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Precipitation, adsorption and rhizosphere effect: The mechanisms for Phosphate-induced Pb immobilization in soils—A review

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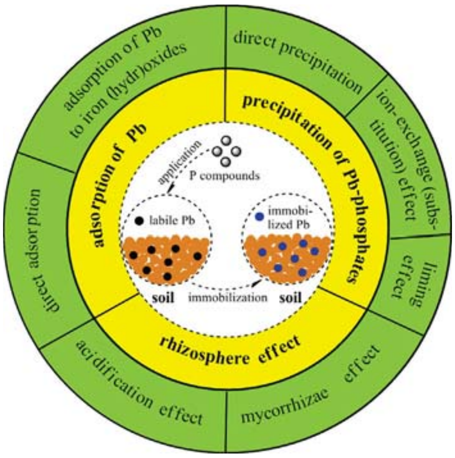
HIGHLIGHTS

- Mechanisms about phosphate-induced Pb-immobilization are summarized.
- Precipitation of Pb-phosphates is the main mechanism along with the adsorption effect and rhizosphere effect.
- The relationships between the three mechanisms were discussed.
- How to overcome the adverse impacts during the P application is of great importance.

GRAPHICAL ABSTRACT



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ABSTRACT

Lead (Pb) is one of the most toxic heavy metals that pose a direct threat to organisms and it can not been degraded through microbial activities or chemical reaction. Bioavaibility and eco-toxicity of Pb which mostly depend on Pb chemical speciation play an important role in the remediation of Pb-contaminated soils. Phosphate (P) amendments which could transfer Pb from unstable fraction to stable fraction are commonly used to immobilize Pb in soils and have been extensively studied by researchers during decades. Based on the previous study, it can be concluded that three principal mechanisms may be responsible for P-induced Pb immobilization: 1) the precipitation of Pb-phosphates, including direct precipitation, ion-exchange (or substitution) effect and liming effect; 2) the adsorption of Pb, including the direct adsorption and the adsorption of Pb to iron (hydr)oxides; 3) the rhizosphere effect, including acidification effect and mycorrhizae effect. In this review, these mechanisms have been completely discussed and the internal relationships among them were summarized to give a better understanding of P-induced Pb immobilization in soils and promote the development of P-based remediation technology.

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Contents

1. Introduction

Lead (Pb) metal, an important structural and industrial material, comes into the soil through both pedogenic and anthropogenic processes such as smelting, weathering, shooting, and hunting [1]. Pb can be retained in the soil through a series of reactions such as adsorption, ionic exchange and precipitation, forming various Pb-compounds [2–4]. The total concentration of Pb could maintain for a long time in the environment once Pb was introduced in soils since most of Pb compounds do not undergo microbial or chemical degradation [5–8]. Though most of the Pb-compounds in soils are relatively insoluble, they could be dissolved and remobilized when the conditions are changed to acidity [9,10]. In general, the Pb-compounds with high mobility are more environmental risk [11–15]. According to the BCR (European Community Bureau of Reference) sequential extraction method proposed by A. M. Ure et al. in 1993, heavy metal has been divided into four speciations: soluble/exchangeable fraction (F1), reducible fraction (F2), oxidizable fraction (F3) and residual fraction (F4); and the mobility is decreased in the order of: F1 > F2 > F3 > F4 [16]. The F4 of Pb, such as pyromorphite, has been recognized as the most stable fraction since it is strongly bound in the crystal minerals and even unreactive in a wide range of nature conditions while F1, F2 and F3 are thermodynamically unstable and could be easily affected by environmental changes, releasing more soluble Pb to the environment [17]. Based on this theory, the remediation strategies designed to promote the transformation of Pb from unstable fraction (F1, F2 and F3) to mineral structure (F4) with the using of soil amendments become a promising technique and has been extensively studied [18].

P (phosphate)-based materials, such as triple superphosphate (TSP), diammonium phosphate (DAP), hydroxyapatite (HA), and synthetic P materials have been proved to be extremely effective and attractive for the stabilization of heavy metals [e.g. Pb, Cd (cadmium), Fe (ferri)] in soils, water and sediment [19,20]. Based on the previous studies, almost 49 elements could combine with PO_4^{3-} and form ~300 minerals, by which most of the toxicity metals could be immobilized, especially the Pb [21]. It has been reported that the Pb-phosphates are at least 44 orders of magnitude less soluble than other Pb minerals in soils such as anglesite ($PbSO_4$), galena (PbS), cerussite ($PbCO_3$), and litharge (PbO) [21,22]. In the presence of adequate P, the Pb could be immobilized into a mineral phase like pyromorphite, which is presented as $Pb_5(PO_4)_3X$ [X = F (fluorine), Cl (chlorine), Br (bromine), OH (hydroxy); *Ksp* (solubility product) = $10^{-71.6}$, $10^{-84.4}$, $10^{-78.1}$, $10^{-76.8}$, respectively] [9,21]. Once the Pb in contaminated soils was converted into Pb-phosphate, it would be immobilized and its bioavailability would be reduced [23]. Numerous researchers have confirmed that P treatment can minimize the leachability of Pb and reduce Pb plant uptake in the soil since the pyromorphite has a special crystal structure for ionic substitution, replacing the Ca^{2+} (calcium) by Pb^{2+} [21,24]. Moreover, the Best Management Practices (BMPs) for Pb in outdoor shooting ranges proposed by U.S. Environmental Protection Agency (USEPA) is the P remediation technology [25]. The literatures about P-induced Pb immobilization in soils during several decades are summarized and presented in Table S1 (shown in Supplementary Material). However, with the widely application of P for Pb immobilization, the most important aspects need to be taken into consideration are the *in situ* viability and environmental sustainability since the P-based materials may induce eutrophication in water environment and Pb may be remobilized by plants, posing a secondary pollution [24,26–28]. Additionally, the application of P may enhance the leaching of As (arsenic), Se (selenium), Sb (antimony) and W (tungsten) since these oxoanions and phosphate will compete for the adsorption site in soils or around plant roots [25,29–32]. These factors must be taken into consideration during the application of P-based materials for Pb remediation in soils. Consequently, get a better understanding about the mechanisms during the immobilization of Pb by P-based materials is of great importance to control Pb bioavailability and mobility in contaminated soils and at the same time avoids the adverse impacts.

Relying on the obtained results, it can be concluded that P could induce Pb immobilization in soils through various processes, the principal mechanisms involved include: the precipitation of Pb-phosphates, the adsorption of Pb and the rhizosphere effect [2,33,34]. All of these mechanisms have been reported in the literatures previously and the details are summarized in Fig. 1. Theoretically speaking, the real mechanism about P-induced Pb immobilization in soil is influenced by various factors such as the solubility of P sources, the pH value, the Pb speciation and particle size and so on [21,25]; these factors could affect each other through various reactions and these reactions make it more difficult to predict the immobilization mechanisms. In this paper, we provide a review which focuses on the possible mechanisms in P-induced Pb immobilization to make a better understanding of Pb stabilization by P in soils and promote the development of P-based remediation technology.

2. The precipitation of Pb-phosphates

As has been reported by Nriagu during 1970s, the formation of Pb-phosphates is of crucial importance in the dispersion and fixation of Pb in the environment since their solubilities are much lower than other Pb-compounds [35–38]. The solubilities of several Pb-phosphates have been listed in Table 1 [2,35–41]. It can be seen

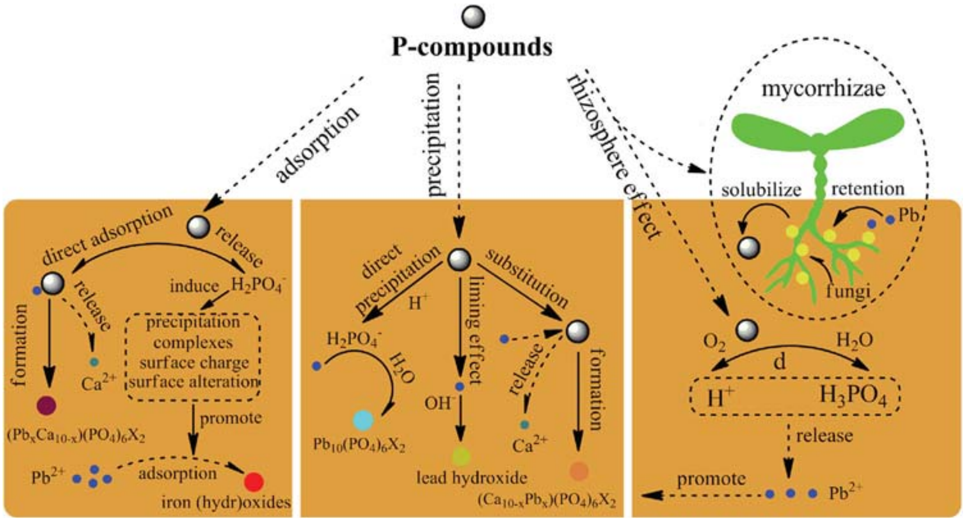

Fig. 1. The mechanisms involved in P-induced Pb immobilization.

