

1 Novel Thermal Modification of Phosphate Tailings for Enhanced Heavy Metals
2 Immobilization in Soil

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Abstract

Recent interest in amendments derived from industrial by-products has highlighted their potential for both resource recycling and heavy metal remediation. Phosphate tailings (PT), primarily dolomite-based solid waste with low utilization rates, offer a promising yet underexplored solution. This study pioneers the thermal modification of PT into a novel amendment, thermally modified phosphate tailings (TPT), to assess its adsorption performance, underlying mechanisms, and effectiveness in immobilizing heavy metals in soils. The thermal modification process transformed dolomite in PT into calcite and periclase, dramatically enhancing the maximum adsorption capacities by 28-fold for Cd^{2+} and Cu^{2+} , and 7-fold for Pb^{2+} , with the capacities reaching 248, 531, and 433 $\text{mg}\cdot\text{g}^{-1}$ for Cd^{2+} , Pb^{2+} , and Cu^{2+} , respectively. The dominant removal mechanism for TPT was surface precipitation, complemented by electrostatic adsorption, surface complexation, and ion exchange. Practical applications of TPT in contaminated soil reduced TCLP-extracted Cd, Pb, and Cu by up to 44%, 60%, and 61%, respectively, effectively transforming heavy metals into relatively stable form. This study demonstrates the potential of TPT as a novel amendment for heavy metal immobilization, providing both effective contamination control and enhanced resource utilization, thus addressing a critical gap in the remediation of contaminated soils. Given its low-cost nature derived from industrial waste, TPT holds significant promise for large-scale application, making it a practical and sustainable solution for soil remediation.

Keywords:

Phosphate flotation tailings, thermal modification, heavy metal contamination, soil remediation

1 Introduction

Heavy metal contamination of soil poses significant risks to ecosystems and human health, necessitating the development of effective remediation strategies. Over the past two decades, in situ chemical immobilization has emerged as a widely adopted approach due to its rapid implementation, commercial feasibility, and ability to reduce metal mobility and bioavailability in soils (Liu et al., 2024). This method employs various amendments, such as biochar, animal waste, clay minerals, liming agents, and phosphate compounds, to stabilize heavy metals through mechanisms including surface adsorption, complexation, ion exchange, and precipitation (Gao et al., 2023). Specifically, amendments derived from industrial by-product, such as steel slag, red mud and phosphogypsum, have received significant attention for their demonstrated efficiency in immobilizing heavy metals and cost-reduction potential for soil remediation through industrial waste recycling (Hassandoost et al., 2022; Hassandoost et al., 2024; Zhang et al., 2024a). This strategy not only alleviates heavy metal contamination but also promotes circular resource utilization, aligning with the principles of green remediation.

Phosphate tailings (PT), a by-product of phosphate rock beneficiation, represent an underutilized resource with significant potential for heavy metal remediation. During

beneficiation, 30-40% of the raw phosphate ore is discarded as tailings, resulting in the accumulation of vast quantities of waste (Gu et al., 2022). As of 2020, China had approximately 1.2 billion tons of PT, yet only 17% had been utilized (Guo et al., 2023). However, current applications, such as mine backfilling, fertilizer production, and construction materials, fail to address the growing environmental and land-use challenges associated with PT accumulation. This insufficiency is largely attributable to the increasing generation of PT from declining ore grades, as well as the limited scalability of these approaches due to constraints such as high transportation and production costs (Guo et al., 2023; Li et al., 2024; Yu and Du, 2023). Consequently, developing efficient methods to transform PT into valuable environmental remediation resources has become imperative.

PT, primarily composed of dolomite, offers a promising pathway for heavy metals immobilization, as evidenced by the established efficacy of dolomite in remediation (Gu et al., 2022; Yu and Du, 2023). Dolomite, a typical carbonate mineral with inherent alkalinity, reduces bioavailability of metals in soil through elevating the soil pH to promote precipitation and releasing CO_3^{2-} to form stable carbonate precipitates (Chen et al., 2024), as demonstrated by reductions in extractable Cd (19%-26%) and Zn (52%-70%) (Vrînceanu et al., 2019), and a 46.9% decrease in Cd content in early rice following application (Chen et al., 2024). However, initial studies indicate poor metal retention performance for unmodified PT, which may be attributed to limited exposure of reactive sites, and the stable crystalline structure of dolomite in PT restricting the release of $\text{Ca}^{2+}/\text{CO}_3^{2-}$ necessary for co-precipitation (Liu et al., 2021; Ouyang et al.,

2021; Wang et al., 2025), thus necessitating appropriate modification techniques to enhance their effectiveness.

