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Effective remediation of cadmium and lead contaminated soils by a novel slow-release phosphate amendment

YAO Wen-bin(姚文斌)[1], HUANG Lei(黄磊)[2], ZHAO Fei-ping(赵飞平)[1],
YANG Zhi-hui(杨志辉)[1]*, LIU Yi(刘奕)[1], SU Chang-qing(苏长青)[3, 4]

1. School of Metallurgy and Environment, Central South University, Changsha 410083, China;
2. Guangzhou University-Linköping University Research Center on Urban Sustainable Development, Guangzhou University, Guangzhou 510006, China;
3. School of Energy Science and Engineering, Central South University, Changsha 410083, China;
4. Institute of Big Data and Internet Innovations, Hunan University of Technology and Business, Changsha 410205, China

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Abstract: Phosphate is widely used to immobilize cadmium (Cd) and lead (Pb) in soils through the insoluble metal phosphate precipitation. However, an increase in the phosphorus content of the environment can cause new pollution. In this study, five slow-release phosphate amendments (SRPAs) were synthesized and their characteristics including BET, SEM, FTIR, swelling ratio, and thephosphorus release were determined. The results show that SRPA was a sphere with a network structure with a specific surface area of 5 to 7.18 m^2/g andcontained phosphate, hydroxyl, carboxyl and other functional groups. Among five SRPAs, S3 sample showed good performance for phosphate release. Phosphate release from SRPA was well fitted with Ritger-Peppas model with constant n between 0.45 and 0.85, indicating that the phosphate release was in accordance with non-Fickian diffusion. As compared with monocalcium phosphate (MCP), SRPA application led to a lower concentration of water-soluble phosphorus in the soil sample and higher remediation efficiencies of Cd and Pb. The remediation efficiencies of water-soluble Cd and Pb in soil with SRPA were 97.1% and 97.9%, respectively. The remediation efficiencies of bioavailable Cd and Pb were 71.85% and 76.47%, respectively. The results of Tessier extraction showed that the exchangeable and carbonatebound fractions of Cd and Pb in the soil sample after SRPA application significantly reduced,while the residual fraction increased, indicating the stability of heavy metals increased.

Key words: heavy metal; phosphate; slow-release amendment; soil remediation

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1 Introduction

Heavy metal contamination in paddy soils is a serious issue for rice production and management in China. The joint report on national soil pollution from the Ministry of Environmental Protection Department and Chinese Ministry of Land and Resources showed that about 16.1% of soil samples collected from land (600 km^2) in China were polluted. The inorganic ions including cadmium (Cd) and lead (Pb) were defined as the main

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Corresponding author: YANG Zhi-hui, PhD, Professor; Tel: +86-731-88830875; Fax: +86-731-88710171; E-mail: yangzh@csu.edu.cn

pollutants. Therefore, the development and research of remediation technology for Pb and Cd contaminated soil has received widespread attention. In recent years, a great deal of research has been done on physical remediation technology, biological remediation technology, and electric remediation technology. However, chemical remediation technology has the advantages of high efficiency, reliability, and cheapness as a large-scale remediation method used in the practice [1]. Therefore, research on controlling secondary pollution caused by chemical remediation has extremely potential application. Phosphate, widely known for causing eutrophication in water bodies, is a very effective amendment for the remediation Pb and Cd-contaminated soil [2, 3]. Monocalcium phosphate (MCP) can form insoluble phosphate with Pb and Cd, thereby reducing the bioavailability of Pb and Cd in the soil. However, a considerable part of phosphate will permeate into the groundwater with the flow of water, which on the causes water pollution and hand reduces the remediation efficiency. In order to control the secondary pollution caused by phosphate in the environment and improve the remediation efficiency, a phosphate slow-release amendment (SRPA) was proposed in this article. Sodium alginate (SA), a raw material produced from brown seaweeds, has been chosen to synthesize the amendment, due to its biodegradability, unique biocompatibility, and non-toxicity. Sodium alginate is able to adsorb soluble metal ions because of the abundant carboxyl groups. However, as an amendment, pure SA beads could be crushed in the soil and dissolved under alkaline conditions. In previous research, sodium alginate was confirmed to be crosslinked by calcium ion [4]. In addition, polyvinyl alcohol (PVA) was successfully applied to prepare slow-release fertilizers [5, 6]. Accordingly, it is reasonable to prepare a novel slow-release amendment with calcium phosphate, SA, and PVA for the remediation of heavy metal contaminated soils. Therefore, the objectives of this study were to prepare a slow-release phosphate amendment (SRPA) for the immobilization of Cd and Pb in contaminated soil, evaluate phosphate release from the slow-release amendments, and investigate the effectiveness of Cd and Pb remediation by this SRPA.

2 Materials and methods

2.1 Materials

Sodium alginate (SA) and polyvinyl alcohol (PVA) were purchased from Fengchuan Chemical Reagent Technologies Co., Ltd. (Tianjin, China) and Kemiou Chemical Reagent Co. Ltd. (Tianjin, China), respectively. Bicarbonate sodium (BS) and monocalcium phosphate (MCP) were from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals used in this study were of analytical reagent (AR) grade. The non-polluted soil (raw soil) was collected from farmland near Yanghu park (112° 55′57″E, 28° 7′12″N) in Changsha city. The air-dried soil samples (collected at 0−30 cm) were ground by mortar and then removed weeds, plant roots, and gravels by 2-mm sieve. The modified Walkley and Black method was used to detect organic matter in soil [7]. The soil pH was detected by pH meter with 1:5 (*w*/*v*) ratio of soil and water. After digesting with HNO_3-HF-$HClO_4$ mixture, the total Cd and Pb concentrations were determined by ICP-OES (Agilent 5100).

The contaminated soil was prepared by spiking the soil with $Pb(NO_3)_2$ and $Cd(NO_3)_2$ according to the concentrations of Pb and Cd in soils being 1300 and 16.0 mg/kg respectively. The spiked soil was aged for 84 d at room temperature. After aging, the concentrations of water-soluble Cd and Pb were determined 0.3 and 5.4 mg/kg, respectively.

Table 1 Properties of raw soil

Property	Value
pH	6.82
OM/($g\cdot kg^{-1}$)	11.55
CEC/($cmol\cdot kg^{-1}$)	8.16
Total Cd/($mg\cdot kg^{-1}$)	0.69
Total Pb/($mg\cdot kg^{-1}$)	91.51
Clay in mass/%	39.08
Sand in mass/%	35.87
Silt in mass/%	25.05

2.2 Synthesis of slow-release phosphate amendment

Based on the different concentrations of SA, PVA, BS, and MCP, five samples of SRPA (numbered S1, S2, S3, S4, S5) were synthesized using the procedures described by the previous study [8]and the ingredients of SRPA are shown in Table 2. Briefly, 50−60 g PVA powder was dissolved in 1 L distilled water in a thermostat water bath of 353 K to prepare the PVA solution. A certain amount of MCP was put into the above PVA solution until fully dissolved, and 6 g BS was added into the above mixture. Thereafter, 25−30 g SA powder was added into the mixture and dissolved by continuous magnetic stirring. The aqueous dispersion was sucked and put into 100 mL 1.5% (*w*/*v*) $CaCl_2$-saturated H_3BO_4 solutions by a syringe. After stirring at 100 r/min, the spherical, smooth and homogenous SRPA beads were formed, collected and washed twice with the distilled water and air-dried at 323 K.