Table 1
The solubility of common Pb-phosphates.

Metal(loid) Phosphate	Chemical Formula	Log K_{sp}
Fluropyromorphite	$Pb_{10}(PO_4)_6F_2$	−71.6
Chloropyromorphite	$Pb_{10}(PO_4)_6Cl_2$	−84.4
Hydroxypyromorphite	$Pb_{10}(PO_4)_6(OH)_2$	−76.8
Lead phosphate	$PbHPO_4$	−11.43
Lead orthophosphate	$Pb_3(PO_4)_2$	−44.4
Plumbogummite	$PbAl_3(PO_4)_2(OH)_5{\cdot}H_2O$	−99.3
Dumontite	$Pb_2(UO_2)_4(PO_4)_2(OH)_4$	−91.4
Corkite	$PbFe_3(PO_4)(OH)_6SO_4$	−112.6
Hinsdalite	$PbAl_3(PO_4)(OH)_6SO_4$	−99.1
Parsonsite	$Pb_2UO_2(PO_4)_2{\cdot}2H_2O$	−45.8
Dewindtite	$Pb(UO_2)_4(PO_4)_2(OH)_4{\cdot}8H_2O$	−92.6
Renardite	$Pb(UO_2)_4(PO_4)_2(OH)_4{\cdot}7H_2O$	−93.7
Przhevalskite	$Pb(UO_2)_4(PO_4)_2{\cdot}4H_2O$	−47.4
Bromopyromorphite	$Pb_{10}(PO_4)_6Br_2$	−78.1
Tsumebite	$Pb_2Cu(PO_4)_2(OH)_3{\cdot}3H_2O$	−51.3

that the stability fields of pyromorphites [$Pb_5(PO_4)_3X$, where X = F, Cl, Br, OH] and plumbogummite [$PbAl_3(PO_4)_2(OH)_5{\cdot}H_2O$] predominate strongly over other Pb-phosphates in the environment under a wide range of chemical conditions [1,2,38,42]. Many studies have demonstrated that P-materials could induce the formation of Pb-phosphates and Cao et al. confirmed that P [MCP (monocalcium phosphate) + KCl (potassium chloride)] addition can effectively transform various Pb minerals into insoluble chloropyromorphite in soils [43]. They also indicated that the P-induced precipitation of chloropyromorphite was greatly influenced by the pH. Therefore, the precipitation of Pb-phosphates, including direct precipitation, ion-exchange (or substitution) effect and liming effect, has been recognized as the main mechanism for P-based remediation technology in Pb contaminated soils, especially in substrates with high concentration of Pb [5].

2.1. Direct precipitation

In 1993, Ma et al. hypothesized that the Pb was immobilized to hydroxypyromorphite through the dissolution of hydroxyapatite [HA, $Ca_{10}(PO_4)_6(OH)_2$] and the precipitation of hydroxypyromorphite [$Pb_{10}(PO_4)_6(OH)_2$] [42], which put forward the direct precipitation of Pb-phosphates in soils. Additionally, Mavropoulos et al. demonstrated that the dissolution of HA and the formation of an intermediate phase [$Pb_{(10-x)}Ca_x(PO_4)_6(OH)_2$, in which Pb ions will gradually occupy Ca(II) sites until it reaches the structure of a pure hydroxypyromorphite: $Pb_{10}(PO_4)_6(OH)_2$] were the main mechanisms of Pb uptake by HA in the solutions [44] and it was subsequently confirmed by electron microscopy analysis [45]. Therefore, on the basis of the geochemical computer speciation models, Basta et al. has reported that DAP could decrease solution Pb by forming Pb-phosphate precipitation [$Pb_{10}(PO_4)_6(OH)_2$] with low solubility [46]. Simultaneously, Khan M. J. investigated the effects of composts, lime and DAP on the phytoavailability of Pb in a copper mine tailing soil in 2009, results showed that DAP was more effective to reduce the phytoavailability of Pb than the other two materials, which is in agreement with other researches [41,46–48].

According to the direct precipitation process of Pb-phosphate presented in Eqs. (1) and (2), the dissolution of P from P-materials and the liberation of Pb were usually the limiting factors during the reactions. Sima et al. investigated the remediation effect of TSP and phosphate rock (PR) on three kinds of Pb-contaminated soils [$Pb(NO_3)_2$, $PbSO_4$, and $PbCO_3$] by using toxicity characteristic leaching procedure (TCLP) assessment [49]. They not only found that TSP was more effective in forming insoluble $PbHPO_4$ and $Pb_5(PO_4)_3Cl$ by precipitatation with Pb than PR, but also reported that precipitation of Pb-phosphate was simultaneously limited by the dissolution of the original Pb compounds [49]. The related schematic diagram was shown in Fig. 2. Many of the studies revealed that precipitation of Pb-phosphate in less soluble-P treated soils was limited when compared with soluble-P, thus the soluble P materials which could provide sufficient P immediately attracted lots of attentions [20,43,46,50]. Problem associated with the widely use of soluble P materials was the water eutrophication while the application of insoluble P was limited by its dissolving capacity and mobility [1]. Therefore, many researchers tried to modify the insoluble P materials using various agents such as sodium carboxymethyl cellulose (CMC), sodium dodecyl sulfate (SDS) and biochar to get stabilized and nano-sized P materials for Pb immobilization [1,24,51–53]. The laboratory flowchart of SDS-stabilized chlorapatite was shown in Fig. 3. Results showed that the CMC, SDS and biochar could greatly promote the Pb remediation efficiency by enhancing its mobility and increasing the available P in the samples, and they also demonstrated that the use of modified P materials could also reduce the eutrophication risk than the application of soluble P. Additionally, Kpomblekou-A et al. have reported that organic acids could enhance the release of P from low and medium reactive PR in 2003 [54]. Based on the study of Kpomblekou-A et al., Zhu et al. investigated the effects of γ-polyglutamic acid (γ-PGA), PR, and γ-PGA-activated PR (γ-PGA-PR)

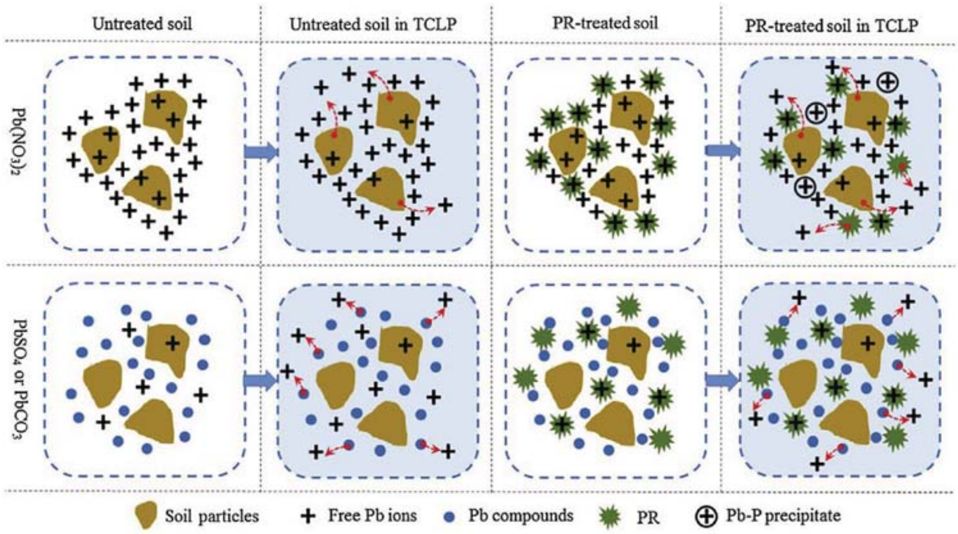

Fig. 2. Schematic diagram of reactions between Pb and PR in soils and TCLP tests [49]. Copyright 2015 Elsevier Ltd.

