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Influence of different phosphates on adsorption and leaching of Cu and Zn in red soil

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Abstract: Batch and soil column experiments were conducted to evaluate the influence of KH_2PO_4, $(NH_4)H_2PO_4$ and $Ca(H_2PO_4)_2$ on the adsorption and leaching characteristics of Cu and Zn in red soil. The results show that all the three phosphates can greatly improve the adsorption capacity of red soil for Cu and Zn, and the effect of different phosphates on Cu and Zn adsorption follows the order of $Ca(H_2PO_4)_2$ >KH_2PO_4>$(NH_4)H_2PO_4$. The addition of phosphate has little effect on the mobility of Cu. $Ca(H_2PO_4)_2$ and $(NH_4)H_2PO_4$ show a strong ability in immobilizing Zn while the immobilization ability of KH_2PO_4 is much weaker. All the three phosphates are helpful for modifying the partitioning of Cu and Zn from the non-residual phase to the residual phase; however, they could also enhance the contents of Cu and Zn associated with exchangeable and carbonates fractions.

Key words: Cu; Zn; phosphate; adsorption; leaching; red soil

1 Introduction

In the past decades, heavy metal pollution has been considered as one of the most environment concern around the world and received more and more attention. Anthropogenic industrial and agriculture activities including sewage discharge, stack of solid waste and application of chemical fertilization are the major sources of metal enrichment in soil [1−3]. Heavy metals are easily retained by the surface layer soil which has a strong metal ions adsorption capacity, and they can withstand microbial or chemical degradation, thus persist for a long time after their introduction in soils [4]. Excessive accumulation of heavy metals in top-soil will not only affect soil quality, crop growth and further contaminate groundwater by leaching, but finally pose a great threat to human health through the food chain [5−7]. In China, due to rapid economic development and delay of environmental protection in recent 30 years, a great amount of heavy metals were released into municipal and rural soils with the result that the pollution situation in some areas is quite severe [8]. According to a previous report [9], unrecycled and unused industrial waste and domestic trash were dumped into open fields around most cities, polluting soil and taking over or damaging 1×10^5 km^2 of cropland in China.

Many physicochemical and biological (phytoremediation and microbial methods) remedy techniques were applied to mobilizing or immobilizing heavy metals in polluted soil. Among these techniques, the application of phosphate amendments was proved to significantly reduce the availability of heavy metals in soil in addition to providing nutrition for crops and therefore identified as a cost-effective method in soil situ remediation [10−12]. Phosphate compounds immobilize heavy metals in soil mainly through reactions including P-induced directly/indirectly metal adsorption, precipitation of metals with solution phosphate [1,13]. Many researchers suggested that the effectiveness of lead

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immobilization in contaminated soil can be improved by mixing P sources with higher solubility (i.e., KH_2PO_4, CaH_2PO_4 and H_3PO_4) and rock phosphate [11,14,15]. Soluble phosphates were also found to be highly effective in increasing the adsorption of Pb and Zn in soil [10,16]; however, some researchers pointed out that the leachability of metals in soils amended with soluble phosphates was much higher [17,18]. On the other hand, soil properties such as pH, organic matter and soluble salts contents also affect the stabilization of metals. Soil pH is considered to be the most important factor in deciding the chemical forms of metals in soils [19−21] and can influence the reaction between metal ions and phosphates. CAO et al [22] found that acidic condition (pH<5) was favorable for the transformation of Pb from PbO, $PbCO_3$ and $PbSO_4$ to sparingly soluble chloropyromorphite in the presence of soils added with $Ca(H_2PO_4)_2$ while the contents of soluble Cu and Zn could be increased by the acidification of soil via H_3PO_4 addition. On the whole, previous studies on chemical immobilization of heavy metals by P addition were mainly carried out with the subject of Pb, while other metals such as Cu and Zn were less concerned. Furthermore, there were only a limited number of studies focused on the effect of soluble phosphate on the leaching of metals in soil, especially in acid soil with low pH value.