Table 2 Material composition of slow-release phospate amendment

Slow-release phospate amendment	Concentration/(g·L^{-1})			
	SA	PVA	BS	MCP
S1	30	50	6	0
S2	30	50	6	10
S3	30	60	6	10
S4	25	60	0	10
S5	25	60	6	10

SA: Sodium alginate; PVA: Polyvinyl alcohol; BS: Bicarbonate sodium; MCP: Morocalcium phosphate.

2.3 Determination of phosphorus encapsulation efficiency

0.05 g of SRPA beads were digested for 6 h in the complexed acid of 18.5 mol/L HCl and 18.5 mol/L HNO_3 (3 : 1 v/v). After digesting, the solution was diluted with deionized water to 10 mL. The concentration of phosphorus in the above solution was determined by a spectrophotometer with ammonium molybdate. The encapsulation efficiency E_e of an agent was expressed as follows:

$$E_e = (C_{\mathrm{mp,\,SPRA}}/C_{\mathrm{aap,\,SPRA}}) \times 100\% \tag{1}$$

where $C_{\mathrm{mp,\,SPRA}}$ is the measured phosphorus content in SPRA, and $C_{\mathrm{aap,\,SPRA}}$ is the actually added phosphorus content in SPRA.

2.4 Swelling experiment

100 g SRPA beads were placed in 500 mL distilled water, and then the pH value was buffered close to 2, 4, 6, 7, 9 and 10, respectively, with 0.1 mol/L hydrochloric acid and 0.1 mol/L sodium hydroxide solution. Thereafter, the SRPA beads were placed in a water bath at 298 K for 8 h. The SRPA beads were collected every 30 min, sucked off the water with a tissue paper and weighed. The swelling ratio (R_s) can be calculated by the following equation:

$$R_s = \frac{W_t - W_0}{W_0} \tag{2}$$

where W_t is the weight of the SRPA beads at time *t* and W_0 is the initial weight at the initial time.

2.5 Phosphorus release experiment

The following procedures were conducted to analyze the release of phosphorus from SRPA in aqueous solution. 5.00 g of SRPA was added into 100 mL distilled water (the pH value was adjusted to 7.0) and placed at room temperature. 10 mL solution was taken at 0.5, 1, 2, 4, 6 and 8 h and used for determining phosphorus concentration. The concentration of phosphorus in solution was detected by an UV-visible spectrophotometer. Phosphorus release kinetics was simulated with the following models.

Zero-order kinetics of phosphorus release can be represented as:

$$Q = Q_0 + Kt \tag{3}$$

where Q means the amount of phosphorus released; Q_0 means the initial amount of phosphorus in solution; K is a constant.

The first-order kinetics equation can be expressed as follows:

$$\ln\left(\frac{C_s}{C_s - C_t}\right) = K_F t \tag{4}$$

where C_s means the balance concentration of phosphorus; C_t means the concentration of phosphorus at time *t*; K_F is a rate constant.

The release of an agent from an insoluble matrix as the square root of a time-dependent process based on Higuchi diffusion was elaborated by the following equation:

$$Q_t = k_H (t)^{0.5} \tag{5}$$

Where Q_t means the amount of phosphorus released at time *t*; k_H means a release rate constant.

The Ritger-Peppas model can be described with the following equation [9]:

$$\frac{M_t}{M_\infty} = kt^n \tag{6}$$

where M_t/M_∞ means the fraction of phosphorus released at time t; k is a constant; n means the diffusion exponent.

2.6 Effect of pH on releasing of phosphate

To study the effect of pH value on the release of phosphate, pH value was buffered close to 2, 4, 6, 7, 9 and 10, respectively, with 0.1 mol/L hydrochloric acid and 0.1 mol/L sodium hydroxide solution. 5.00 g of SRPA was added into 100 mL buffered solution at room temperature for 2 h. The concentration of phosphorus in solution was detected with an UV-visible spectrophotometer.

2.7 Characterization of SRPA

The morphology of SRPA was observed with a SEM (JSM-5600LV, JEOL, Japan) at an acceleration voltage of 5 kV. The functional groups were determined with a FTIR (Thermo Nicolet, NEXUS, TM, USA) by scanning the sample from 400 to 4000 cm^{-1} at 4 cm^{-1} resolution. The specific surface area was measured with a micrometrics instrument (NOVA-1000, China).

2.8 Immobilization remediation experiment of Pb and Cd-contaminated soil

To simulate paddy farmland, 2.5 g SRPA was added into 10 g soil, mixed up with 10 mL water, maintained flooded in a 50 mL plastic tube and placed at room temperature. Parallelly, 0.25 g MCP with identical phosphorus content to SRPA was used as a control. After 7, 14, 28, 42, 56, 70 and 84 d, the bioavailable and waster-soluble Cd and Pb were extracted with diethylene triamine pentaacetate acid (DTPA) solution and distilled water at 1∶10 ratio (w/v). To investigate the fractions of Cd and Pb, sequential extractions of soil samples following the protocol of Tessier were conducted after 84 d. The concentrations of Cd and Pb in extracted solution were measured with ICP-OES (Agilent, USA).

3 Results and discussion

3.1 Characterization of SRPA

As shown in the spectra of pure SA (Figure 1 (a)), there was a strong and broad adsorption band at 3410 cm^{-1} in the presence of bounded —OH groups. Besides, there were some additional peaks at 2828, 1647, 1417, and 1103 cm^{-1}, due to stretching of C—H, —C═O (asymmetric), C—C and C—O—C, respectively [10]. As to the pure PVA, there were two adsorption bands, the 3451 cm^{-1} for —OH groups, and 1653 cm^{-1} for C—H band [11]. After crosslinking with sodium bicarbonate, the peak intensity of S1 at 3450 and 3441 cm^{-1} decreased (Figure 1(c)), confirming that the hydroxyl group is cross-linked with calcium ions and boric acid [12]. After loading calcium phosphate, there were new peaks at 1130 and 926 cm^{-1} in the spectra of S2, S3, S4 and S5. The study of STOCH et al [13] pointed out the peaks reflected the stretching of P—O. The results indicated that the phosphate was successfully loaded in the S2, S3, S4 and S5.