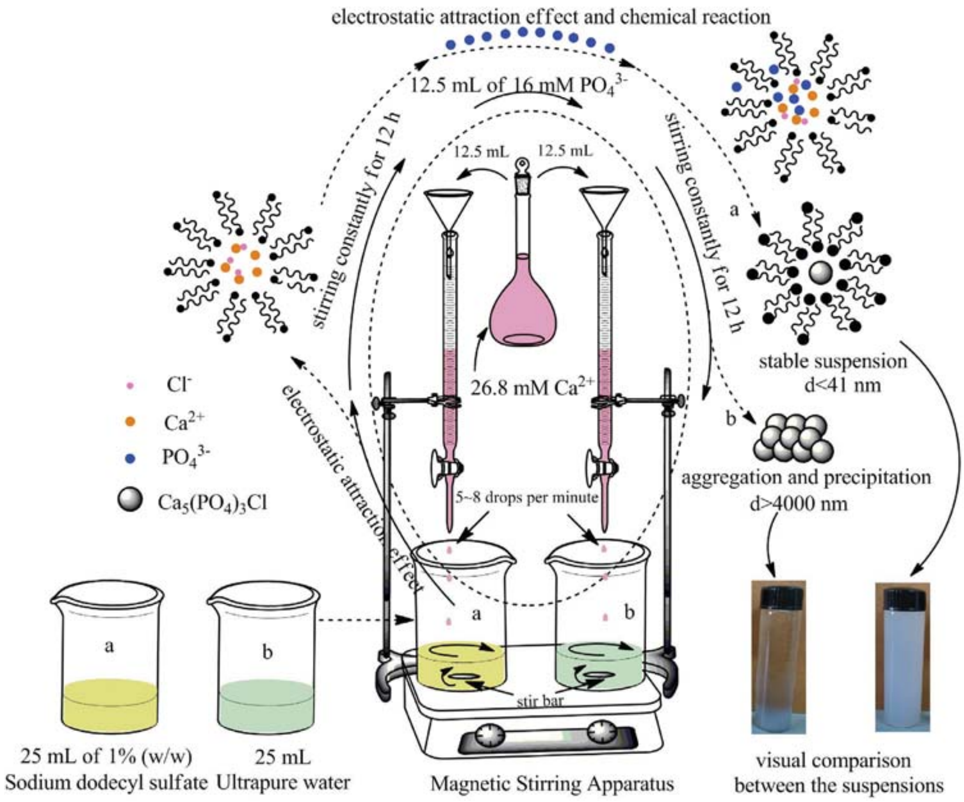

Fig. 3. The laboratory flowchart of SDS-stabilized chlorapatite [1]. Copyright 2016 Elsevier Ltd.

on Pb immobilization and phytotoxicity in contaminated soils [55]. γ-PGA was confirmed to be effective in promoting the release of P from PR and increasing the available P in soils, thus facilitating the precipitation of Pb-phosphate in soils [55]. Simultaneously, Huang et al. also employed bone meal (BM), PR, super phosphate (SP), calcium carbonate (CC) and oxalic acid-activated PR (APR) to evaluate the heavy metal immobilization effect of these materials in a co-contaminated soils [56]. From the analysis of the results, they indicated that APR was the most effective amendment for the immobilization of Pb, Cd and Cu (copper), which mostly attribute to the high content of soluble P induced by the oxalic acid. Thus the modification and acidification of P materials may be promising ways to improve the Pb immobilization efficiency of insoluble P and at the same time decrease the eutrophication risk.

$$Ca_{10}(PO_4)_6(OH)_2 + 14H^+ \underset{dissolution}{\rightarrow} 10Ca^{2+} + 6H_2PO_4^- + 2H_2O \quad (1)$$

$$10Pb^{2+} + 6H_2PO_4^- + 2H_2O \underset{precipitation}{\rightarrow} Pb_{10}(PO_4)_6(OH)_2 \quad (2)$$

2.2. Ion-exchange (or substitution) effect

Another process for the formation of Pb-phosphates with $Ca_{10}(PO_4)_6(OH)_2$ (hydroxyapatite, HAP) has been proposed by Suzuki et al. and Takeuchi et al. in 1984 and 1988, respectively.

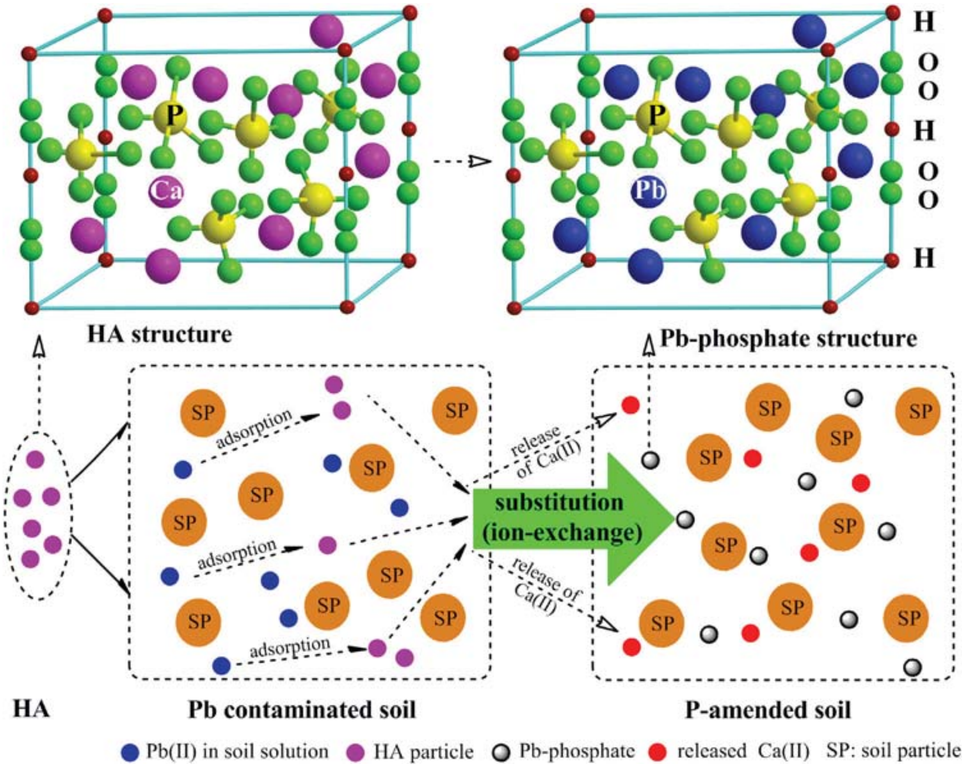

Fig. 4. The ion-exchange (or substitution) process during P-induced Pb remediation in Pb polluted soil.

They put forward that the ion-exchange (or substitution) effect, shown in Eq. (3), may be the main mechanism during the removal of Pb^{2+} by $Ca_{10}(PO_4)_6(OH)_2$ in solutions [2,57,58]. In the early study of Takeuchi and Arai in 1990, HAP was proved to be effective in removing Pb^{2+} from the aqueous solutions through uptaking and ion exchange process, which was irreversible [59]. Theoretically speaking, ion-exchange (or substitution) effect would be helpful for interpreting the *in situ* Pb immobilization in soils induced by P-compounds since Pb ions may also exist in soil solutions. According to the study of Takeuchi et al., HA (calcium phosphate compound) was found to have a very high capacity to substitute divalent heavy metals for Ca^{2+} when there were heavy metal ions in water surrounding the HA [58]. Ma et al. thought that precipitation, cation substitution and surface adsorption were the main types that controlled Pb immobilization by HA [42]. They also demonstrated that apatite could not only provide P for precipitation of Pb-phosphate but also supply Ca^{2+} for ion-exchange, which was of vital importance in remediation of Pb contaminated soils and other solid wastes [42]. As demonstrated by other researchers, apatite structure has a high flexibility that calcium ions in the apatite crystal lattice were easily exchangeable with other ions, especially with divalent ions, such as lead, cadmium, and copper [60–63]. That is to say, Pb can substitute for Ca in the structure of $Ca_{10}(PO_4)_6(OH)_2$ during the reaction, thus the Pb could be immobilized to $Pb_{10}(PO_4)_6(OH)_2$, and it has been proved by some researchers [9,25,63]. This property has been widely investigated for heavy metal immobilization in both soils and aqueous environment [60]. In 2010, Zhu et al. found that Ca in M(2) site could be preferentially replaced by Pb ions in solid solutions due to its special crystal structure [63]. The process of ion-exchange (or substitution) effect during P-induced Pb immobilization in Pb contaminated soils was shown in Fig. 4. From the ion-exchange (or substitution) process shown in Fig. 4 it can be concluded that the Pb liberation from soil particles was also the limiting factor in this mechanism, which was in accordance with the direct precipitation mechanism. In general, both of two theories mentioned above are powerful evidences for the precipitation of Pb^{2+} and formation of pyromorphite.

$$Ca_{10}(PO_4)_6(OH)_2 + xPb^{2+} \underset{substitution}{\rightarrow} (Ca_{10-x}Pb_x)(PO_4)_6(OH)_2 + xCa^{2+} \quad (3)$$

2.3. Liming effect

Some studies have reported that the addition of some P-compounds such as apatite could alkalify the soils through the consumption of H^+ during the dissolution process, or the P-compounds itself contained free calcium carbonate ($CaCO_3$), serving as a liming agent [2,48,64,65]. PR was confirmed to be the most liming-riched P material since 1000 kg of PR was equal to 450–560 kg $CaCO_3$ during the dissolution process, providing sufficient OH^- for reducing the heavy metal concentrations in soil solutions by forming insoluble metal precipitates, complexes, and secondary minerals [2,34,66]. Dissolution of apatite could increase the soil pH while the dissolution of soluble phosphates such as SSP (single superphosphate) and MKP (monopotassium phosphate) was acid-generating [67]. In a dissolution kinetics and metal removal study conducted by Oliva et al., the biogenic hydroxyapatite (Apatite II^{TM}) was found to increase the pH from 3.0 to 6.3, 5.0–7.6 in the two experiments, respectively [64]. The increase of pH was attributed to the generation of hydroxyls during the dissolution of hydroxyapatite (released from Apatite II^{TM}) according to Eq. (4) [64].