In order to evaluate the stability of Cu and Zn in soil with P fertilization addition, in this work, batch and soil column experiments were conducted to investigate the adsorption behavior and leaching characteristics of Cu and Zn in red soil added with different soluble phosphates (KH_2PO_4, $(NH_4)H_2PO_4$ and $Ca(H_2PO_4)_2$). The results of the experiments were expected to provide helpful information for governing heavy metal pollution in red soil by using method of phosphate application.

2 Experimental

2.1 Soil sample

The soil samples used in this experiment were collected in an orchard in the Shaoyang soil and Water Conservation Research Institutes (27°17′56.04″N, 111°31′45.48″E), Hunan province, China. The agrotype is a typical red soil widely distributed in southern China. Soils from the surface layer (0−20 cm), subsurface layer (20−40 cm) and deep layer (40−60 cm) were collected respectively by digging an l m-depth hole, and then they were taken back to laboratory. Impurity matters such as stone, leaves, grasses in soils were removed, after that, the sampled soils were allowed to air-dry and passed through a 2 mm-nylon sieve. The basic properties of the soil are presented in Table 1.

2.2 Adsorption experiments

As there was no obvious difference among properties of the soil samples in different layers, only the surface layer soil was selected for the adsorption experiments. Soil sample aliquot (5 g) was placed into a 100 mL polypropylene centrifuge tube, 50 mL of 0.01 mol/L $NaNO_3$ solution containing a series concentrations (0, 0.5, 1, 5, 10, 20, 50, 100 mg/L) of Cu (as $Cu(NO_3)_2$) or Zn (as $Zn(NO_3)_2$) was added to each tube. Phosphate (KH_2PO_4, $(NH_4)H_2PO_4$ or $Ca(H_2PO_4)_2$) was also added at n(P): n(Cu/Zn)=2:1. The suspensions were shaken at 160 r/min for 2.0 h and then kept still for 20.0 h at a constant temperature of (25±2) °C. At the end of each adsorption period, the suspensions were centrifuged at 4000 r/min for 20 min and supernatant was filtrated for measurement of metal concentrations.

Langmuir and Freundlich equations [23] were applied to fitting the data from the isotherm studies:

$$q_e = \frac{K_L q_m \rho_e}{1 + K_L \rho_e} \quad (1)$$

$$q_e = K_F \rho_e^{1/n} \quad (2)$$

where q_e is the amount of adsorbed metal concentration at equilibrium; ρ_e is the concentration of the metal in solution at equilibrium; q_m is the maximum adsorption amount of metal on soil; K_L, K_F and $1/n$ are constants.

2.3 Soil column experiments

Leaching experiment was conducted at room temperature using four columns which were made of polypropylene with the inner diameter of 10 cm and the length of 60 cm. Prior to the leaching experiments, the columns were washed with diluted HNO_3 (5%, volume fraction) and distilled water. A plastic plate with 50 cavities was placed at the bottom to facilitate the outflow

Table 1 Basic properties of soils used in this study

Soil sampling depth/cm	pH	Cation exchange capacity/ (cmol(+)·kg^{-1})	w(Cu)/ (mg·kg^{-1})	w(Zn)/ (mg·kg^{-1})	w(P)/ (mg·kg^{-1})	w(Sand)/ %	w(Silt)/ %	w(Clay)/ %
0−20	4.3	9.5	1.31	2.81	4.62	38.88	30.28	30.84
20−40	4.2	8.8	0.85	2.12	3.60	35.52	27.80	30.40
40−60	4.1	8.3	0.57	1.80	3.33	38.24	30.40	31.36