Limited research has explored PT modification for heavy metal immobilization, with most focusing on acid activation for phosphate release. Liu et al.(2021) achieved 5%-10% higher immobilization efficiency of dolomite phosphate rock for Pb and Cd through humic acid activation, while Zhang et al.(2024b) reduced Pb leaching by up to 99.60% using phosphoric acid. Wu et al.(2023) further developed a hydroxyapatite-based material from PT with improved adsorption capacities of Cd, Pb, and Zn. However, these wet modification approaches often involves multiple washing and filtering cycles, leading to time-consuming and operationally complex procedures. In contrast, thermal modification could potentially serve as a promising strategy for improving the performance of PT. This single-step process decomposes dolomite into magnesium oxide and calcium carbonate, thereby increasing adsorption and precipitation capacities for metal ions, which was evidenced by a sevenfold increase in Zn^{2+} adsorption capacity on modified dolomite (Calugaru et al., 2016; Salameh et al., 2015). Likewise, thermally activated fluorapatite, another major component of PT, also showed improved Pb immobilization (Aklil et al., 2004; Mouflih et al., 2005). These findings highlight the potential of thermal modification for improving heavy metal immobilization capacity of PT. However, the effect and mechanism of thermal modification applied to PT remain unclear.

This study investigates the potential of thermally modified phosphate tailings (TPT) as a sustainable solution for heavy metal remediation in contaminated soils. Cd,

Pb and Cu were selected as representative metals in this study, as they are widespread inorganic soil contaminants which can cause phytotoxicity and threaten human health through the food chain (Xiao et al., 2024). The objectives of this study were (a) to prepare and characterize TPT; (b) to investigate the adsorption performance and mechanism of TPT for Cd, Pb and Cu ions using batch sorption experiments; and (c) to evaluate the effectiveness of TPT for simultaneous remediation of Cd, Pb, and Cu in contaminated soil using incubation experiments.

2 Materials and methods

2.1 Preparation of thermally modified phosphate tailings

Phosphate tailings powder from Yunnan phosphate group Co., LTD (China) was calcined in muffle furnace at 700°C for 2 h and then sieved to 0.15-mm. The product was named as the thermally modified phosphate tailings (TPT).

2.2 TPT characterization

The pH was determined using the STARTER 3100/F pH meter (Ohaus Inc., China) with a solid:liquid ratio of 1:2.5. The main chemical composition in oxides of PT and TPT was determined by X-ray Fluorescence (XRF, Axios-MAX, PANalytical, Netherlands). The mineralogical analysis of PT, TPT and TPT after heavy metal adsorption were obtained through X-ray Diffraction (XRD, X'Pert Pro, Almelo, Netherlands) with CuK α radiation for 2 θ from 5° to 90° at 0.190°·s⁻¹. The surface functional groups were identified by Fourier transform infrared spectroscopy (FT-IR,

Nicolet iS10, Thermo, USA) at the range of 400-4000 cm^{-1} . The Scanning Electron Microscope (SEM, S-4800, Hitachi, Japan) was used to analyze the surface morphologies of materials with gold coated before. The X-ray photoelectron spectrometer (Axis Supra, Shimadzu, Japan) was utilized to analyze the surface composition of materials.

2.3 Batch sorption experiment

The adsorption behavior of Cd^{2+} , Pb^{2+} and Cu^{2+} on PT and TPT was investigated by batch sorption experiment in 15 mL polyethylene centrifuge tubes. The solution contained Cd^{2+} , Pb^{2+} or Cu^{2+} was prepared by dissolving $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with 0.01 M NaNO_3 as the background electrolyte. The initial pH of the metal solution was adjusted to $\text{pH } 5.00 \pm 0.05$ using 1 $\text{mol} \cdot \text{L}^{-1}$ HNO_3 and 1 $\text{mol} \cdot \text{L}^{-1}$ NaOH to avoid metal ions precipitation (Wu et al., 2021).

The adsorption isotherm experiments were carried out at 298 K with Cd^{2+} , Pb^{2+} and Cu^{2+} solution with the initial concentrations of 2-1500 $\text{mg} \cdot \text{L}^{-1}$, 50-1500 $\text{mg} \cdot \text{L}^{-1}$ and 50-1400 $\text{mg} \cdot \text{L}^{-1}$, respectively. 10 mg of PT or TPT were added to polyethylene centrifuge tubes with 10 mL Cd^{2+} , Pb^{2+} or Cu^{2+} solutions. The mixture was shaken at 150 rpm for 48 h, and then the suspensions were passed through 0.22 μm filter membrane. The concentration of heavy metals in filtrate was determined by the inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 7000DV, PerkinElmer, US) after being diluted by 0.5% HNO_3 solution.