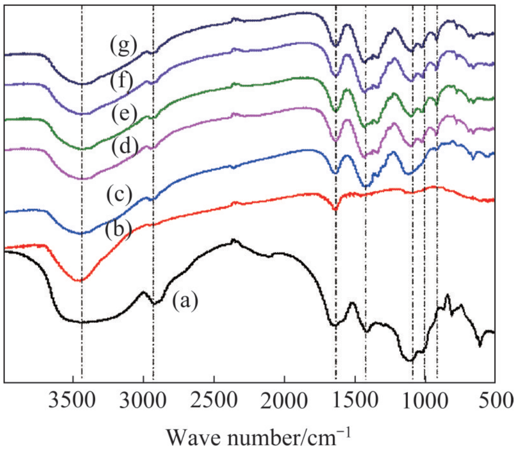

Figure 1 FTIR spectra of pure SA(a), pure PVA(b), S1 (c), S2 (d), S3(e), S4(f) and S5(g)

As illustrated in Figure 2, SEM images indicated that all the SRPA possessed an appropriate network structure. However, the structure characterization differed for the five SRPAs due to the alteration of their polymer density. S1 without calcium phosphate exhibited a cohesive and compact structure (Figure 2(a)), indicating that the beads were collapsed. The specific surface area of S1 was only 2.3 m^2/g. With monocalcium phosphate (MCP) addition, the network of SRPA was more regular and the specific surface area increased to 7.9 m^2/g. The result attributes to calcium ions, which promoted the crosslinking of SA. Moreover, S2 had a nice network structure and the aperture was the minimum. After adding more dosage of PVA and SA, the S3 and S5 are with large aperture and their specific surface area is 5.03 and 4.78 m^2/g, respectively. In other words, the PVA and SA might play a role in adjusting the network structure. However, without BS addition, there were unregular holes in S4 and its specific surface area was 4.0 m^2/g, indicating that sodium bicarbonate was critical for crosslinking. The results implied that the calcium phosphate and sodium bicarbonate benefited the formation of network structure of SRPA. The PVA and SA played a role in adjusting the network structure.

Table 3 BET surface area of various slow-release phospate amendment (m^2/g)

S1	S2	S3	S4	S5
2.36	7.90	5.03	4.00	4.78

3.2 Swelling behavior of slow-release phospate amendment

The swelling process was important for SRPA. After swelling, the size and weight were enlarged and the release of phosphate might be accelerated. The swelling characteristic can be indicated by the swelling ratio. The swelling ratio for SRPA in 8 h ranged from 2.3 to 4.6. The lowest swelling ratio was observed for S1 with 2.3, while S4 showed the maximum swelling ratio with a value of 4.6. The result revealed that increasing SA content in S4 instead of the polymer content in S1 significantly decreased the swelling ratio. This phenomenon might be attributed to 1) the high crosslink degree that decreased the swelling capacity of the network when carboxylate group existed; 2) the phosphate chelate with calcium ions of the network that caused the ionization of groups, increasing electrostatic repelling and leading to expansion of network; 3) the lesser absorption of H_2O and restricted transportation of H_2O, the penetration of free radical and monomer molecules might be decreased by denser network and viscous medium[14]. The larger swelling ratio might indicate burst release at initialtion [15]. The samples with a large swelling ratio and relatively less phosphate content might release all the phosphate at initialtion. The swelling

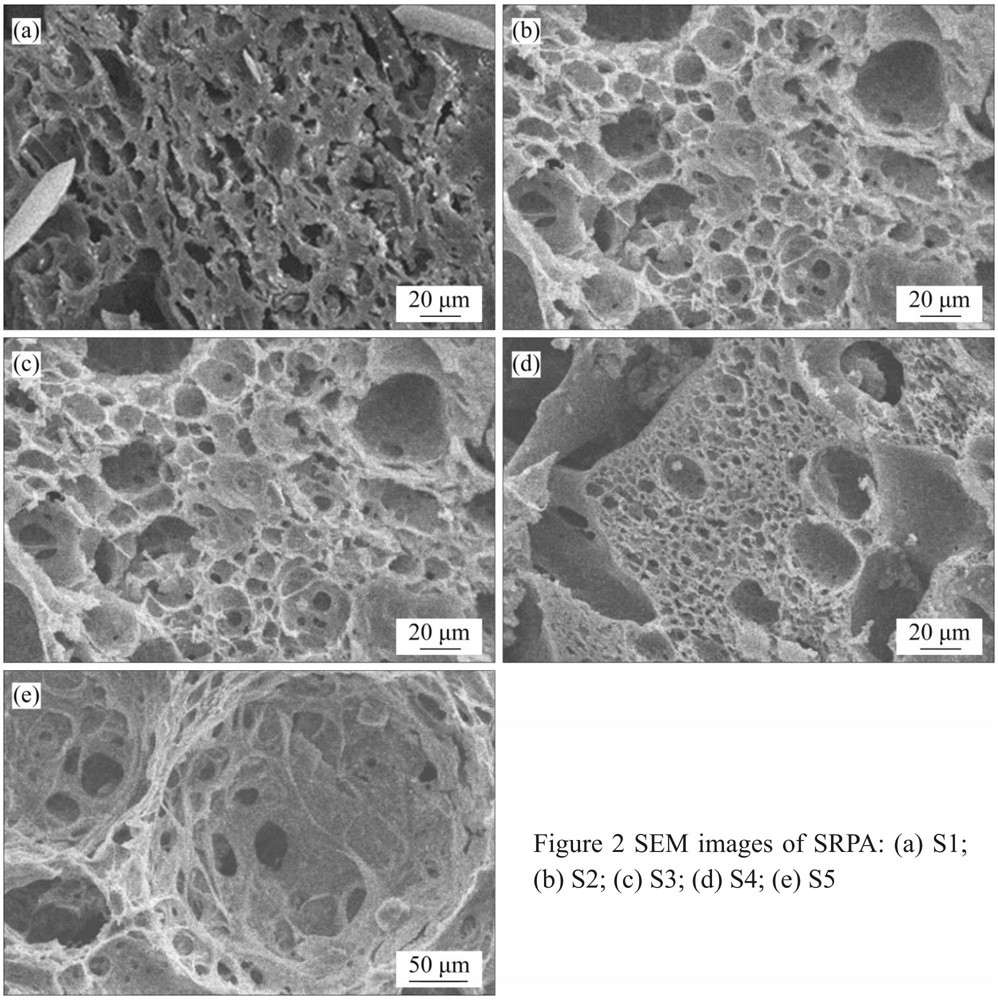

Figure 2 SEM images of SRPA: (a) S1; (b) S2; (c) S3; (d) S4; (e) S5

ratio of SRPA was also pH-dependent (Figure 3(b)). In this study, the minimum swelling ratio was found in neutral conditions, which was consistent with the other study [16]. The result might attribute to the presence of hydrogels. At acidic (or basic) condition, positive (or negative) electric charges in PVA-SA chains caused the swell process and generated the water diffusion effect into SRPA [17]. From the result of swelling ratio, the release of phosphate might be accelerated in acid condition, in which the heavy metal was activated.