of leachate. Two pieces of filter papers were placed on the plastic plate to avoid the outflow of soil particles from the soil column. Soils from the three layers (surface, subsurface and deep layers) were subsequently filled into the columns with 20 cm per layer and compacted according to their actual bulk density. The soil columns were initially washed from the top with deionized water by using a peristaltic pump (BT100-EA/DG−4, Chongqing Jieheng Peristaltic Pump Co., Ltd., China). Then, heavy metals Cu and Zn were slowly poured into each soil column from the top in the form of $Cu(NO_3)_2$ and $Zn(NO_3)_2$ solution (200 mL). The contents of metals in the soil columns were 50 mg/kg for Cu and 200 mg/kg for Zn according to the second level criterion of Stand of Soil Environment [24]. The soil columns were kept standing for two weeks. Phosphates (KH_2PO_4, $(NH_4)H_2PO_4$ or $Ca(H_2PO_4)_2$) were dissolved in 200 mL deionized water and added into each soil column from the top. The average fertilization quantity was 15−30 mg/kg in cropland of south China, so the content of P was set at 20 mg/kg. The soil column added with KH_2PO_4, $(NH_4)H_2PO_4$ and $Ca(H_2PO_4)_2$ were named as K1, K2 and K3, respectively. The fourth column named as CK was served as the control group without any phosphate added. 11250 mL of deionized water equivalent to the precipitation of ten years of the local area was pumped into the columns (1125 mL/d). Leachates from the columns were collected daily in plastic containers and filtered for the determination of pH, electrical conductivity and heavy metal concentrations. After the leaching process, soils in different layers were taken out respectively and dried. Fractionation of metals in the soil was measured by the sequential extraction procedure of the Tessier method [25].

2.4 Analytical methods

Soil pH was measured in deionized water at a soil/solution mass ratio of 1:2.5 using HI 3221 pH meter (Hanna Instruments Inc., USA). Cation exchange capacity (CEC) was determined by $BaCl_2$ displaced method [26]. Total phosphate was measured using the method in Ref. [27]. Soil particle size distribution analysis was measured by pipette method [28]. Electronic conductivity was determined by DDSJ−308A conductivity meter (INESA Scientific Instrument Inc., China). Total metal content in soil after HNO_3−HF−$HClO_4$ digestion process sample (0.5 g) was transferred to a Teflon vial and 10 mL HCl was added and allowed to near dryness (100 °C). This was followed by the addition of 5 mL HNO_3, 5 mL HF, and 4 mL $HClO_4$. The solution was subsequently heated at 160 °C for 1 h and at 200 °C to near dryness. Then, the solution was transferred to a 50 mL volumetric flask by adding distilled water and leachate was determined by atomic absorption spectrometry (AA700, PerkinElmer, USA). Reference standard soil from sediment of Xiangjiang River (GBW07457, Institute of Geophysical and Geochemical Exploration CAGS, China) and reagent blanks were used as the quality control sample during the analysis procedures. Fractionation of heavy metals was determined by the sequential extraction procedure of Tessier method [25]. Statistical analyses were conducted using SPSS 10.0 software.

3 Result and discussion

3.1 Effect of different phosphates on Cu and Zn adsorption in red soil

Experimental data and adsorption isotherms for Cu and Zn onto red soil with different phosphates are shown in Figs. 1(a) and (b), respectively. As can be seen, all the three phosphates can greatly improve the adsorption capacity of red soil for Cu and Zn. The addition of P made the adsorption amount increase linearly, and Cu and Zn were almost completely adsorbed (adsorption rate ranged from 95.0% to 99.6% and 93.8% to 98.4%, respectively) within the initial concentration range of 0.5−100 mg/L. When the initial concentrations exceed 20 mg/L, the adsorption rates of the two metals decrease significantly (around 50% at the maximum initial concentration of 100 mg/L) in the case of no phosphate addition. Table 2 presents Langmuir and Freundlich isotherm parameters and the calculated R^2 values ranging from 0.9891 to 0.9954 and 0.9055 to 0.9943, respectively, indicating that the two models well describe the adsorption characteristics of the two metals. The higher K_F values observed for Cu (phosphate application: 227.44−354.76 L/kg and red soil: 61.35 L/kg) suggest a stronger bonding affinity compared with Zn (phosphate application: 195.95−249.24 L/kg and red soil: 50.63 L/mg), and this is consistent with many other studies [29−31]. For the different phosphates, the K_F of both Cu and Zn decreased in the order of $Ca(H_2PO_4)_2$> KH_2PO_4> $(NH_4)H_2PO_4$. The result of batch experiment is in agreement with some previous reports [32−34], finding that Cu and Zn adsorption in soils is higher in the presence of P. SAEED and FOX [35] attributed the enhanced adsorption capacity of Zn to the increase of the negative charge on iron and aluminum oxides system in the soil of variable charge types. Some other researchers indicated that the formation of new specific adsorption sites as result of P interaction with soil colloids was another potential mechanism [33,36,37]. Different promotion effects of the phosphates were caused by their different cations. NH_4^+ might reduce the pH of solution, hence the promotion effect was the minimum. More K^+ cations existed in the solution in the case of the same P