Under alkaline conditions, Pb could form hydrocerussite [$Pb_3(CO_3)_2(OH)_2$] and lead oxide fluoride (Pb_2OF_2) during the apatite treatment [68]. The liming effects on Pb, Cd, Ni (nickel), Zn (zinc), and Cu accumulation in wheat, carrots, and spinach which grown on previously sludge-applied soils have been extensively investigated by Hooda et al. in 1996 [69]. Their outdoor experiment showed that liming the soils from pH = 5.95 to 7.0 before sowing could significantly reduce the metal uptake by the crops. Feng et al. put forward that the concomitant precipitation of metal hydroxides can be one of the mechanisms to remove the heavy metals from waste water, the related mechanism was shown in Eqs. (5)–(7) [70]. Some researchers also employed PR, lime-stabilized biosolid (LSB), and anaerobic biosolid (AB) to reduce extractability, phytoavailability and gastrointestinal (GI) bioavailability of Pb, Cd, and Zn in contaminated soils in smelter sites [66]. LSB could reduce the extractability and phytoavailability of Pb efficiently but not GI availability of Pb since the LSB treated products of Pb were not stable under the acid condition (pH = 2.0) during the PBET (physiologically based extraction test) procedure [66]. On the other hand, PR was the only amendment in this study which could reduce GI-available Pb in GI solutions, that was to say the alkaline-treated product of Pb (such as lead hydroxide) was not that stable than Pb-phosphates (product of PR-treated soil). Except the formation of hydroxide and other Pb complexes, the alkaline treatment was also effective to decrease the risk of human from exposure to Pb by reducing Zn phytotoxicity in contaminated sites [66]. The liming effect of PR, apatite and other Ca containing P-compounds on Pb immobilization was mainly caused by an increase of pH in soils, which was not stable under long term remediation since acidification would induce the release of Pb and highly alkaline conditions (pH >11–12) may increase the Pb mobility and pose an adverse effect on contaminated soils [71]. Therefore, the alkaline remediation may be more useful as an assistant amendment for the Pb immobilization in acid soils or it can be used with the combination of acid-generating phosphates such as SSP and MKP [71]. Based on this theory, Karalić et al. investigated the influence of acid soils liming and initial soil acidity on availability of Pb, Cd, Cr, and Zn [72]. Liming treatments resulted in a strongest heavy metals availability decrement in extremely acid soils (initial soil pH <4) with highest initial heavy metal concentrations, in which Pb was the only one that has a significantly decrease in its availability under both extremely acid soils and heavily acid soils (initial soil pH: 4–5) conditions [72].

$$Ca_5(PO_4)_3OH \Leftrightarrow 5Ca^{2+} + 3PO_4{}^{3-} + OH^- \tag{4}$$

$$M^{2+} + OH^- \rightarrow M(OH)^+ \tag{5}$$

$$M(OH)^+ + OH^- \rightarrow M(OH)_2 \tag{6}$$

$$M(OH)_2 + OH^- \rightarrow M(OH)_3^- \tag{7}$$

Where M^{2+} represents divalent heavy metals.

3. The adsorption of Pb

The adsorption of Pb to soil particles, P-compounds, iron (hydr)oxides, and other soil complexes could be another way for retaining Pb in soils and make the Pb more stable [2]. Pb complexations with the phosphates and iron (hydr)oxides were relatively stable in the environment than other Pb fractions. Application of P-compounds may induce the direct adsorption to P compounds and promote the adsorption of Pb to iron (hydr)oxides in soil, thus significantly improving the Pb immobilization in contaminated soils.

3.1. The direct adsorption

The direct adsorption of Pb to P-compounds was considered as another important mechanism for the immobilization of Pb in soils. Mavropoulos et al. studied the mechanism of lead immobilization by HA using X-ray diffractometry (XRD) associated with Rietveld methodology, chemical analysis, and pH studies [44]. After the comparison between the amount of the totally immobilized Pb^{2+} and the immobilized Pb in hydroxypyromorphite structure, they concluded that adsorption or complexation could be the potential mechanisms involved in Pb immobilization by HA, which occupied over 30% of immobilized Pb. The related process was written as equations below:

$$\equiv POH + Pb^{2+} = \equiv POPb^+ + H^+ \tag{8}$$

$$\equiv PO^- + Pb^{2+} = POPb^+ \tag{9}$$

$$\equiv CaOH + Pb^{2+} = \equiv CaOPb^+ + H^+ \tag{10}$$

Chen et al. investigated the influence of pH on the sorption of Pb^{2+}, Cd^{2+}, and Zn^{2+} onto mineral apatite [68]. They demonstrated that the internal competition (competition with the same metal) and the competition with H^+ for adsorption sites on the apatite were the main competitive effects in metal individually adsorption while the competition with other metals was also involved in the combination adsorption of two or more kinds of heavy metals. On the other hand, they also found that Pb was almost removed with 100% efficiency for most of the pH conditions, which was not pH dependent but the adsorption products was pH-dependent, the conclusions were also in accordance with the study of Smičiklas et al. (Table 2) [68,73]. Smičiklas et al. also proposed that specific cation sorption was the contribution mechanism for the precipitation of hydroxypyromorphite $[Pb_{10}(PO_4)_6(OH)_2]$ [73]. Other researchers who used carbonate hydroxyapatite (CHAP) for Pb removal in aqueous solutions proposed that the maximum uptake amount (101 mg/g) of Pb by CHAP occurred at pH = 6.0 [74]. Except the pH, crystallinity and specific surface area were also the main factors that influence the Pb adsorption process induced by HAP. Stötzel et al. investigated the Pb adsorption behavior of several kinds of HAP with different crystallinity and specific surface area, they concluded that the adsorption capacity of HAP had a positive correlation with specific surface area while it showed a negative relation with crystallinity [75]. As reported by Zhu et al., the direct adsorption of heavy metals onto apatite may be facilitated by the exchange of Ca^{2+} (from the apatite) with the heavy metals in the soil solutions [2,63,76]. In some extent, the direct adsorption mechanism is intensified by the substitution of metal cation (Pb^{2+}) for Ca^{2+} (in P-compounds), which may be equal to the ion-exchange (or substitution) effect we mentioned in Section 2.2 with respect to the same process and results in it (Eq. (11)) [34]. On the other hand, the direct adsorption of Pb stimulated by P-compounds could also induce the formation of surface complexes and their coprecipitation [34]. For instance, a new class of HAP gel (Ca-HA) was synthesized and applied for Pb removal in aqueous solution. Lead hydroxyapatite and lead oxide were found on the surface of Ca-HA particles after the adsorption experiment, which indicated that surface complexation was involved (Fig. 5) [77]. In the study of Meski et al., they demonstrated that the mechanisms for Pb removal from solution by CHAP depended on the initial Pb concentrations: the dissolution and precipitation mechanism was dominant at low Pb concentration (20–200 mg/L) while the adsorption mechanism (Pb^{2+} adsorbed on CHAP surface) and ion exchange mechanism were dominant at high Pb concentration (500–700 mg/L) [78].

$$Ca_{10}(PO_4)_6(OH)_2 + xM^{2+} \underset{directadsorption}{\rightarrow} (M_x,Ca_{10\text{-}x})(PO_4)_6(OH)_2 + xCa^{2+} \tag{11}$$

Recently, efforts have been made to enhance the Pb adsorption capacity of HAP by using various materials such as porous methyltrimethoxysilane, magnetite, manganese dioxide, porous chitosan (CS) and apple pomace to get improved HAP materials [79–83]. Nano-HAP/CS porous materials (HCPMs) fabricated by Lei et al. showed a good adsorption property for Pb^{2+} and the adsorption capacity increased from 208.0 to 548.9 mg/g with the pH decreasing from 7.0 to 2.5 [83]. They indicated that Pb ions were chemically adsorbed on HCPMs during the fluxion, following by the formation of lead hydroxyapatite and CS-Pb complex, the details were shown in Fig. 6 [83]. The maximum Pb adsorption capacity for methyltrimethoxysilane coated hydroxyapatite

Table 2
The adsorption products of Pb^{2+} in reaction with apatite in aqueous solutions with respect to pH [68].