The adsorption kinetics experiments were conducted in the same conditions as

adsorption isotherm experiments, with solution containing of 30-1000 mg·L⁻¹ Cd²⁺, Pb²⁺ and Cu²⁺ for 0-90 h, respectively, and aliquots of samples were collected and filtered at different time intervals. To investigate the influence of pH on adsorption, the initial pH of the solutions was adjusted to specific values within the ranges of 1.0-8.0, 1.0-6.0, and 1.0-5.0 for Cd²⁺, Pb²⁺ and Cu²⁺, respectively, using 1 mol·L⁻¹ HNO₃ and 1 mol·L⁻¹ NaOH. These pH ranges were set to ensure that the metal ions remained in their ionic state, and no additional adjustments were made during the 48-hour equilibration period.

2.4 Soil incubation experiment

Two contaminated soils were collected from the surface layer (0-20 cm) of two agricultural lands in Longyan (S1, Fujian Province, China) and Liuyang (S2, Hunan Province, China), respectively. The samples were mixed evenly, air-dried and passed through a 2-mm sieve. The physic-chemical properties of the tested soils are shown in Table S1. The Cd and Pb concentrations in the two soils are all exceeding the risk intervention values according to the China's Ministry of Environment Protection (GB15618-2018), and the total Cu concentrations are exceeding the risk screening values.

Incubation experiment was conducted to evaluate the influence of obtained material on mobility of heavy metals in soils after applying. Three treatment groups were set up in soil mesocosms: (1) CK: control treatment group, no application of TPT; (2) TPT-5%: application of 5% (mass%) TPT; (3) TPT-10%: application of 10%

(mass%) TPT. Each treatment was taken in 500 mL plastic beakers with 320 g soil and five parallel repeats were set. After mixing homogenously, all the treatments were incubated at 298 K for 60 days and the ultrapure water was added every three days to maintain 80% water holding capacity. Soil samples were collected at 60 days and freeze-dried and then ground to pass through a 2-mm sieve before the further analysis.

The Potassium Dichromate Heating Oxidation-Volumetric Method was employed to measure the soil organic matter (OM) and NH_4 -acetate buffer solution (pH=7) was used to determine cation exchange capacity (CEC) in soils. The concentration of extractable metals in soils was measured by the toxicity characteristic leaching procedure (TCLP) (EPA, 1992). An improved sequential extraction procedure BCR (European Community Bureau of Reference) was employed to determine the chemical speciation of heavy metals in soils (Rauret et al., 1999), and the metal contents in extractant were measured using Inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500cx, Agilent, America).

2.5 Statistical analysis

Statistical analyses were performed using SPSS 26.0. One-way analysis of variance (ANOVA) was applied to compare the effects of different treatments, followed by post-hoc multiple comparisons using the Least Significant Difference (LSD) test at a significance level of $P < 0.05$. When $P < 0.05$, the differences were considered significant.

3 Results and discussion

3.1 Characterization of materials

Thermal modification significantly increased the pH of PT, while the main chemical components remain largely unchanged, predominantly consisting of CaO and P₂O₅, with MgO and SiO₂ following (Table S2). The XRD analysis revealed that dolomite, fluorapatite and quartz were the main components of PT (Fig. 1). However, the characteristic peaks of dolomite disappeared after thermal treatment while the peaks corresponding to calcite and periclase emerged, indicating that dolomite decomposed into calcite and periclase. This change was further confirmed by FT-IR (Fig. S1). For PT, the band located at 729 and 881 cm⁻¹ were ascribed to the in-plane bending and the out-of-plane bending modes of CO₃²⁻ group, respectively, while the broad and weak adsorption bands detected at 2523, 2627 and 3020 cm⁻¹ resulted from the combinations involving CO₃²⁻, confirming the presence of dolomite (Gunasekaran and Anbalagan, 2007; Nguyen et al., 1991). However, the characteristic band at 2627 cm⁻¹ disappeared after modification, indicating that dolomite had transformed to calcite (Park et al., 2011), which was further supported by the shift of all other bands. The decomposition transformed PT particles from randomly shaped with broad size distribution to smaller, denser and irregular morphologies (Fig. S2) due to the release of CO₂ from the carbonate-rich areas (Wilson et al., 2008). The introduction of calcite and periclase added pronounced alkalinity of TPT and helped with the affinity for metal ions, potentially improving the adsorption performance of the material (Calugaru et al., 2016;

Salameh et al., 2015).