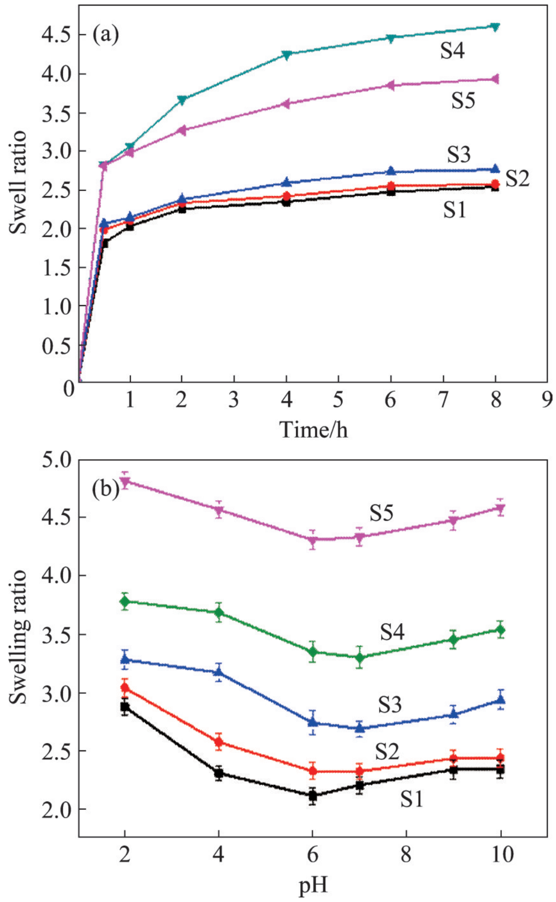

Figure 3 Swell ratio of SRPA at different time (a) and various pH values (b)

3.3 Phosphorus content and phosphorus release of SRPA

Phosphorus plays the most critical role to immobilize the heavy metal. Thus, phosphorus content was an important index to evaluate the SRPA characteristic. The SRPA containing more phosphorus might display more ability to immobilize heavy metal. The practical phosphorus contents for SRPAs (S2, S3, S4, S5) varied from 5.91% to 8.17%, which were a little higher than the similar amendments with 5.4% [18]. Besides the phosphorus contents, the encapsulation efficiency should also be considered. More encapsulation efficiency indicated less cost of production. The order of phosphorus contents was S3>S5>S4>S2. And the order of encapsulation efficiency was S3> S5> S4>S2. The result indicated the increase of SA and PVA benefit embedding of phosphate.

Several studies found that swell behavior would affect the releasing process in similar products [19, 20]. Thereby the phosphorus release was determined in various pH relating to the swelling behavior in this study. The phosphorus concentration releasing from SRPAs after 4 h in various pH values (from 2 to 10) is shown in Figure 4. Under acidic condition, the phosphorus concentration releasing from SRPA was much higher than that under the neutral condition as expected for the swelling process (Figure 4(a)). Nevertheless, the phosphorus concentration decreased when the pH value was over 7.0. As reported by MARSHALL et al [21], phosphate preferred to dissolve under acid condition and precipitated under basic condition. Thus, it could be induced that the release of phosphorus increased under acidic conditions, while decreased under basic condition.

Table 4 Phosphorus content of various amendments

Amendment	Measured phosphorus content/%	Actually added phosphorus content/%	Encapsulation efficiency/%
S2	5.91	10.63	55.6
S3	8.17	9.60	85.0
S4	6.96	10.52	66.1
S5	7.11	10.01	70.4

Most of the pH values of paddy soil were near 7.0. Thus, the phosphorus release kinetics of all these SRPA was tested at pH 7.0. The less amount of phosphorus was released from SRPA at initial stage (2 h) (Figure 4(b)), probably due to phosphate release from the surface adhered particle. Thereafter, phosphate release increased with prolonging time. Moreover, the largest phosphate release was obtained in S3 and S4 after 4 h. The result could be explained by the possibility of more phosphate content in S3 and the relative compact network preventing the release of phosphate in S2,

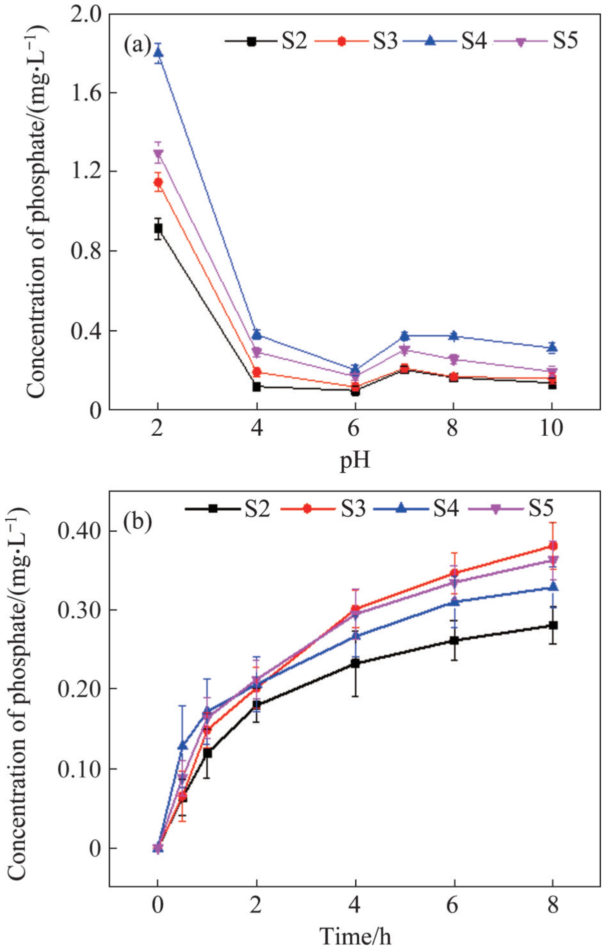

Figure 4 Phosphorus release of various amendments with different pH (a) and prolonged time (b)

S4 and S5 [11, 22].

The curve fitting coefficients of phosphate release kinetics with different models are shown in Table 5. The phosphorus release from S2, S3 and S5 that contained phosphate and sodium bicarbonate was consistent with both of Higuchi model (R^2 in the range of 0.9713 − 0.9848) and Ritger-Peppas model (R^2 in the range of 0.9506−0.9642) during a period of 8 h. In particular, the n values for S2, S3 and S5 were higher than 0.45 (Table 6), indicating non-Fickian mechanism for phosphorus release [23]. According to previous studies [24], the mechanism of phosphate transporting included both the diffusion and corrosion controlling phosphorus released from S2, S3 and S5. However, phosphorus release from S4 without sodium bicarbonate was found to match Ritger-Peppas model (R^2=0.9957). The N of S4 was 0.3339, indicting that the diffusion mainly controlled phosphorus release (concentrate of phosphate determined the release rate) and the release rate was sharply decreased in the first 2 h.