Initial pH	Final pH	Main reactions	The adsorption products
1.1–2.0	3.1–6.2	$Ca_{10}(PO_4)_{6-x}(CO_3)_xF_{2+x}(c) + 12H^+ \rightarrow$ $10Ca^{2+} + (6-x)H_2PO_4^- + xH_2CO_3^0 + (2+x)F^-$ $10Pb^{2+} + 6H_2PO_4^- + 2F^- \rightarrow Pb_{10}(PO_4)_6F_2(c) + 12H^+$	fluoropyromorphite
2.7–5.1	6.6–6.8	$Ca_{10}(PO_4)_{6-x}(CO_3)_xF_{2+x}(c) + (12-x)H^+ \rightarrow$ $10Ca^{2+} + (6-x)H_2PO_4^- + xHCO_3^- + (2+x)F^-$ $10Pb^{2+} + 6H_2PO_4^- + 2(F^-, OH^-) \rightarrow Pb_{10}(PO_4)_6(F,OH)_2(c) + 12H^+$	hydroxyl fluoropyromorphite
6.0–8.4	7.1–10.6	$Ca_{10}(PO_4)_{6-x}(CO_3)_xF_{2+x}(c) + 6H^+ \rightarrow$ $10Ca^{2+} + (6-x)HPO_4^{2-} + xHCO_3^- + (2+x)F^-$ $10Pb^{2+} + 6(HPO_4^{2-}, HCO_3^-) + 2(F^-, OH^-) \rightarrow Pb_{10}(PO_4, CO_3)_6(F,OH)_2(c) + 6H^+$	carbonate hydroxyl fluoropyromorphite
6.0–12.1	7.1–11.9	$Ca_{10}(PO_4)_{6-x}(CO_3)_xF_{2+x}(c) + 6H^+ \rightarrow$ $10Ca^{2+} + (6-x)HPO_4^{2-} + xHCO_3^- + (2+x)F^-$ $3PbOH^+ + 2HCO_3^- + OH^- \rightarrow Pb_3(CO_3)_2(OH)_2(c) + 2H_2O$	hydrocerussite
10.7–12.1	10.7–11.9	$Ca_{10}(PO_4)_{6-x}(CO_3)_xF_{2+x}(c) + (6-x)H^+ \rightarrow$ $10Ca^{2+} + (6-x)HPO_4^{2-} + xCO_3^{2-} + (2+x)F^-$ $3Pb(OH)_3^- + 2CO_3^{2-} + OH^- \rightarrow Pb_3(CO_3)_2(OH)_2(c) + 7OH^-$ $10PbOH_3^- + 6HPO_4^{2-} \rightarrow Pb_{10}(PO_4)_6(OH)_2(c) + 6H_2O + 22OH^-$ $2PbOH_3^- + 2F^- \rightarrow Pb_2OF_2(c) + H_2O + 4OH^-$	hydroxypyromorphitelead oxide fluoride

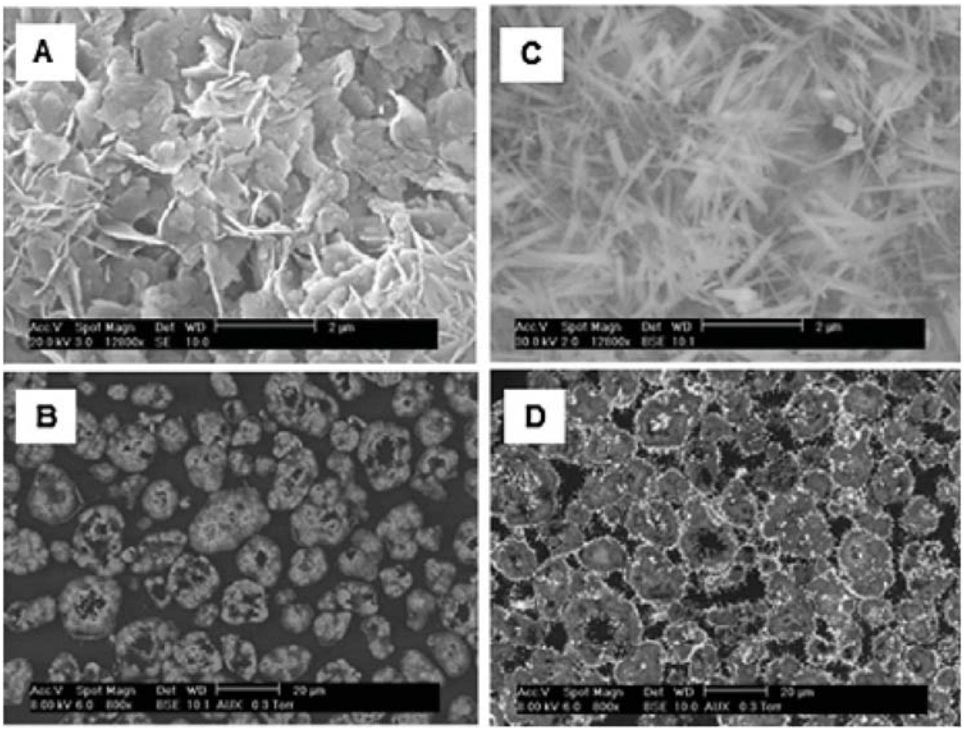

Fig. 5. SEM images of Ca-HA particles: (A) Non-polished and before Pb^{2+} sorption; (B) Polished and before Pb^{2+} sorption; (C) Non-polished and after Pb^{2+} sorption; (D) Polished and after Pb^{2+} sorption [77]. Copyright 2013 Elsevier Ltd.

(MTHAp), hydroxyapatite/apple pomace (HANP@AP), hydroxyapatite/magnetite (HAp/Fe_3O_4), and hydroxyapatite/manganese dioxide (HAp/MnO_2) were 105.485, 303.0, 598.8, and 769 mg/g according to the relative studies, respectively, presenting perfect adsorption effects on Pb ion in polluted solutions [79–82]. Therefore, the surface property can be another greater factor that influences the Pb adsorption efficiency of P-materials.

3.2. The adsorption of Pb to iron (hydr)oxides

Additionally, the P-compounds could also promote the adsorption of Pb to iron (hydr)oxides in soil, thus increasing the amorphous Fe oxide (AFeO) fraction [84,85]. It has been well known for a long time that Pb ions are strongly bound to iron (hydr)oxides, thus the increase of Pb adsorption to iron (hydr)oxides is important for the remediation of Pb in soils or sediments [86–88]. X-ray adsorption fine-structure spectroscopy (XAFS) and X-ray adsorption spectroscopy investigations conducted by Bargar et al. and Roe et al. found that Pb could adsorb to goethite by forming inner-sphere surface complexes with the surface hydroxyl groups (≡FeOH) [89,90]. Hayes and Leckie put forward a mechanism (Eq. (12)) involved in Pb adsorption to goethite by using a surface complexation model (SCM), and Gunneriusson et al. who used other SCMs also concluded two other reactions about the adsorption of Pb (Eqs. (13) and (14)) [91,92]. As reported by Abbaspour and Golchin in 2011, the Pb was increased in AFeO fraction with the application of di-ammonium phosphate in amended soils [84]. Simultaneously, Tiberg et al. also found that the phosphate could greatly enhance the Pb adsorption to ferrihydrite at pH <6, and it is more effective on Pb than Cu [85]. Evidences also showed that the Pb sorption on the iron oxide-water interface could be enhanced by phosphates [93]. And Xie et al. proposed 4 reasons for

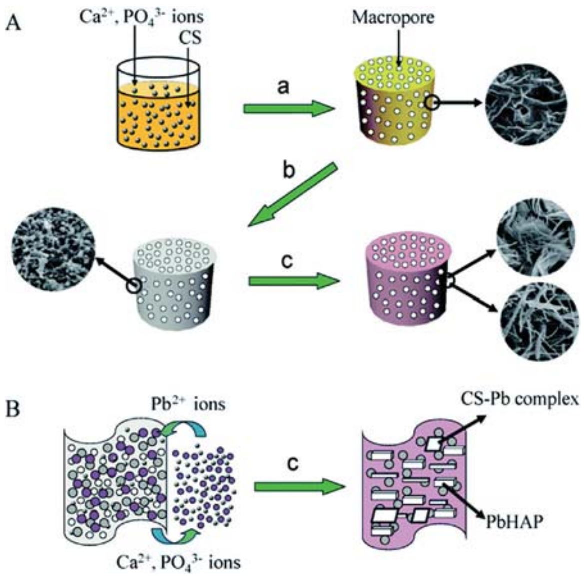

Fig. 6. (A) Illustration of the preparation process of HCPMs and their adsorption process for Pb^{2+} in aqueous solutions under flow conditions: (a) fabrication of BCPMs from CS solutions including Ca^{2+} ions and PO_4^{3-} ions by freeze-drying method; (b) conversion of HCPMs from BCPMs after NaOH solution treatment; (c) adsorption of Pb^{2+} ions on HCPMs under flow conditions to form PbHAP rods and CS-Pb complex. (B) Illustration of adsorption mechanism of HCPMs for Pb^{2+} ions in aqueous solutions [83]. Copyright 2015 Royal Society of Chemistry.

the P-induced enhancement: 1) changes of surface charge which makes the adsorption more favorable; 2) formation of surface complexes (ternary lead-phosphate-iron oxide); 3) precipitation of lead-phosphate; 4) surface alteration [2,93].