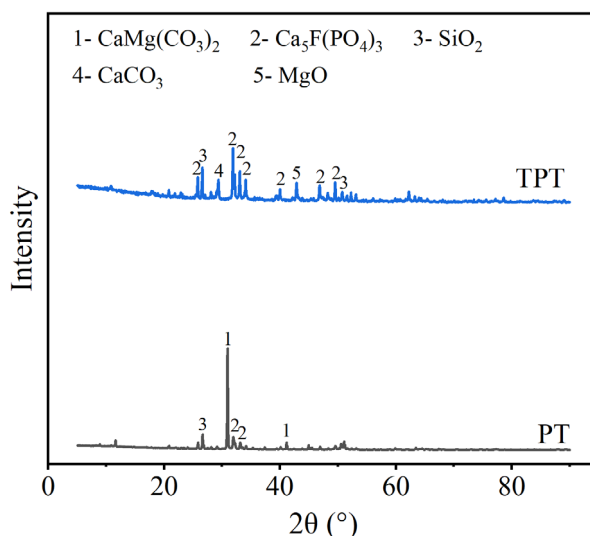


Fig. 1 XRD of PT and TPT

3.2 Adsorption behavior of TPT for metals

3.2.1 Adsorption kinetics

The adsorption of PT for Cd^{2+} and Cu^{2+} occurred rapidly in the first hour, then gradually became slow and reached equilibrium in 12 h (Fig. 2a-c). In contrast, the adsorption of Pb^{2+} required 48 h to achieve equilibrium. For TPT, the rapid adsorption of metals persisted for 10-12 h before the rates decline, with equilibrium achieved at approximately 72 h.

Pseudo-first-order and pseudo-second-order model were employed to further explore the adsorption behavior (Table S3). Higher correlation coefficients (R^2) for the pseudo-second-order model indicated the adsorption on both PT and TPT was mainly controlled by chemisorption (Kong et al., 2024). This chemisorption behavior is likely attributed to surface precipitation, as CO_3^{2-} or OH^- ions released from dolomite-based PT react with metal ions to form stable carbonate or hydroxide precipitates (Liu et al.,

2021), while the thermal modification might enhance this precipitation pathway in TPT.

Notably, the rate constant (k_2) decreased for TPT compared to PT, suggesting a decreased adsorption rate after modification. This slowdown might be attributed to the two-step adsorption of heavy metals on calcite: initial surface adsorption followed by rate-limiting surface precipitation, which required calcite dissolution to supply CO_3^{2-} for metal ion reaction (Du et al., 2011). For TPT, the denser structure likely suppressed the release of CO_3^{2-} , consequently diminishing the adsorption efficiency and saturation time (Ruiz-Agudo et al., 2014; Zhou et al., 2017). Despite the smoother curve in adsorption, TPT showed significantly higher metal ion adsorption capacities than PT within the same time, indicating a marked improvement in metal removal efficiency achieved through thermal modification.