Table 5 R^2 of dynamic models of phosphate release

Sample	Zero order	First order	Higuchi diffusion	Ritger-Peppas
S2	0.3349	0.3360	0.9713	0.9506
S3	0.6192	0.6200	0.9848	0.9515
S4	0.3588	0.5964	0.9337	0.9957
S5	0.3338	0.3347	0.9798	0.9642

Table 6 Parameters of Ritger-Peppas model

Parameter	K	N
S2	0.0091	0.5162
S3	0.0075	0.6010
S4	0.0119	0.3339
S5	0.0100	0.4862

3.4 Concentration of phosphorus in soil after SRPA application

The concentration of phosphorus in soil with SRPA addition is depicted in Figure 5. In the first week, the water-soluble phosphorus of SRPA treated soil was 0.05 mg/kg. At the 28th day, the concentration of water-soluble phosphorus was fluctuated to 0.36 mg/kg. After being treated for 80 d, the concentration of water-soluble phosphorus maintained at 0.31 mg/kg. As for MCP, the water-soluble phosphorus of soil sharply increased to 10.21 mg/kg in the first week. Due to the adsorption, the concentration of phosphorus reduced to 5.34 mg/kg at the 14th day. After 80 d, the water-soluble phosphate was 3.12 mg/kg. The total phosphorus concentration in soil was also continuously monitored for 80 d. Because of a slow release of phosphorus, the overall trend of total phosphorus (TP) of SRPA treated soil gradually rose. The initial TP of soil was 42.26 mg/kg. After being treated by SRPA, the TP increased to 42.35 mg/kg in the first week and maintained at 44.03 mg/kg finally. The TP in the MCP treated soil increased to 43.98 mg/kg in the first week.

3.5 Remediation efficiency

According to CIZMECIOGLU et al [25], the soluble heavy metal in soil, which was the main form to transport into crops, was used as an indicator of remediation efficiency. The phosphate could react with Cd and Pb to form precipitation.

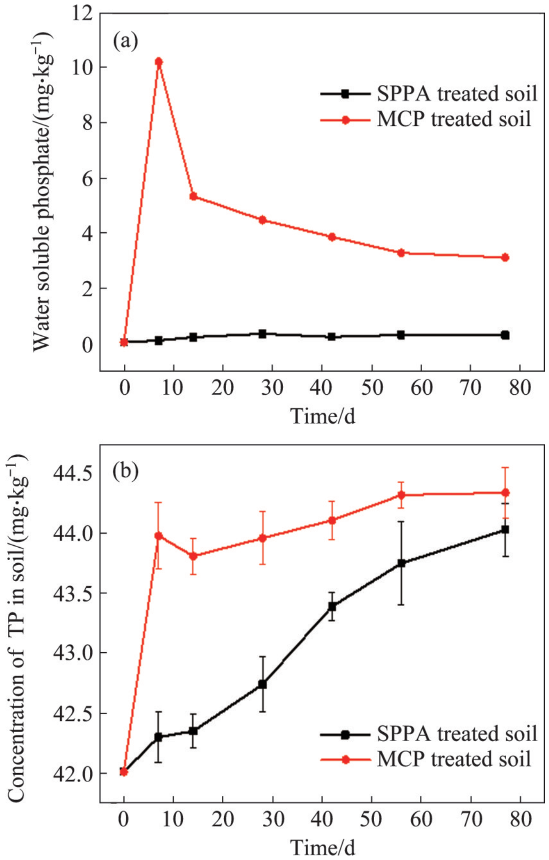

Figure 5 Phosphorus release of SRPA in soil: (a) Water soluble phosphorus; (b) Total phosphorus

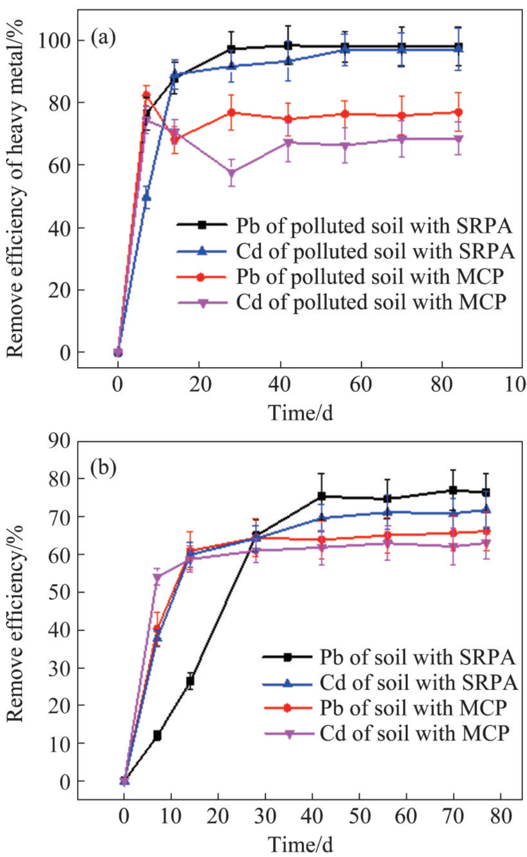

Figure 6 Remediation effective of Pb and Cd by SRPA: (a) Water-soluble Pb and Cd; (b) Bioavailable Pb and Cd

The removal efficiency of water-soluble Pb and Cd by MCP reached 82.33% and 74.34%, respectively, on the 7th day (Figure 6). Subsequently, the removal rates of water-soluble Pb and Cd decreased to 68.12% and 70.52%, respectively. This may be caused by the reduction of iron in the soil and the release of Pb and Cd from the soil into the solution [26]. It was 68.58% for Cd and 76.95% for Pb when the reaction time extended to 80 d. As expected, the SRPA showed far more excellent capacity of immobilizing soluble heavy metals than MCP. With SRPA, the removal of water-soluble Pb and Cd steadily rises. Although the remediation efficiency was 49.74% for Cd and 86.8% for Pb on the 7th day, the final remediation efficiency reached 97.1% for Cd and 97.9% for Pb.

Besides, the heavy metals in mineral and organic matter fraction caused by microbial, exchanging of ions, reduction, and oxidation in soil, could be taken up by crops also, namely, bioavailable heavy metal [27]. Therefore, bioavailable heavy metal is another critical index for the soil remediation. For the evaluation of bioavailability to heavy metal, a single-step extraction method was used with DTPA [28]. From Figure 5, the removal efficiencies of bioavailable Pb and Cd by MCP increased rapidly to 40.23% and 54.13% on the 7th day, and thereafter reached equilibrium on the 14th day with 58.75% for Cd and 60.96% for Pb in the contaminated soil. After the 80th day, the removal efficiencies of bioavailable Pb and Cd were 66.21% and 63.09%, respectively. As to SRPA, the removal efficiencies of bioavailable Pb and Cd were 11.9% and 37.37% on the 7th day, and reached equilibrium at the 21st day with 64.93% and 64.28% for Pb and Cd, respectively. After 80 d, 76.47% and 71.85% of bioavailable Pb and Cd were removed by SRPA, which were significantly higher than those by MCP. Thus, the results imply that the removal of Pb and Cd by SRPA is more stable, longer-lasting, and more efficient.