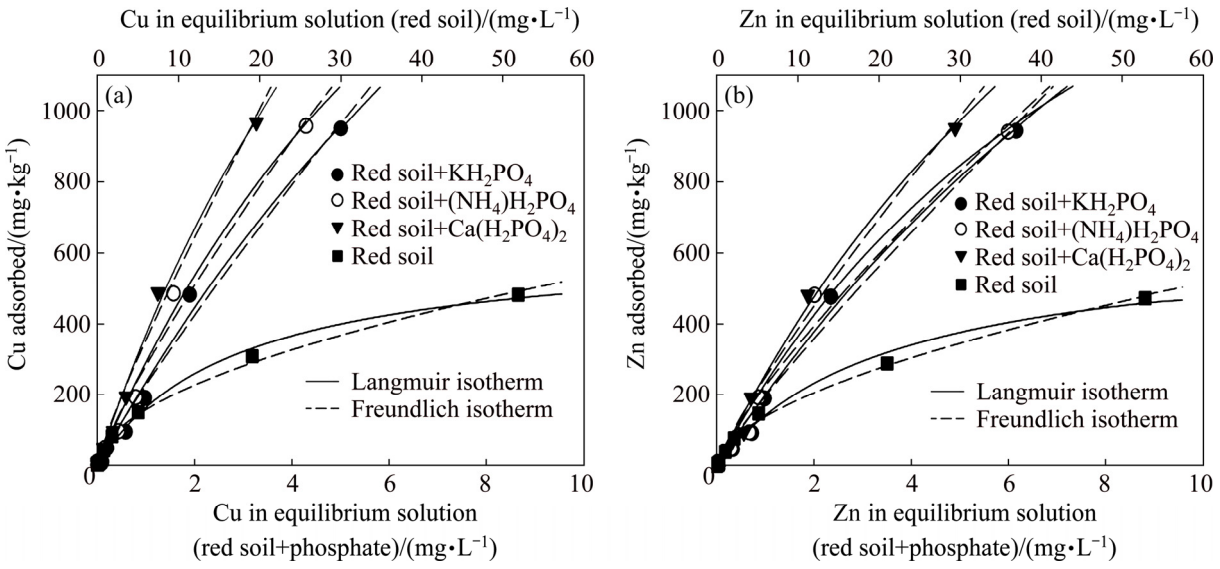

Fig. 1 Adsorption isotherms of Cu (a) and Zn (b) onto red soil with different phosphates

Table 2 Langmuir and Freundlich model parameters and *R*-squared values calculated from adsorption experimental data of Cu and Zn