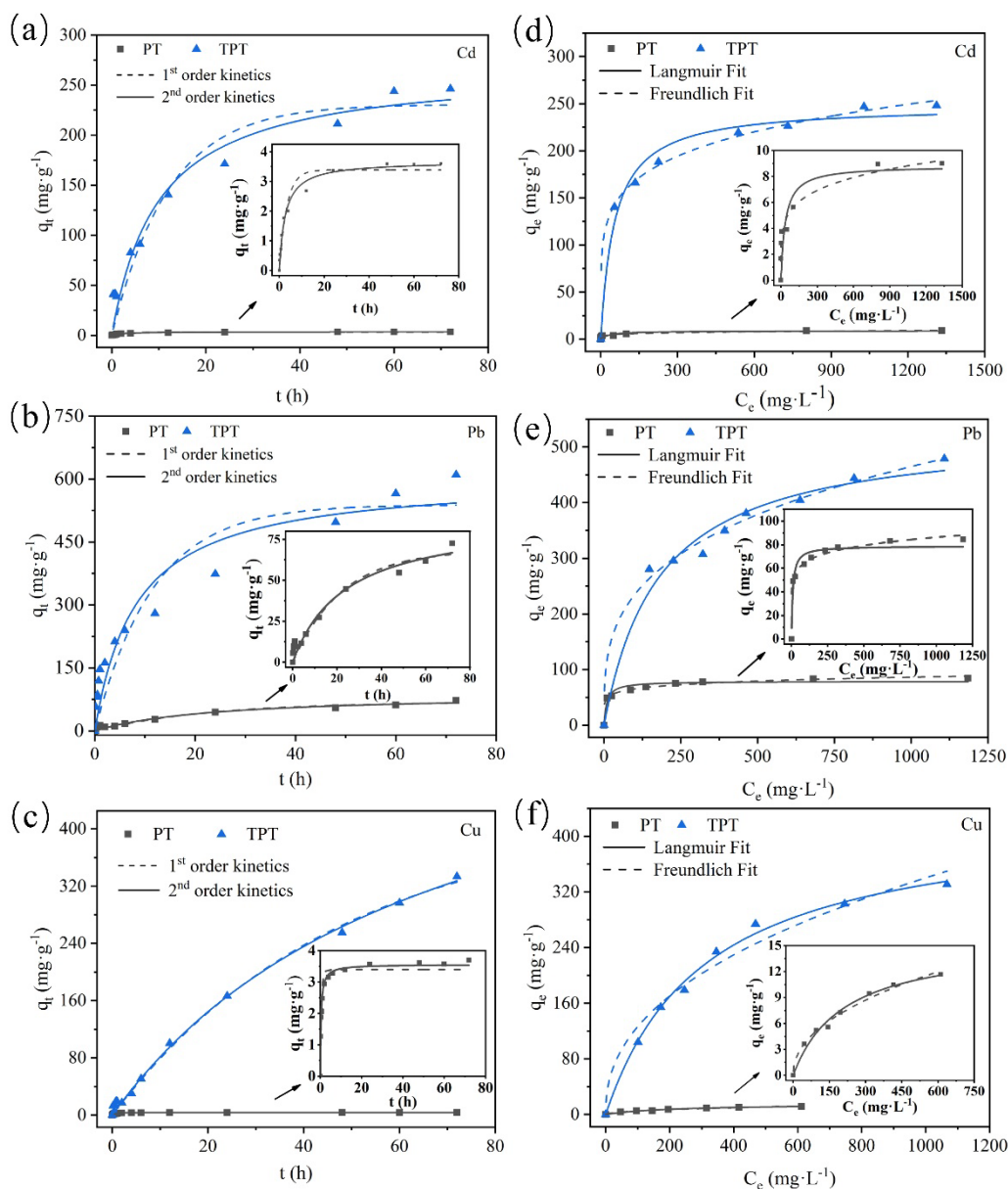


Fig. 2 Adsorption kinetics(a-c) and isotherms(d-f) of Cd^{2+} , Pb^{2+} and Cu^{2+} onto PT and TPT

3.2.2 Adsorption isotherms

The adsorption capacity of PT and TPT for Cd^{2+} , Pb^{2+} and Cu^{2+} increased with the initial concentration of metal ions until equilibrium was reached (Fig. 2d-f). The Langmuir and Freundlich model were used to investigate the adsorption performance of metals on adsorbents (Table S4). Based on the correlation coefficients (R^2), the

Freundlich model better described the adsorption process of Cd^{2+} and Pb^{2+} on PT and TPT, as well as Cu^{2+} on PT, suggesting the multilayer adsorption process on the heterogeneous surface of adsorbents. In contrast, the adsorption of Cu^{2+} on TPT followed Langmuir isotherm model, indicating the monolayer adsorption on homogenous surface (Wu et al., 2021). According to the Langmuir models, the maximum adsorption abilities of TPT for Cd^{2+} , Pb^{2+} and Cu^{2+} were $248.27 \text{ mg}\cdot\text{g}^{-1}$, $531.45 \text{ mg}\cdot\text{g}^{-1}$ and $433.30 \text{ mg}\cdot\text{g}^{-1}$, respectively, which were 7 to 28 times higher than that of PT, confirming the substantial enhancement from the thermal modification. Compared to other modified adsorbents with adsorption capacities for Cd, Pb, and Cu ranging from 10 to $240 \text{ mg}\cdot\text{g}^{-1}$, 2 to $480 \text{ mg}\cdot\text{g}^{-1}$, and 33 to $1111 \text{ mg}\cdot\text{g}^{-1}$, respectively (Table S5), TPT exhibited relatively superior adsorption capacity for metal ions among them, demonstrating its promising potential for metal ions retention. Meanwhile, utilizing low-cost industrial waste and the simple thermal modification process contribute to cost reduction and enhance the feasibility of large-scale production, further highlighting the practical advantage of TPT as an amendment.

3.2.3 Effect of solution pH

The pH of solution is a critical variable during the adsorption process, affecting both metal speciation and the surface charge of adsorbent (Chen et al., 2007). The adsorption capacities of materials for metal ions increased with the initial pH of solution, with a more pronounced effect observed in TPT (Fig. 3). When the initial pH rose from

1 to 3, the adsorption capacity for Cd^{2+} , Pb^{2+} and Cu^{2+} increased sharply by 711, 23 and 11 times, respectively. After $\text{pH} > 3$, the increase slowed, with only a 0.07-0.23 times enhancement at $\text{pH}=5$ compared to $\text{pH}=3$. In contrast, PT showed a relatively modest response, especially for Cd and Cu (3 and 2 times increases, respectively), while the adsorption capacity for Pb increased 12 times at $\text{pH}=3$ compared to $\text{pH}=1$.

These trends were likely attributed to the surface charge modulation by pH: at low pH, the protonated surfaces of PT and TPT would experience competition between H^+ ions and metal ions for binding sites, limiting adsorption. As pH increased, surface deprotonation generated increased negative charge, facilitating electrostatic attraction between adsorbents and metal ions (Mostofa et al., 2022). Notably, under identical pH conditions, TPT consistently exhibited significantly higher adsorption capacities than PT ($P < 0.05$), indicating that thermal modification effectively enhanced the adsorption performance of material on heavy metal ions.