In a study of Liu and Zhao, iron phosphate (vivianite) nanoparticles were synthesized using CMC as a stabilizer for Pb immobilization in soils, results showed that the synthesized nanoparticles were effective to reduce the TCLP leachability and PBET bioaccessibility of Pb with a maximum reduction of 95% and 47%, respectively [94]. Simultaneously, the decrease of exchangeable and carbonate-bound Pb fractions were observed while residual-Pb fraction was increased, indicating that the Pb in soils was transferred to a more stable fraction with the application of the synthesized nanoparticles. They also found that the combination of iron and phosphate would also decrease the P leaching to the environment. Additionally, other researchers also demonstrated that ferrous phosphate nanoparticles [$Fe_3(PO_4)_2$, $FeHPO_4$ and $Fe(H_2PO_4)_2$] could not only reduce the bioaccessibility and toxicity of heavy metals but also decrease the leaching of P, which was more environmental friendly [95]. In a recent study, Guo et al. investigated the $FePO_4$ or $AlPO_4$ based surface coating for Pb immobilization in a shooting range soil, data showed that both of the two materials could effectively prevent the Pb from weathering and significantly reduce TCLP-leachable Pb in soils [96]. Therefore, the combination of iron and phosphate may be a promising technology for Pb immobilization in soils.

On the other hand, P could adsorb on hydrous metal oxides such as goethite (α-FeOOH) and akaganeite (β-FeOOH), and the iron oxide-based sorbents have been extensively studied for the removal of P from wastewater in recent years [97–103]. It has been proved that both α-FeOOH and β-FeOOH could adsorb P selectively among a large amount of other cations in seawater, especially the β-FeOOH, which exhibited stable chemical property and excellent adsorption ability even after 10 cycles [97]. Others demonstrated that P adsorption may make the hydrous metal oxides more negative charged and occupied the adsorption sites, which has a dual effect on the adsorption of Pb to iron (hydr)oxides [104]. However,

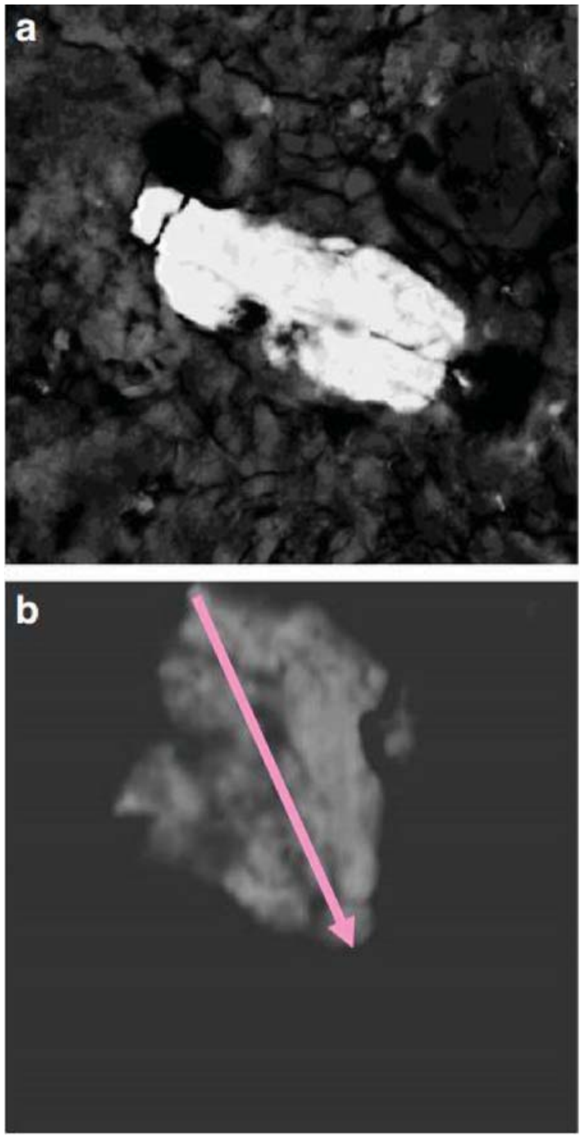

Fig. 7. Observation of Pb-phosphates in pea rhizosphere by SEM image and EDS analysis. **a** for soluble KH_2PO_4 amendment, $Pb_5(PO_4)_3(OH)_2$ (Hydroxypyromorphite) was observed. **b** for solid hydroxyapatite, the following Pb-Ca-P associations were observed: (1) $Ca_{4.5}Pb_{0.5}(PO_4)_3OH$, (2) $Ca_{4.0}Pb_{0.9}(PO_4)_3OH$, (3) $Ca_{3.3}Pb_{1.7}(PO_4)_3OH$, and (4) $Ca_{3.0}Pb_{2.0}(PO_4)_3OH$. (The pink arrow showed the detection area during the observation) [115] Copyright 2014 Springer Ltd.

the precipitation of Pb-phosphate, which was considered as the main mechanism for P-induced Pb immobilization, could be limited with the presence of iron (hydr)oxides since the iron (hydr)oxides could remove the P from the soil solution through adsorption or precipitation process. Therefore, the effect of the P-compounds on Pb adsorption to iron (hydr)oxides was complicated since the interaction between iron and P was variable and can not be predicted, which needs to be further studied.

$$\equiv FeOH + Pb^{2+} = \equiv FeOPb^{+} + H^{+} \quad (12)$$

$$\equiv FeOH + Pb^{2+} = \equiv FeOHPb^{2+} \quad (13)$$

$$\equiv FeOH + Pb^{2+} + H_2O = \equiv FeOPbOH + 2H^{+} \quad (14)$$

4. The rhizosphere effect

Except the precipitation and adsorption mechanisms, Selim has illustrated the relevant literatures in decades and proposed that

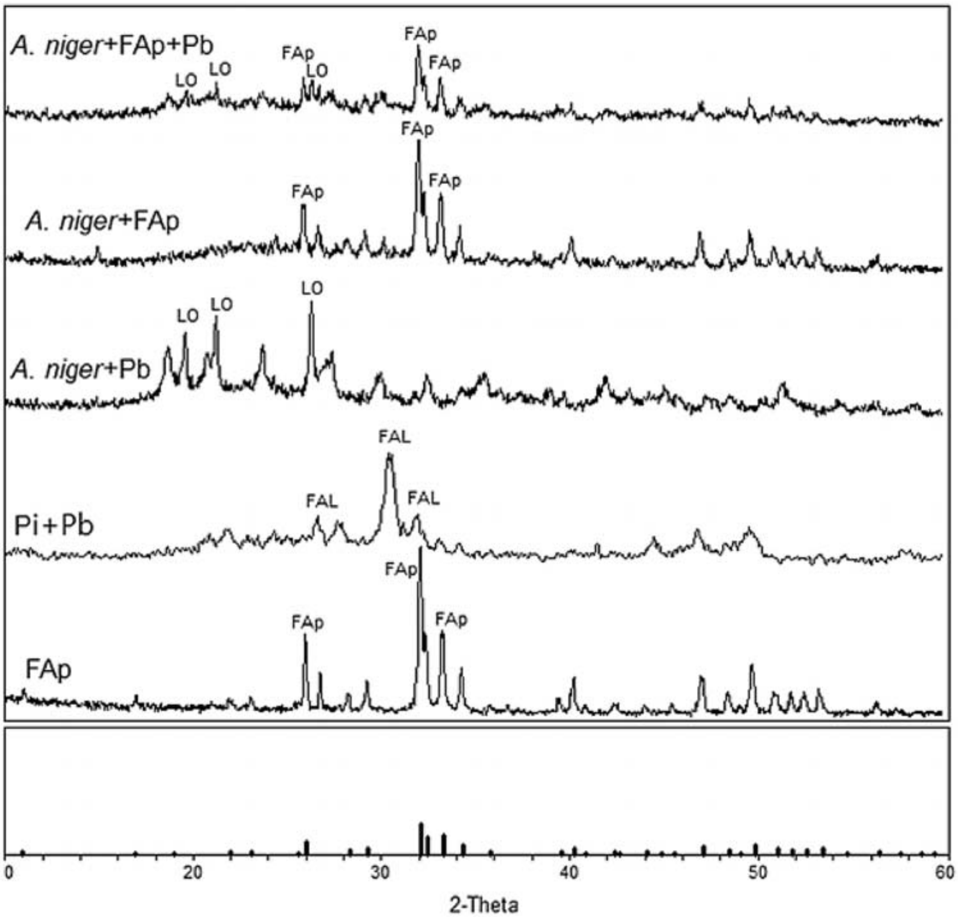

Fig. 8. XRD patterns of the precipitation in four treatments and FAp mineral. LO = lead oxalate, FAL = fluoropyromorphite. The pattern of standard FAp (ICDD database) is shown at the bottom. [114] Copyright 2016 Elsevier Ltd.