3.6 Fractions of Pb and Cd in soil

The fractions of Pb and Cd were analyzed by sequential extraction techniques, which are suitable to indicate the stabilization of heavy metal in soil

[29]. The method divided the heavy metal as five fractions: exchangeable fraction, carbonate bound fraction, Fe-Mn oxide bound fraction, organic matter (OM) bound fraction and residual fraction. Among these five fractions, the exchangeable and carbonate bound heavy metal are active in soil and would be easily released in soil. Fe-Mn oxide bound and organics bound fractions are relatively stable in soil for the chemical complex of metal ion with Fe-Mn oxides and organic matter. The residual heavy metal is regarded as a fairly stable form which was hardly released to soil. As illustrated in Table 7, in the soils without MCP and SRPA addition, the exchangeable, carbonate bound, Fe-Mn oxide bound, OM bound and residual Cd were 55.76%, 9.80%, 25.14%, 3.88%, and 5.41%, respectively. Lead mainly exists in Fe-Mn oxide bound fraction. The exchangeable, carbonate bound, Fe-Mn oxide bound, OM bound and residual Pb were 9.94%, 2.32%, 57.74%, 19.80% and 10.20%, respectively.

The MCP addition decreased the exchangeable and carbonate bound Cd to 43.12% and 4.12%, respectively. The Fe-Mn oxide bound, OM bound, and residual fractions increased to 27.45%, 10.57%, and 14.74%, respectively. Similar to Cd, the exchangeable, carbonate, Fe-Mn oxides boundand residual Pb decreased to 2.95%, 0.38% and 47.35%, respectively. Otherwise, the OM bound and residual Pb increased to 30.39% and 18.93%, respectively. The results obviously indicated that the highly active Cd and Pb greatly reduced, and the relatively stable fractions increased after adding MCP. The SRPA has more efficiency for immobilizing Pb and Cd. For instance, SRPA decreased the exchangeable and carbonate bound Cd to 43.13% and 3.00%, respectively. The Fe-Mn oxides bound, OM bound and residual Cd fractions increased to 27.62%, the 5.82% and 21.41%, respectively. Illustrated by previous study [30], the Cd immobilization by phosphate was fairly stable because of the formation of insoluble phosphate cadmium. The SRPA contained phosphate and prevented the contact of phosphate with soil mineral. The produced cadmium phosphate and lead phosphate were fairly stable and insoluble in soil. Thus, Cd and Pb prefer to exist in the formation of residual formation in soil.

3.7 Explanation of remediation mechanism

Heavy metals in soil can be divided into the following categories: bioavailable heavy metals (having the potential to be taken up by plants) and stable heavy metals (hardly taken up by plats). The bioavailable heavy metals include those fractions of water-soluble (existing in soil solution and easily migrate into plants) and adsorbed on the surface of soil particles. However, the flooding process will cause the dissolution of iron and manganese oxides in the soil, which will cause the release of heavy metals and increase the content of bioavailable heavy metals [26]. As reported by previous studies, increasing pH value might cause immobilizing heavy metal[31, 32]. However, pH value would be adjusted to 7.0 after flooding [33, 34]. Thus, the use of phosphorus was more effective for immobilizing heavy metals in paddy soil. After phosphate enters the soil, on the one hand, it forms insoluble phosphate with free Cd in the soil, and on the other hand, it complexes with aluminum or iron in clay minerals or iron-manganese oxides to increase the soil electronegativity and promote the complexation [35 − 38]. Forming insoluble phosphorus with other ions like iron in the soil might affect the effect of immobilizing heavy metals [39 − 41]. However, the excessive phosphate would introduce the eutrophication of environment. Thus, the SPRA was

Table 7 Percentages of different fractions of Pb and Cd in soils (%)

Element	Treatment	Exchangeable	Carbonate	Fe-Mn oxide	OM	Residual
Pb	CK	9.94^{a}*	2.32^{a}	57.74^{a}	19.80^{b}	10.20^{c}
	MCP	2.95^{b}	0.38^{b}	47.35^{b}	30.39^{a}	18.93^{a}
	SRPA	1.23^{c}	0.51^{b}	49.78^{b}	32.45^{a}	16.03^{b}
Cd	CK	55.76^{A}	9.80^{A}	25.14^{A}	3.88^{B}	5.41^{C}
	MCP	43.12^{B}	4.12^{B}	27.45^{A}	10.57^{A}	14.74^{B}
	SRPA	42.13^{B}	3.00^{B}	27.62^{A}	5.82^{B}	21.41^{A}

Note: *Values followed by different lowercase letters are significantly different for each fraction of Pb at $p<0.05$. Values followed by different uppercase letters are significantly different for each fraction of Cd at $p<0.05$.

synthetized to treat heavy metal contamination. MCP is a commonly used soil remediation agent, which can form stable phosphate precipitation with cadmium ions. In SPRA, MCP plays an important role in immobilizing cadmium. SA is a widely used sustained-release material, which can form grid structure by crosslinking with divalent cations. However, SA is fragile in physical structure and easy to be crushed by extrusion, so it is usually used in combination with PVA. BS can consume excess hydrogen ions of SA, promoting the crosslinking process of SA-PVA, adjusting the formed grid structure, affecting the concentration of phosphate in SPRA. In the beginning, the organic shell of SRPA can effectively protect phosphate from binding with other ions in the soil and adsorption sites on the soil surface. After absorbing water in the soil, the surface of the SRPA swelled, and phosphate was released from the SRPA in a non-Fickian diffusing manner. Therefore, unlike directly applying phosphate to the soil, the concentration of water-soluble phosphorus in SRPA is controlled to a lower level. The removal rate of water-soluble heavy metals reached more than 80%, which was slightly higher than that of MCP. The calcium ions and hydrogen ions in calcium dihydrogen phosphate of SRPA can compete for the reaction sites of Pb and Cd in the soil and affect the removal rate of heavy metals. However, the complexation of calcium by sodium alginate effectively inhibited this competition and improved the removal rates of heavy metals. With the slow-release process, the contents of total phosphorus in the soil increased and the contents of bioavailable heavy metals continued to decrease. After SRPA addition, the removal rates of bioavailable heavy metals reached 76.47% and 71.85% for Pb and Cd, respectively. And the residual heavy metals remarkably increased from 10.20% to 16.03% for Pb and from 5.41% to 21.41% for Cd. This result indicates that the SRPA effectively reduces the activity of heavy metals in the soil and has a good barrier effect against heavy metals.

4 Conclusions

Five SRPAs were synthesized by different rates of SA, PAV, MCP and BS. Among these SRPAs, S3 synthesized by using 30 g/L SA, 60 g/L PVA, 10 g/L MCP and 6 g/L BS showed a good performance for phosphate release. As compared with MCP, SRPA resulted in a lower water-soluble phosphorous content in soil within 80 d, implying that phosphate was slowly released from SRPA. Phosphate release from SRPA was well fitted with Ritger-Peppas model with constant *n* between 0.45 and 0.85, indicating that the phosphate release was in accordance with non-Fickian diffusion. With SRPA application to the contaminated soil, the removal rates of water soluble and bioavailable Pb and Cd were significantly higher than that with MCP. Moreover, the exchangeable fractions of Pb and Cd in the soil after SRPA remediation significantly declined and the residue fractions increased, indicating the activity of Pb and Cd in the soil significantly reduced.

References

[1] ÁLVAREZ-AYUSO E, GARCíA-SÁNCHEZ A. Sepiolite as a feasible soil additive for the immobilization of cadmium and zinc [J]. Science of the Total Environment, 2003, 305(1−3): 1−12. DOI: 10.1016/S0048-9697(02)00468-0.