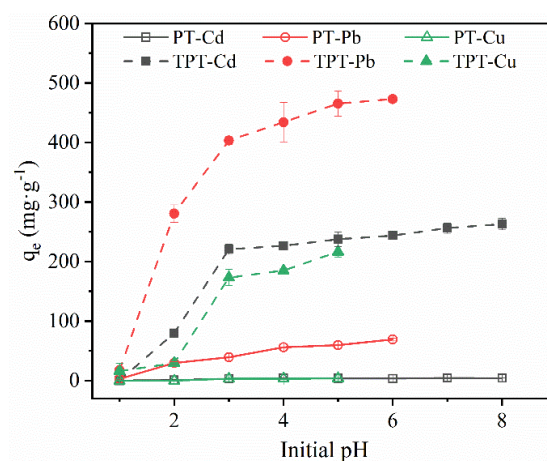


Fig. 3 Effects of pH on Cd^{2+} , Pb^{2+} and Cu^{2+} adsorption onto PT and TPT

3.2.4 Adsorption mechanism

A series of characterizations were conducted to elucidate the interaction mechanism between TPT and heavy metals, revealing four major pathways: precipitation, complexation, ion exchange, and electrostatic adsorption.

Heavy metals can be removed by TPT through surface precipitation. XRD spectra (Fig. 4a) revealed the formation of $\text{Cd}(\text{OH})_2$, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, $\text{Cu}_2(\text{OH})_3\text{NO}_3$ and $\text{Cu}_2(\text{OH})_2\text{CO}_3$ on TPT after adsorption, accompanied by the disappearance of the peaks of MgO . The characteristic peaks of CaCO_3 also disappeared after the adsorption of Pb^{2+} and Cu^{2+} . These results demonstrated that Cd, Pb and Cu precipitated on the surface of material with MgO and CaCO_3 in TPT potentially involved (Zhao et al., 2020). FT-IR spectra (Fig. S3) confirmed these findings, revealing new peaks consistent with these Pb and Cu precipitates and a peak at 3604 cm^{-1} ($-\text{OH}$) contributed to $\text{Cd}(\text{OH})_2$ (Chen et al., 2020; Da Cunha et al., 2014; Srikhaow and Smith, 2013). XPS further validated this mechanism (Fig. 4c-e), revealing decomposed spectra of $\text{Cd}3\text{d}_{5/2}$, $\text{Pb}4\text{f}_{7/2}$ and $\text{Cu}2\text{p}_{3/2}$ into two peaks: $\text{Cd}(\text{OH})_2$ (404.97 eV) and Cd-O bonding (405.88 eV), $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (138.20 eV) and Pb-O bonding (138.95 eV), $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (933.80 eV) and $\text{Cu}_2(\text{OH})_3\text{NO}_3$ (934.93 eV) (Chufarova et al., 2019; Quan et al., 2020; Singh et al., 2006; Wen et al., 2019), respectively. These results further confirmed the formation of Cd, Pb and Cu precipitates after adsorption, along with the formation of Cd/Pb-O bonding on the surface of TPT. This bonding is attributed to the complex reaction between metal ions and oxygen functional groups, representing another form of $\text{Cd}^{2+}/\text{Pb}^{2+}$ on the surface. Notably, $\text{Cd}(\text{OH})_2$ and $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ were the main forms of Cd and Pb adsorbed on TPT, respectively, due to a higher peak area ratio compared

with corresponding value of Cd/Pb-O bonding.

Precipitation of heavy metals was driven by the increasing solution pH, which created an alkaline environment. OH^- released during MgO hydration could react with heavy metals to form the precipitates. Additionally, the CO_3^{2-} produced from calcite dissolution facilitated the formation of $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ and $\text{Cu}_2(\text{OH})_2\text{CO}_3$. In this study, $\text{Cu}(\text{OH})_2$ also converted to $\text{Cu}_2(\text{OH})_3\text{NO}_3$ due to the NO_3^- in solution.

Metal ions can also be retained through complexation with functional groups which have been confirmed in the spectra of $\text{Cd}3d_{5/2}$, $\text{Pb}4f_{7/2}$ and $\text{Cu}2p_{3/2}$. FT-IR (Fig. S3) also showed a decrease in Si-O band at 799 cm^{-1} after adsorption, suggesting the involvement of Si-O (Criado et al., 2007), which was further evidenced by XPS analysis. The O1s spectra of TPT (Fig. S4) could be decomposed into five parts with binding energies of 532.90 eV (metal hydroxides or -OH), 532.20 eV (SiO_2), 531.53 eV (CO_3^{2-}), 530.70 eV (PO_4^{3-}) and 530.04 eV (MgO) (Chi et al., 2017; Grimes et al., 1995; Qin et al., 2018; Yue et al., 2019; Zheng et al., 2010), with peaks corresponding to SiO_2 shifted to higher binding energies after adsorption. This change indicated the complexation between surface O-containing functional groups and metal ions, reducing the electron cloud density around O1s (He et al., 2014).