P-compounds may also affect the metal transformation in the rhizosphere through acidification effect and mycorrhizae effect [2]. Since Pb is one of the most toxic heavy metals and can be easily uptake by plants [1,3,105,106], this mechanism is also of great importance for interpreting the transformation of Pb in soils with the presence of P-compounds.

4.1. Acidification effect

Many researchers observed that the application of P-compounds may cause acidification in soils, which could enhance the mobilization of metals [33,107]. Acidification mostly occurred during the application of water-soluble P-compounds such as SSP and ammonium phosphate (AMP) in soils [41]. SSP such as MCP could dissolve in soils with the formation of dicalcium phosphate (DCP) and phosphoric acid (H_3PO_4) (Eq. (15)). Then H_3PO_4 subsequently dissociates into dihydrogen phosphate ($H_2PO_4^-$) and hydrogen ions (protons-H^+), reducing the pH to a low level (Eq. (16)) [2,33]. For AMPs, the nitrogen-containing P-compounds, they could dissociate into NH_4^+ and $H_2PO_4^-$ (Eq. (17)), then produce H^+ and NO_3^- through nitrification and lower the pH (Eq. (18)) [46]. Simultaneously, NO_3^- which are not strongly bind to soils could induce the leaching of basic cations to keep the balance of charge in soils, thus accelerating the acidification process [33]. In the case of legume-based systems, application of P-compounds may promote the nitrogen fixation, thereby indirectly causing soil acidification [33].

Researchers have observed that DAP would increase Pb solubility and mobility through the acidification [41,46,47], which is benefit for the subsequent precipitation of Pb-phosphate (according to the Eqs. (1) and (2)) [2,18]. Other researchers also demonstrated that the application of soluble and acidic phosphate sources was necessary for successful *in situ* treatment [25]. In the application of insoluble P-compounds, the acidification induced by the organic acids in root exudates was effective to dissolve the phosphate and increase Pb solubility and mobility around the rhizosphere, which could accelerate the Pb immobilization process through the precipitation of Pb-phosphates [108–110]. A recent study conducted by Zhu et al. showed that the γ-polyglutamic acid (γ-PGA), secreted by microorganism, could activate the PR to enhance the Pb immobilization and reduce the phytotoxicity of Pb [55]. However, the only use of γ-PGA was found to have an adverse impact on the growth of *pak choi* and increase Pb accumulation in the plant while the combination use with PR could reverse the results. That is to say, application of PR associated with γ-PGA could protect the plant from the acidification effect of γ-PGA and at the same time enhance the Pb immobilization efficiency of PR through the acidification effect. Thus, the acidification effect directly or indirectly induced by the organisms around the rhizosphere could cooperate well with P-compounds and enhance the P-induced Pb-immobilization in soils. It was also a promising way to develop environment friendly and cost effective technologies for *in situ* Pb remediation in the future.

$$Ca(H_2PO_4)_2 + H_2O \rightarrow CaHPO_4 \cdot H_2O + H_3PO_4 \quad (15)$$

$$H_3PO_4 \rightarrow H_2PO_4^- + H^+ \quad (16)$$

$$NH_4H_2PO_4 \rightarrow NH_4^+ + H_2PO_4^- \quad (17)$$

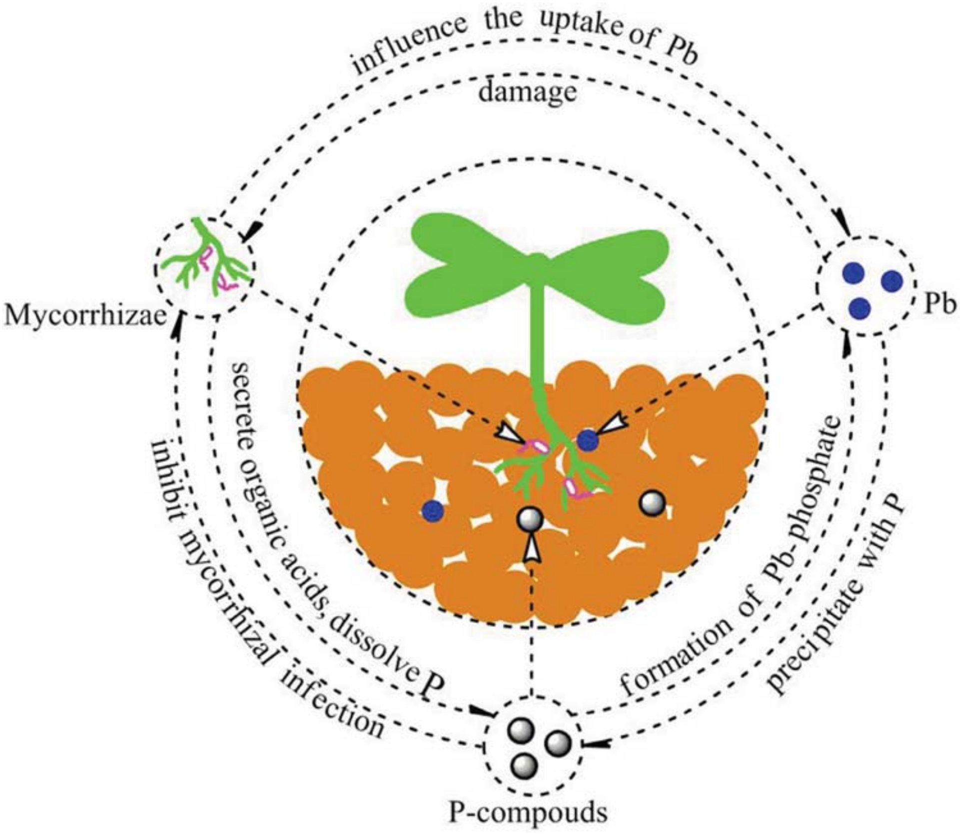

Fig. 9. The links among the P-compounds, Pb, and Mycorrhizae in root system.

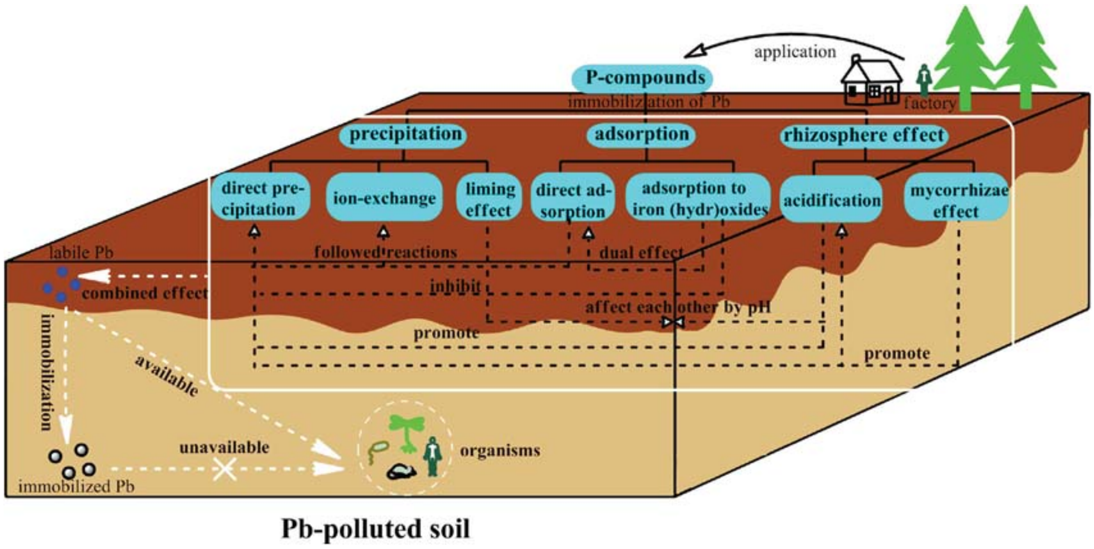

Fig. 10. The internal relationships among the three mechanisms about P-induced Pb immobilization in polluted soils.