[2] HUANG Guo-yong, SU Xiao-juan, RIZWAN M S, et al. Chemical immobilization of Pb, Cu, and Cd by phosphate materials and calcium carbonate in contaminated soils [J]. Environmental Science and Pollution Research, 2016, 23(16): 16845−16856. DOI: 10.1007/s11356-016-6885-9.

[3] MIGNARDI S, CORAMI A, FERRINI V. Evaluation of the effectiveness of phosphate treatment for the remediation of mine waste soils contaminated with Cd, Cu, Pb, and Zn [J]. Chemosphere, 2012, 86(4): 354 − 360. DOI: 10.1016/j.chemosphere.2011.09.050.

[4] MARTÍNEZ-GÓMEZ F, GUERRERO J, MATSUHIRO B, et al. In vitro release of metformin hydrochloride from sodium alginate/polyvinyl alcohol hydrogels [J]. Carbohydrate Polymers, 2017, 155: 182−191. DOI: 10.1016/j.carbpol.2016.08.079.

[5] ANITHA T, KUMAR P S, KUMAR K S, et al. Biosorption of lead(II) ions onto nano-sized chitosan particle blended polyvinyl alcohol (PVA): Adsorption isotherms, kinetics and equilibrium studies [J]. Desalination and Water Treatment, 2016, 57(29): 13711 − 13721. DOI: 10.1080/19443994.2015.1061951.

[6] ZHANG Dan, ZHANG Yu, SHEN Fei, et al. Removal of cadmium and lead from heavy metals loaded PVA ‑ SA immobilizedLentinus edodes [J]. Desalination and Water Treatment, 2014, 52(25 − 27): 4792 − 4801. DOI: 10.1080/19443994.2013.809936.

[7] MIKHAILOVA E A, NOBLE R R P, POST C J. Comparison of soil organic carbon recovery by walkley-black and dry combustion methods in the Russian chernozem [J]. Communications in Soil Science and Plant Analysis, 2003, 34(13, 14): 1853−1860. DOI: 10.1081/css-120023220.

[8] WANG Yun-yan, YAO Wen-bin, WANG Qing-wei, et al. Synthesis of phosphate-embedded calcium alginate beads for Pb(II) and Cd(II) sorption and immobilization in aqueous solutions [J]. Transactions of Nonferrous Metals Society of China, 2016, 26(8): 2230−2237. DOI: 10.1016/S1003-6326(16)64340-6.

[9] JIN Lan, LIU Qing, SUN Zhi-yong, et al. Preparation of 5-fluorouracil/β-cyclodextrin complex intercalated in layered double hydroxide and the controlled drug release properties [J]. Industrial & Engineering Chemistry Research, 2010, 49(22): 11176−11181. DOI: 10.1021/ie100990z.

[10] LAWRIE G, KEEN I, DREW B, et al. Interactions between alginate and chitosan biopolymers characterized using FTIR and XPS [J]. Biomacromolecules, 2007, 8(8): 2533−2541. DOI: 10.1021/bm070014y.

[11] HASNAIN M S, NAYAK A K, SINGH M, et al. Alginate-based bipolymeric-nanobioceramic composite matrices for sustained drug release [J]. International Journal of Biological Macromolecules, 2016, 83: 71 − 77. DOI: 10.1016/j.ijbiomac.2015.11.044.

[12] HUQ T, FRASCHINI C, KHAN A, et al. Alginate based nanocomposite for microencapsulation of probiotic: Effect of cellulose nanocrystal (CNC) and lecithin [J]. Carbohydrate Polymers, 2017, 168: 61−69. DOI: 10.1016/j.carbpol.2017.03.032.

[13] STOCH P, STOCH A, CIECINSKA M, et al. Structure of phosphate and iron-phosphate glasses by DFT calculations and FTIR/Raman spectroscopy [J]. Journal of Non-Crystalline Solids, 2016, 450: 48 − 60. DOI: 10.1016/j.jnoncrysol.2016.07.027.

[14] HASNAIN M S, NAYAK A K, SINGH M, et al. Alginate-based bipolymeric-nanobioceramic composite matrices for sustained drug release [J]. International Journal of Biological Macromolecules, 2016, 83: 71 − 77. DOI: 10.1016/j.ijbiomac.2015.11.044.

[15] XU Shi-mei, WU Rong-lan, HUANG Xiao-juan, et al. Effect of the anionic-group/cationic-group ratio on the swelling behavior and controlled release of agrochemicals of the amphoteric, superabsorbent polymer poly(acrylic acid-co-diallyldimethylammonium chloride) [J]. Journal of Applied Polymer Science, 2006, 102(2): 986−991. DOI: 10.1002/app.23990.

[16] HUA Shui-bo, MA Hai-zhen, LI Xun, et al. pH-sensitive sodium alginate/poly(vinyl alcohol) hydrogel beads prepared by combined Ca^{2+} crosslinking and freeze-thawing cycles for controlled release of diclofenac sodium [J]. International Journal of Biological Macromolecules, 2010, 46(5): 517−523. DOI: 10.1016/j.ijbiomac.2010.03.004.

[17] SILVA D, PINTO L F V, BOZUKOVA D, et al. Chitosan/alginate based multilayers to control drug release from ophthalmic lens [J]. Colloids and Surfaces B: Biointerfaces, 2016, 147: 81−89. DOI: 10.1016/j.colsurfb.2016.07.047.

[18] ZHAO Ling, CAO Xin-de, ZHENG Wei, et al. Copyrolysis of biomass with phosphate fertilizers to improve biochar carbon retention, slow nutrient release, and stabilize heavy metals in soil [J]. ACS Sustainable Chemistry & Engineering, 2016, 4(3): 1630−1636. DOI: 10.1021/acssuschemeng.5b01570.

[19] PEDACCHIA A, ADROVER A. Study of release kinetics and diffusion coefficients in swellable cellulosic thin films by means of a simple spectrophotometric technique [J]. Chemical Engineering Research and Design, 2014, 92(11): 2550−2556. DOI: 10.1016/j.cherd.2014.03.017.

[20] TAJAROBI F, LARSSON A, MATIC H, et al. The influence of crystallization inhibition of HPMC and HPMCAS on model substance dissolution and release in swellable matrix tablets [J]. European Journal of Pharmaceutics and Biopharmaceutics, 2011, 78(1): 125−133. DOI: 10.1016/j.ejpb.2010.11.020.

[21] MARSHALL J A, MORTON B J, MUHLACK R, et al. Recovery of phosphate from calcium-containing aqueous solution resulting from biochar-induced calcium phosphate precipitation [J]. Journal of Cleaner Production, 2017, 165: 27−35. DOI: 10.1016/j.jclepro.2017.07.042.

[22] SILVA D, PINTO L F V, BOZUKOVA D, et al. Chitosan/alginate based multilayers to control drug release from ophthalmic lens [J]. Colloids and Surfaces B: Biointerfaces, 2016, 147: 81−89. DOI: 10.1016/j.colsurfb.2016.07.047.