Metal adsorbed	Treatment	Langmuir model			Freundlich model		
		K_L/(L·mg^{-1})	q_m/(mg·kg^{-1})	R^2	K_F/(L·mg^{-1})	n^{-1}	R^2
Cu	Red soil +KH_2PO_4	0.1204	3446.72	0.9954	227.44	0.8990	0.9936
	Red soil+$(NH_4)H_2PO_4$	0.1004	3204.56	0.9927	282.03	0.8501	0.9890
	Red soil+$Ca(H_2PO_4)_2$	0.0061	4076.51	0.9906	354.76	0.8591	0.9924
	Red soil	0.0592	624.21	0.9938	61.35	1.8868	0.9943
Zn	Red soil+KH_2PO_4	0.0609	3398.8	0.9931	195.95	0.8741	0.9894
	Red soil+ $(NH_4)H_2PO_4$	0.1034	2480.53	0.9891	224.74	0.8107	0.9822
	Red soil+$Ca(H_2PO_4)_2$	0.0888	3154.72	0.9942	249.24	0.8522	0.9055
	Red soil	0.0476	641.76	0.9903	50.36	1.7544	0.9924

concentration, thereby KH_2PO_4 showed stronger ability to complete adsorption sites with Cu^{2+} and Zn^{2+}.

3.2 Heavy metal concentrations in leachate

The variations of Cu and Zn concentrations in leachates are presented in Figs. 2(a) and (b), respectively. It was observed that the concentration of Cu in leachates continuously increased during the whole leaching process for 10 d while the concentration of Zn increased firstly and then decreased. Less Zn was leached out from the soil columns (K1, K2 and K3) added with different phosphates compared with the CK treatment and the retention ability of the three phosphates followed the order of $Ca(H_2PO_4)_2 \approx (NH_4)H_2PO_4 > KH_2PO_4$. The maximum concentration of Zn in leachate of K1 was 1.134 mg/L, which was a little higher than the third level (1.0 mg/L) criterion of quality standard for ground water (GB/T 14848−9) in China. This means that KH_2PO_4 is unable to effectively immobilize Zn in red soil, groundwater pollution is possible to be contaminated under the conditions similar to the experiment. The concentrations of Cu in the leachates were very low (0.023−0.073 mg/L) and there was no obvious difference in the variations of Cu concentrations among all the four treatments. The most likely reason was that the added Cu was almost all adsorbed in red soil and hardly to be released through leaching effect. It was confirmed that Cu was harder to migrate in soil system due to its stronger bonding affinity in soil compared with Zn [38−40]. Moreover, minerals with lower solubility form first in a system with multiple metals [41]. Solubility products of zinc phosphate are greater than those of Cu phosphate. In general, the result obtained from the leaching experiments agreed with the data presented in adsorption experiments.

Phosphate treatments were reported to effectively reduce Pb dissolution and transport from contaminated soils; however, they were less studied with the objects of