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \quad (18)$$

4.2. Mycorrhizae effect

Plant root and their symbionts were usually recognized as mycorrhizae and it can not be ignored since heavy metal uptake by plants mostly depend on both plant and soil factors [106,111,112]. In addition, some of the fungal hyphae in mycorrhizae can extend several cm into the soil and uptake large amounts of nutrients to the host root plant, even the heavy metals [106,113,114]. Austruy et al. found that solid HAP and KH_2PO_4 even have no effect on the formation of Pb-phosphate with the absence of plants while these P-compounds could cause the immobilization of Pb and form Pb-phosphate complexes with the presence of plants [115]. SEM (scanning electron microscope) image and EDS (energy dispersive spectrometer) results showed that the Pb-phosphate complexes consisted of $Pb_5(PO_4)_3(OH)_2$, $Ca_{4.5}Pb_{0.5}(PO_4)_3OH$, $Ca_{4.0}Pb_{0.9}(PO_4)_3OH$, $Ca_{3.3}Pb_{1.7}(PO_4)_3OH$, and $Ca_{3.0}Pb_{2.0}(PO_4)_3OH$ (Fig. 7) [115]. Therefore, they demonstrated that the plant roots in the rhizosphere may influence the Pb immo-

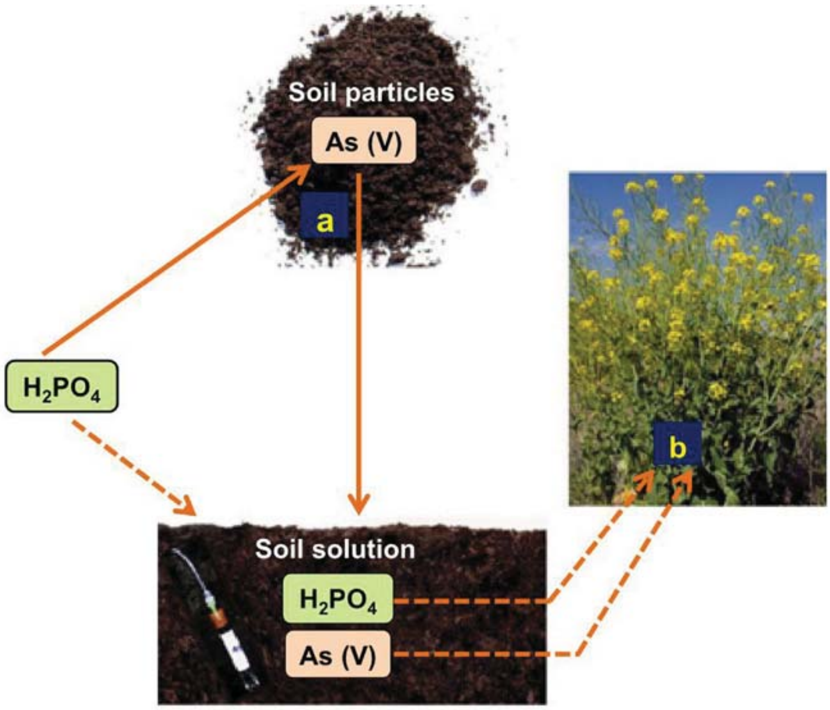

Fig. 11. Phosphate ($H_2PO_4^{-1}$) ions compete for As(V) adsorption by soil particles (a), and for As(V) absorption by plant roots (b). [30] Copyright 2013 Elsevier Ltd.

bilization. In the early study of Bolan et al. and Jayachandran et al., mycorrhizae was thought to be responsible for the liberation of P ions from both organic and inorganic matter, which is benefit for the immobilization of Pb [2,116–118]. Some scholars demonstrated that the release of root exudates, such as organic acids, could increase the availability of P in soils by decreasing the adsorption of P and increasing the solubilization of P compounds (monocalcium phosphate, North Carolina phosphate rock) [108–110,114,119,120]. In Li et al.' recent study, they found that fungus *Aspergillus niger* could enhance the solubility of fluorapatite by secreting organic acids, thus promoting the formation of fluoropyromorphite [$Pb_5(PO_4)_3F$, FAp], which was confirmed by the XRD analysis (Fig. 8) [114]. On the other hand, Menezes-Blackburn et al. speculated that the LMWOAs (Low Molecular Weight Organic Acids)-induced mobilized P may have been sequestered by soil microbes and remained relatively unavailable to plants [112]. That is to say, the mycorrhizae may play an important role in P-induced Pb immobilization through increasing the availability of P in soils or some other ways which need to be further studied.

On the other hand, it has also been reported by scholars that the addition of high level P-compounds may drastically reduce the fungal attachment to the roots and inhibit mycorrhizal infection [121,122]. Some researchers also demonstrated that the addition of P-compounds could alter the composition of root exudates and the amount of inhibitors or activators of *Arbuscular mycorrhizal* fungal development [121,123]. Andrade et al. have reported that the mycorrhizae effects could alleviate the stress caused by excess Pb in soils through maintaining higher P/Pb ratios on the shoots and enhance the P uptake [124]. Additionally, they also found that there were 30% less Pb in the shoots of mycorrhizal-treated plants than non-mycorrhizal treated plants, which suggested a possible Pb retention ability of the mycorrhizal (adsorption to cell walls). Simultaneously, sufficient P was found to reduce the Pb accumulation in rice grain while deficient P tended to enhance the grain Pb [125]. The links among the P-compounds, Pb, and mycorrhizae in root system was summarized in Fig. 9. It can be seen that the interaction among P-compounds, Pb, and mycorrhizae is complicated and it is necessary to be studied completely for promoting the development of P-based Pb-immobilization technology.

5. Conclusion and prospect

P-compounds were usually employed as chemical amendments for Pb immobilization in contaminated soils and they were effective to transfer labile Pb to stable fraction. The mechanism about P-induced Pb immobilization during the remediation is complicated and we have summarized it into three aspects: the precipitation of Pb-phosphates, the adsorption of Pb, and the rhizosphere effect. These three mechanisms were completely discussed and the specific reactions were also presented with respect to the references. Through the deeply discussion into each mechanism, we can see that none of the mechanism is independent and the internal relations among three mechanisms are obvious and we have summarized it in Fig. 10. From Fig. 10 we can see that each of the mechanism could affect and be affected by another, the synergic effects or antagonistic effects between each other cooperate together for the P-induced Pb immobilization. Thus, the effects about P-induced Pb immobilization in soils are difficult to predict and it should take various factors into consideration. In this review, with the particular analysis about each mechanism, we want to give a more particular understanding about P-induced Pb immobilization in contaminated soils and promote the development of P-based remediation technology.

On the other hand, even application of P has been recognized as an effective way to immobilize Pb in soils, the ultimate fate of P, the sustainability of Pb-phosphates, and P-induced adverse impacts should also be considered. Three aspects are concluded in this study:

(1) It can be seen in Table S1 that P-compounds, especially soluble P, were widely used for Pb remediation in soils since soluble P could provide more available P for Pb immobilization and has a high mobility in soils. However, problem associated with the application of soluble P is the eutrophication risk induced by

the leaching of excessive P, which should be taken into consideration during the *in situ* soil remediation.

(2) Formation of Pb-phosphates during the P-induced-remediation always represents the success of Pb immobilization and Pb-phosphates are believed to be stable and unreactive in the environment. However, some studies demonstrated that plants may solubilize insoluble inorganic phosphate compounds by modifying their root system and secreting a series of organic acid to enhance the uptake of P under P starvation [28]. That is to say, the sustainability of Pb-immobilization can be influenced by the biological P-demand of plants and Pb may be remobilized under natural environment.

(3) Some researchers indicated that the application of P would enhance the leaching of As (arsenic) since phosphate and arsenate will compete for the adsorption site in soils or around plant roots (Fig. 11) [2,30]. Similarly, both Se and Sb (behave as oxoanions) can be mobilized by the addition of P in soils through the competition for negative sorption sites with phosphate [31,32]. Additionally, P has once been used for solubilizing W in an Occupational Safety and Health Administration (OSHA) protocol since P could also accelerate the leaching of W in soils [25]. In view of these cases, the leaching of As, Se, Sb and W should be taken into account during the P-induced-remediation to avoid the adverse impacts that induced by P application.

Therefore, based on the extensively comprehension of the mechanisms about P-induced Pb-immobilization in soils, researchers must pay more attention to the ultimate fate of P, the sustainability of Pb-phosphates, and P-induced adverse impacts during the application of P for Pb immobilization in further studies, finding an environmental friendly and cost-effective way to make the best use of P-compounds for Pb remediation and at the same time try the best to reduce the secondary pollution.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2017.05.038.

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