Generally, SiO_2 in TPT exhibits high affinity for metal ions, with surface oxygen atoms hydrolyzing to form silanol group (Si-OH). The acidity of Si-OH determines the dependence of the SiO_2 surface charge on pH, further influencing the surface charge of materials. At low pH, SiOH^+ formed with a positively charged surface of TPT, while a negatively charged surface would prevail with the formation of SiO^- , which can

complex with hydroxides or heavy metal ions (Bayat, 2002; Mohan and Gandhimathi, 2009).

Metal ions can be captured by ion exchange with exchangeable ions (Ca^{2+} , Mg^{2+} , etc.) released from TPT. As indicated in the wide scan spectra (Fig. 4b), the peaks of Cd3d, Pb4f and Cu2p were observed after the adsorption of heavy metals on TPT accompanied by the significant decreases in intensity of Ca2p and Mg2p, indicating potential exchange between metal ions and Ca^{2+} and Mg^{2+} in TPT (Zhang et al., 2021).

Electrostatic adsorption also contributed, particularly at higher pH values where deprotonated surfaces become negatively charged. Previous studies have shown that calcite and fluorapatite adsorb metal ions via electrostatic adsorption (Du et al., 2011; Xiao et al., 2020). In our study, the adsorption capacity of TPT increased at $\text{pH} > 2$, likely due to enhanced electrostatic attraction between negatively charged surfaces and metal cations.