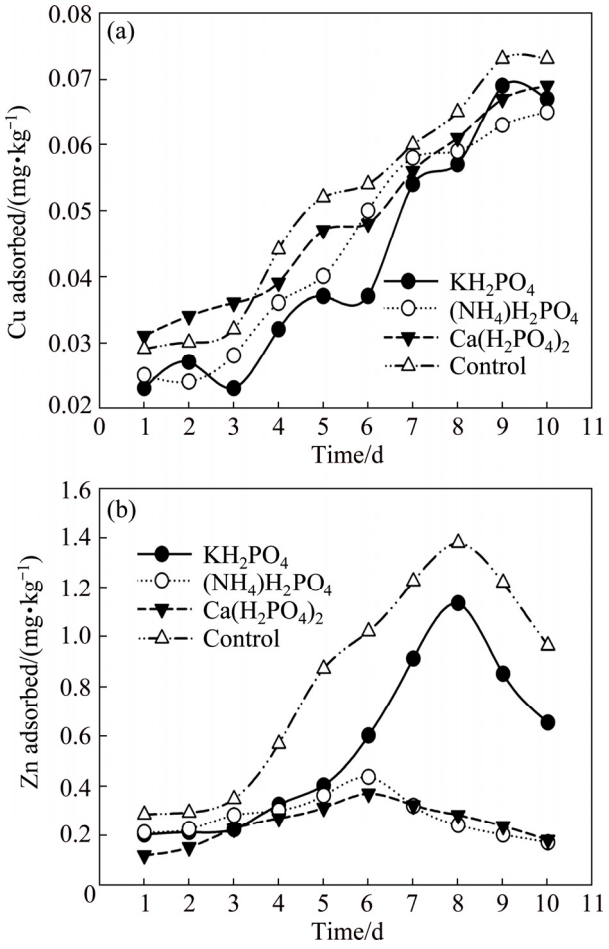

Fig. 2 Concentrations of Cu (a) and Zn (b) in leachates

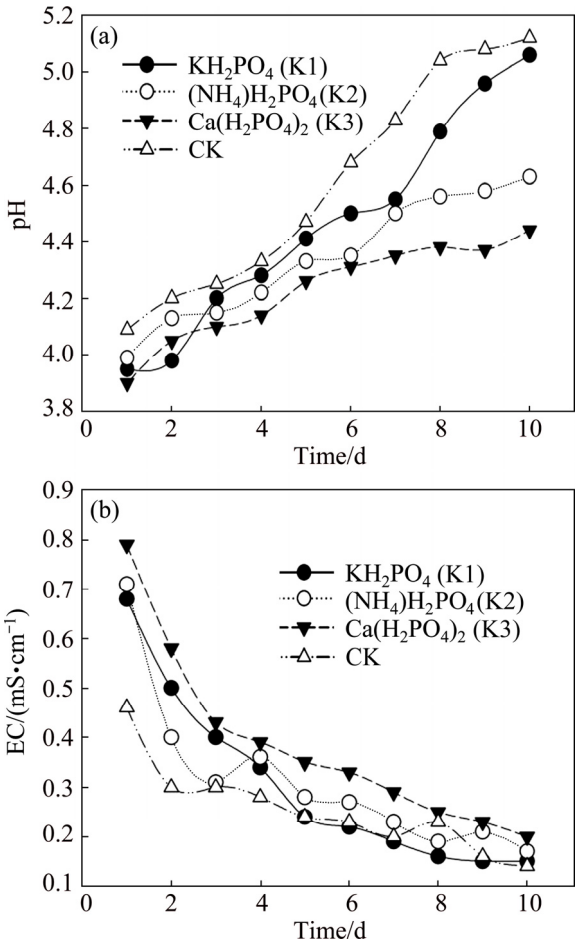

Fig. 3 pH (a) and electrical conductivity (b) of leachates

Cu, Zn and other metals. Our study showed that $Ca(H_2PO_4)_2$ and $(NH_4)H_2PO_4$ can significantly immobilize Zn in red soil, whereas the immobilization ability of KH_2PO_4 was much weaker. $Ca(H_2PO_4)_2$ and $(NH_4)H_2PO_4$ were also found to be able to immobile Cu and Zn to some extent in some previous studies [10,41]. The formation of pyromorphite is considered as the main mechanism of reducing Pb availability in soils [14], while the immobilization of other metals such as Cu, Zn and Cd is attributed to various processes including ion exchange [42,43], surface complexation [44] and sorption to the phosphate mineral [45], etc. The addition of KH_2PO_4 could cause more decrease in the pH of soil compared with $(NH_4)H_2PO_4$ and provide less $H_2PO_4^-$ than $Ca(H_2PO_4)_2$. The two aspects were possible to be the reasons for the weak immobilize ability of KH_2PO_4 in decreasing the transfer ability of metals in red soil.