[23] CHOURASIYA V, BOHREY S, PANDEY A. Formulation, optimization, characterization and *in-vitro* drug release kinetics of atenolol loaded PLGA nanoparticles using 3^3 factorial design for oral delivery [J]. Materials Discovery, 2016, 5: 1−13. DOI: 10.1016/j.md.2016.12.002.

[24] AGÜERO L, ZALDIVAR-SILVA D, PEÑA L, et al. Alginate microparticles as oral colon drug delivery device: A review [J]. Carbohydrate Polymers, 2017, 168: 32 − 43. DOI: 10.1016/j.carbpol.2017.03.033.

[25] CIZMECIOGLU S C, MUEZZINOGLU A. Solubility of deposited airborne heavy metals [J]. Atmospheric Research, 2008, 89(4): 396−404. DOI: 10.1016/j.atmosres.2008.03.012.

[26] PATRICK W H Jr, HENDERSON R E. Reduction and reoxidation cycles of manganese and iron in flooded soil and in water solution [J]. Soil Science Society of America Journal, 1981, 45(5): 855−859. DOI: 10.2136/sssaj1981.03615995004500050006x.

[27] XIAO Ling, GUAN Dong-sheng, PEART M R, et al. The influence of bioavailable heavy metals and microbial parameters of soil on the metal accumulation in rice grain [J]. Chemosphere, 2017, 185: 868 − 878. DOI: 10.1016/j.chemosphere.2017.07.096.

[28] ESCAMILLA-ROA E, HUERTAS F J, HERNÁNDEZ-LAGUNA A, et al. A DFT study of the adsorption of glycine in the interlayer space of montmorillonite [J]. Physical Chemistry Chemical Physics, 2017, 19(23): 14961−14971. DOI: 10.1039/c7cp02300f.

[29] BAUN D L, CHRISTENSEN T H. Speciation of heavy metals in landfill leachate: A review [J]. Waste Management & Research: the Journal of the International Solid Wastes and Public Cleansing Association, ISWA, 2004, 22(1): 3−23. DOI: 10.1177/0734242X04042146.

[30] MAHAR A, WANG Ping, LI Rong-hua, et al. Immobilization of lead and cadmium in contaminated soil using amendments: A review [J]. Pedosphere, 2015, 25(4): 555−568. DOI: 10.1016/S1002-0160(15)30036-9.

[31] ZHONG Cong, FENG Zi-xu, JIANG Wei, et al. Evaluation of geogenic cadmium bioavailability in soil-rice system with high geochemical background caused by black shales [J]. Journal of Soils and Sediments, 2021, 21(2): 1053−1063. DOI: 10.1007/s11368-020-02802-0.

[32] HOUBEN D, EVRARD L, SONNET P. Mobility, bioavailability and pH-dependent leaching of cadmium, zinc and lead in a contaminated soil amended with biochar [J]. Chemosphere, 2013, 92(11): 1450－1457. DOI: 10.1016/j.chemosphere.2013.03.055.

[33] SUN Li-na, CHEN Su, CHAO Lei, et al. Effects of flooding on changes in Eh, pH and speciation of cadmium and lead in contaminated soil [J]. Bulletin of Environmental Contamination and Toxicology, 2007, 79(5): 514−518. DOI: 10.1007/s00128-007-9274-8.

[34] DING Chang-feng, DU Shu-yang, MA Yi-bing, et al. Changes in the pH of paddy soils after flooding and drainage: Modeling and validation [J]. Geoderma, 2019, 337: 511−513. DOI: 10.1016/j.geoderma.2018.10.012.

[35] KUO S, MCNEAL B L. Effects of pH and phosphate on cadmium sorption by a hydrous ferric oxide [J]. Soil Science Society of America Journal, 1984, 48(5): 1040－1044. DOI: 10.2136/sssaj1984.03615995004800050018x.

[36] KRISHNAMURTI G S R, HUANG P M, KOZAK L M. Sorption and desorption kinetics of cadmium from soils: Influence of phosphate [J]. Soil Science, 1999, 164(12): 888−898. DOI: 10.1097/00010694-199912000-00002.

[37] CAO X D, MA L Q, CHEN M, et al. Impacts of phosphate amendments on lead biogeochemistry at a contaminated site [J]. Environmental Science & Technology, 2002, 36(24): 5296−5304. DOI: 10.1021/es020697j.

[38] YU Huan-yun, LIU Chuan-ping, ZHU Ji-shu, et al. Cadmium availability in rice paddy fields from a mining area: The effects of soil properties highlighting iron fractions and pH value [J]. Environmental Pollution, 2016, 209: 38－45. DOI: 10.1016/j.envpol.2015.11.021.

[39] HAMMOND L L, CHIEN S H, ROY A H, et al. Solubility and agronomic effectiveness of partially acidulated phosphate rocks as influenced by their iron and aluminium oxide content [J]. Fertilizer Research, 1989, 19(2): 93－98. DOI: 10.1007/BF01054680.

[40] BARTOS J M, MULLINS G L, WILLIAMS J C, et al. Water-insoluble impurity effects on phosphorus availability in monoammonium phosphate fertilizers [J]. Soil Science Society of America Journal, 1992, 56(3): 972－976. DOI: 10.2136/sssaj1992.03615995005600030048x.

[41] YLIVAINIO K. Effects of iron(III) chelates on the solubility of heavy metals in calcareous soils [J]. Environmental Pollution, 2010, 158(10): 3194－3200. DOI: 10.1016/j.envpol.2010.07.004.

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中文导读

新型缓释磷酸盐固定剂对镉和铅污染的土壤的修复效果

摘要：磷酸盐通过不溶性金属磷酸盐沉淀而被广泛应用于镉、铅污染土壤的稳定修复。但是，环境中磷含量的增加会引起新的污染，而缓释磷酸盐因兼具稳定重金属和降低二次污染风险的特性而备受关注。本文制备了一种新型的缓释磷酸盐固定剂(SRPA)，对其进行了BET，SEM，FTIR，溶胀率，磷含量等表征。结果表明，SRPA是一种内部具有网状结构的球体，除磷酸盐外，还含有羟基，羧基和其他官能团，比表面积为5~7.18 m^2/g。SRPA的磷酸盐含量从5%增加到8%，Korsmeyer-Peppus模型表明，non-Fickian扩散过程对磷酸盐的释放起着主要控制作用。将SRPA应用于土壤后，我们发现与传统的磷酸盐改良剂相比，土壤中水溶性磷的浓度大大降低。SRPA比传统的磷酸盐改良剂对土壤的修复效果更好。水溶性镉(Cd)和铅(Pb)的修复效率分别从68.57%提高到97.09%，和从76.9%提高到97.89%。可生物利用的Cd和Pb分别从63.09%增加到71.85%，和从66.21%增加到76.47%。提取物的实验结果表明，随着残留重金属的增加，修复后土壤中重金属的可交换和碳酸盐结合的含量显着降低，表明重金属的稳定性增加。

关键词：重金属；磷酸盐；缓释固定剂；土壤修复