations in leachates

As shown in TABLE II, in the first leaching, the Pb and Cd concentrations of treatments A, F, and G are lower than that of the CK, and there are significant differences. The Pb content of treatment G is only 62.3% of CK and the Cd content of treatment A is 66.5% of CK; the Pb and Cd contents are much higher than the CK in the following three subsequent leaching. Compared with CK, the Pb content of G is 748.2% in the second leaching and Cd content is 400% in the third leaching. The reason for this result lies in the environmental material SAP after analysis. SAP absorbs Pb and Cd in the first leaching, but it expands to a giant size after absorbing water, and destroys the soil structure in the column, leading to less adsorption of heavy metal by the original soil colloids. Also, large size of SAP means less specific surface area, which is against the combination of SAP and heavy metals.

Pb and Cd contents of treatments B, C, D and H are lower than that of CK in all four time leaching, meaning the environment materials HA, FS and SS play roles in the solidification of Pb and Cd. This result could also be explained in the leachate EC value measurement result. The high EC value treatments show higher Pb and Cd levels, indicating that most of the ions in the leachates are Pb and Cd ions. However, compared with CK. Pb dissolution in only treatment D reaches significant differences in all the four time leaching, and the same of Cd in treatment C. The Pb total dissolution of treatment D is 57.3% of CK, with only 48.1% in the second leaching; Cd total dissolution of treatment C is 66.4% of CK. These results indicate that SS is the best for heavy metal Pb solidification, and FS for Cd solidification, which is same with Zhang's single Pb or Cd contaminated soil remediation result [12]. SS is a layered magnesium silicate mineral, in which the Mg^{2+} could be replaced by heavy metal cations [13]. Therefore, SS could solidify heavy metals by ion exchange interaction. FS has large specific surface area, and it could fix heavy metal in its interior, passivating heavy metals by adsorption. Also, in the HA molecule, the H^+ in functional

TABLE II. Pb AND Cd CONCENTRATIONS IN LEACHATES (μg/kg)

Treatments	First leach		Second leach		Third leach		Fourth leach	
	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd
CK	35.65±5.08b	7.05±0.12b	33.67±2.53e	3.30±0.23c	32.14±3.26b	2.10±0.12d	25.73±2.24b	2.05±0.10d
A	28.31±0.89c	4.69±0.60d	82.10±1.89d	7.48±0.90b	94.16±6.06a	6.94±0.92b	90.84±9.46a	5.24±0.55b
B	34.01±1.61b	6.88±0.37b	15.75±2.22e	2.02±0.13c	24.85±1.87bc	2.08±0.17d	22.74±1.61b	2.01±0.06d
C	22.82±3.29d	4.40±0.51d	17.40±1.43f	2.25±0.25d	24.71±1.70bc	1.42±0.06e	19.21±1.19bc	1.56±0.04e
D	23.48±2.39d	6.32±0.88b	16.20±1.54f	2.67±0.12c	16.31±1.19c	1.47±0.09e	16.83±0.76c	1.86±0.12de
E	67.93±13.90a	12.61±4.14a	208.70±30.46bc	9.25±0.84a	103.72±4.86a	8.94±0.71a	99.51±11.63a	3.71±0.10c
F	28.13±0.99c	6.04±0.58c	200.32±14.67c	10.58±0.91a	92.32±8.05a	6.98±0.66b	88.83±10.67a	5.69±0.58ab
G	22.22±4.19d	5.18±0.35c	252.13±31.93ab	8.10±0.86ab	96.39±9.57a	8.40±0.35a	85.56±2.55a	6.93±0.79a
H	34.09±3.06b	6.41±0.35b	28.33±1.10e	2.63±0.23c	27.10±1.85b	1.98±0.09d	21.34±1.91b	1.83±0.09de
I	32.44±6.02b	5.51±1.38c	280.06±16.84a	10.16±0.34a	89.65±8.04a	5.35±0.46c	81.90±3.05a	6.10±0.83ab

Different letters in the same column mean significant differences

groups -COOH and -OH could be exchanged by heavy metal cations. Therefore, HA, with a certain degree of complexation property, can restore the heavy metal contamination [14].

IV. CONCLUSIONS

After conducting and analyzing the leaching experiment, conclusions could be reached as follow.

1) The EC values of leachates reduce during the four time leaching in all treatments. Environmental material SAP contributes the increase of leachate EC values, while HA, FS and SS lead to EC values' reduction.

2) A floating change of pH values in different treatments is shown, but there is no significant difference between the treatments. Therefore, the four kinds of environmental materials could hardly change soil pH value.

3) Environmental material SAP promotes the leaching of heavy metal Pb and Cd. However, environmental materials HA, FS and SS could passivate heavy metal Pb and Cd, and lead to less heavy metals in the underground water. Specifically, SS is the best for Pb contaminated soil remediation and FS is the best for Cd contaminated soil restoration.

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