3.3 Changes of pH and electrical conductivity in leachate

In Fig. 3(a), the changes of pH values in the leachates are shown. For all the columns, pH of leachate increased continuously with leaching time. The pH values in experiment groups (K1, K2 and K3) were lower than that in control group (CK). In the first 5 d, there was very little gap among the pH values of leachates from different columns, after that, the gap became wider and wider. At the end of the leaching experiments, the pH values of leachate in K3 were close to the soil pH (4.1−4.3), while the pH values of leachate in K1, K2 and CK were apparently higher (5.06, 5.04 and 4.63, respectively). KH_2PO_4, $(NH_4)H_2PO_4$ and $Ca(H_2PO_4)_2$ were all acidic fertilizer that could reduce the soil pH, which led to lower pH of experiment group compared with CK. As the leaching process continued, H^+ in leachate became less and less, resulting in the increase of pH in leachates. After a period of leaching (5 d), the soil was saturated and the penetrability decreased, in this case, the soil columns were apt to form watered-out zones, which decreased the redox potential and further consumed the H^+ in soil solution. This may partly explain that the pH changed slowly at first and then increased significantly (5−10 d). This finding was similar with the results of SUN et al [45] who observed that soil pH increased with flooding time. The addition of $Ca(H_2PO_4)_2$ can cause more reduction in soil pH compared with KH_2PO_4, and $(NH_4)H_2PO_4$, and thereby keeping the pH of leachate in K3 at a relatively

low level.

The electrical conductivity (EC) indicates the content of salts in solution and is often used as a measure of ions changes in complicated system such as soil and water [46,47]. Figure 3(b) shows the changes of the electrical conductivity of the leachates. In contrary to pH, the EC of leachate was observed to continuously decrease during the leaching process, which indicated that salinity in leachate decreased. In the initial period of leaching, the EC in the experimental group was obviously higher than that in the control. There was a significant decrease of EC in the first three days and then slow decrease in the following 7 d. The EC values of final leachates for the four columns were almost equal to the values between 0.1 and 0.2 mS/cm. The EC of K1 was close to that of K2 and both of them were lower than that of K3. After the phosphates were added into the soil, part of soluble ions such as H^+, Ca^{2+}, NH_4^+ and K^+ outflew with the leachate. EC values of the experiment groups were higher than that of control group since there was no soluble salinity added into the column of the control group. KASCHL et al [48] observed higher EC with higher heavy metal concentrations in leachates during the leaching of municipal solid waste compost in calcareous soils; however, in our research, the change trend of EC and metal concentrations were completely different. This might be because the Cu and Zn concentrations in our research were too low to influence the variation of EC.

3.4 Fraction distributions of Cu and Zn in soil after leaching

Almost all the added Cu and most of Zn were retained in the soil columns after the leaching experiment. The fraction distributions of Cu and Zn in soils of different layers are shown in Figs. 4(a) and (b), respectively. The percentage of residue in experimental groups was higher than that in control group (especially in the 0−20 cm and 20−40 cm soil layer), which showed that phosphate was helpful for modifying the partitioning of Cu and Zn from the non-RES phase to the RES phase. The total percentage of the easy-to-migration fraction (EXC+CAR) of Cu was very small (less than 8%) in all treatments and as a whole the experimental group was observed to have slightly higher proportion (2.19%−7.40%) of this fraction compared with CK group (2.48%−5.31%). The sum of Zn associated with EXC and CAR accounted for 10%−35% of total Zn in different soil layers, which indicates that Zn shows a higher activity than Cu in the soil environment. Furthermore, phosphate addition could also increase the Zn in EXC and CAR fractions and the proportions in the four columns generally follow the order: K1>K2>K3> CK. This order corresponded with that of the decrease in

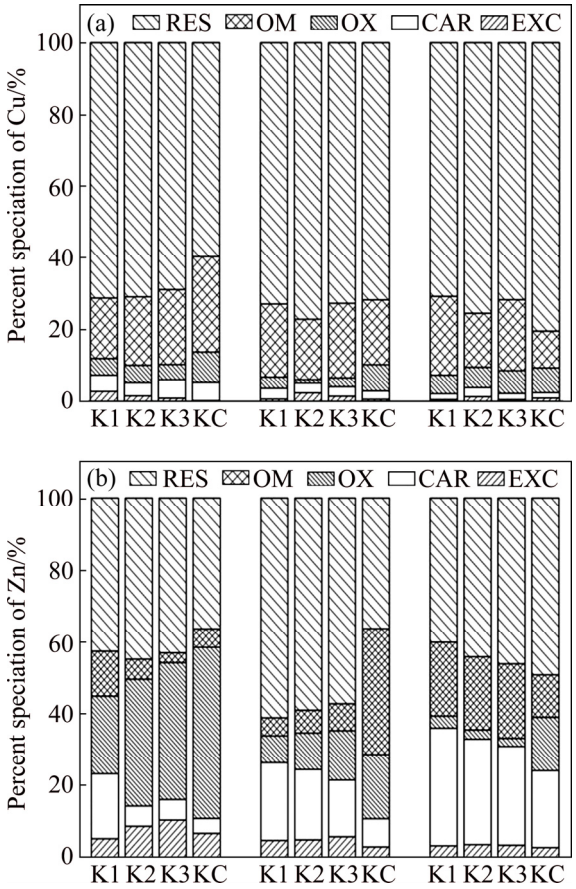

Fig. 4 Fraction distributions of Cu (a) and Zn (b) in soil (RES: Residual fraction; OM: Fraction bound to organic matters; CAR: Fraction bound to carbonates; EXC: Exchangeable fraction; OX: Fraction bound to iron and manganese oxides)

pH of leachates. pH plays the most important role in determining the chemical form of metals in soil and low pH condition can generally enhance their activity [49,50]. Though the addition of KH_2PO_4, $(NH_4)H_2PO_4$ and $Ca(H_2PO_4)_2$ facilitated the formation of residual bounded metals, they lowered the pH of soil, thereby resulting in a great possibility of higher content of Zn in EXC and CAR fractions. Therefore, on one hand, three phosphates can decrease the downward transport ability of Cu and Zn in different degrees, while on the other hand, they cannot well decrease the potential mobility and bioavailability of the two metals in red soil, instead, they are possible to increase their activity. This result is different from that in some former studies [51,52] and it could be due to the difference in physicochemical properties of the used soils. Low pH of red soil made it unable to effectively buffer input of acidity caused by phosphate addition. In conclusion, it may not be appropriate to select adding phosphate fertilizer as the metal immobilization method in red soil. In addition to soil pH, other factors including phosphate concentration, soil moisture condition, etc, are necessary to be

considered to further understand the effect of phosphate on the fractionation and leachability of metals in soil.

4 Conclusions

1) Both the Langmuir and Freundlich models are suitable to describe the adsorption characteristics of Cu and Zn under the condition of phosphate application. All the three phosphates (KH_2PO_4, $(NH_4)H_2PO_4$ and $Ca(H_2PO_4)_2$) could greatly improve the adsorption capacity of red soil for Cu and Zn.

2) Cu is easier to be adsorbed by red soil and more difficult to transport downward. The three phosphates added at the average fertilization quantity level of 20 mg/kg can reduce the transport of Zn in red soil and the retention ability of the phosphates follows the order of $Ca(H_2PO_4)_2 \approx (NH_4)H_2PO_4 > KH_2PO_4$.

3) The application of phosphates could also enhance the content of Zn in bioactive fractions (exchangeable and carbonate) and therefore increase their potential mobility and bioavailability. These phosphates should be used cautiously in immobilizing heavy metals in polluted red soil.

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不同磷酸盐对铜和锌在红壤中吸附和淋溶的影响

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摘 要：采用批式吸附实验和土柱实验研究 KH_2PO_4、$(NH_4)H_2PO_4$ 和 $Ca(H_2PO_4)_2$ 对铜和锌在红壤中的吸附和淋溶特性。结果表明：这 3 种磷酸盐都能极大地提高红壤对铜和锌的吸附能力，其影响大小顺序为 $Ca(H_2PO_4)_2$> KH_2PO_4>$(NH_4)H_2PO_4$。磷酸盐的添加对铜的迁移性影响不大。$Ca(H_2PO_4)_2$ 和 $(NH_4)H_2PO_4$ 能较大地提高锌在红壤中的移动性。3 种磷酸盐都能促进铜和锌的形态由非残渣态向残渣态转化，但是同样会增加其可交换态和碳酸盐结合态的含量。

关键词：铜；锌；磷酸盐；吸附；淋溶；红壤

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