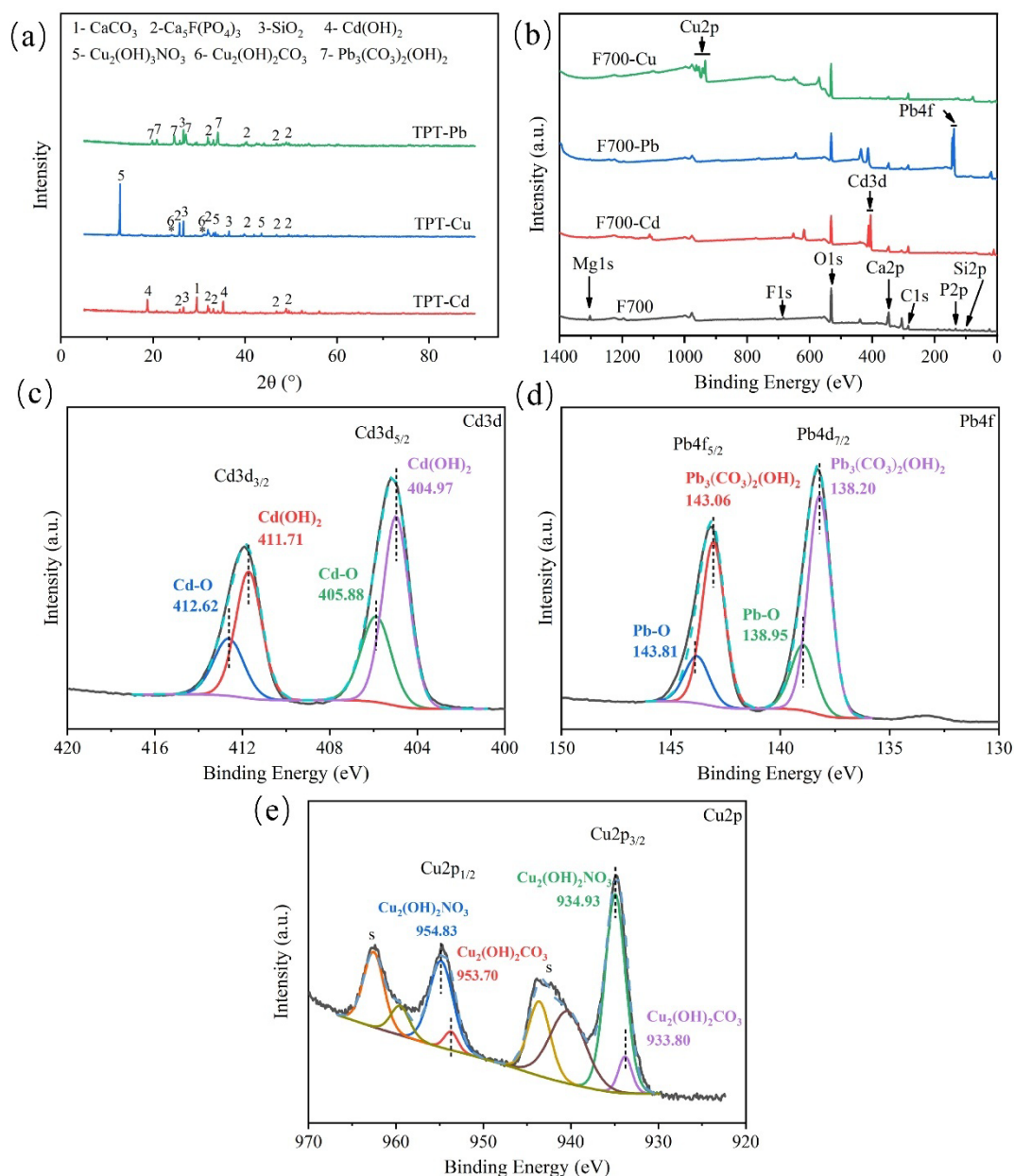


Fig. 4 XRD spectra (a), Full spectra analysis of XPS (b), XPS spectra of Cd 3d (c), Pb 4f (d) and Cu 2p (e) of TPT after adsorbed Cd²⁺, Pb²⁺ and Cu²⁺

In summary, the potential adsorption mechanisms for metal ions of TPT in aqueous solution (Fig. 5) include: (a) surface precipitation with minerals which release anions (e.g., CO₃²⁻ and OH⁻); (b) surface complexation between oxygen functional groups; (c) ion exchange with minerals containing exchangeable ions; (d) electrostatic sorption between ions and adsorbents with negative charged surface. And the dominant

mechanism for metal ions removal was the surface precipitation.

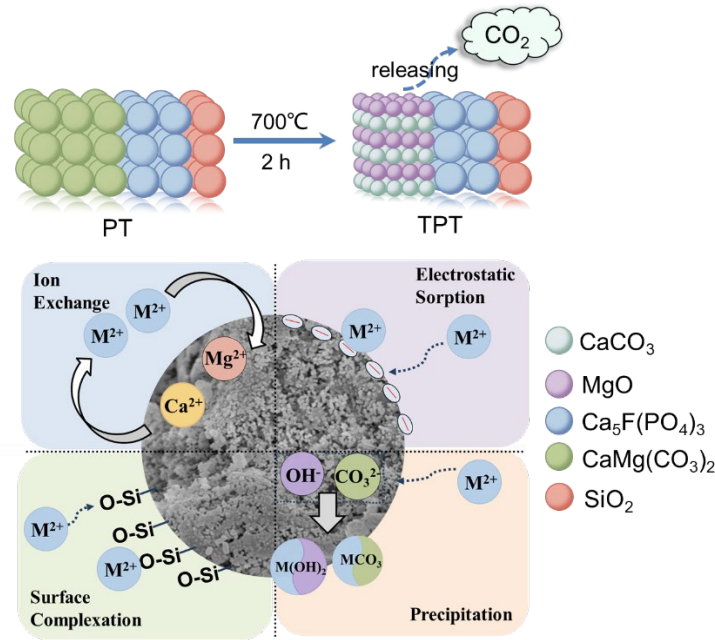


Fig. 5 The mechanisms of Cd²⁺, Pb²⁺ and Cu²⁺ adsorption onto TPT

3.3 Immobilization of Cd, Pb and Cu in soils

3.3.1 Effects of amendments on properties of soil

The effects of TPT application on soil pH, CEC and OM contents are presented in Fig. S5. Compared to the control, soil pH significantly increased with higher addition of TPT ($P < 0.05$), attributed to the high alkalinity and substantial amounts of CaO and MgO in TPT (Yan et al., 2016). Specifically, TPT raised the pH of soil S2 by 3.28-3.97 units, while that of soil S1 increased by 1.00-1.32 units, likely due to the lower initial pH of soil S2. In contrast, TPT decreased soil OM content and CEC in all treatments. In soil S1, the OM content and CEC decreased by 6.47%-6.57% and 29.00%-29.55%, respectively, with no significant change with the increasing addition rates ($P > 0.05$). However, the decreases were more pronounced in soil S2, with OM content dropping

by 6.34%-11.51% and CEC by 18.49%-38.47% as the application rate increased. The observed decrease in OM can be attributed to the alkaline condition induced by TPT application, which may accelerate the decomposition of soil organic matter, consequently diminishing CEC as OM is a major contributor to exchange sites (Xu et al., 2013). The decline in both OM and CEC may have significant implications for soil fertility and functionality (Paes Da Costa et al., 2024), highlighting the need to evaluate the long-term agricultural impacts of TPT use and to explore integrated soil management strategies.

3.3.2 Effects of amendments on TCLP extractable heavy metals

The toxicity characteristic leaching procedure (TCLP) was conducted to evaluate the mobility of heavy metals in TPT-treated soil after two-month incubation (Fig. 6). The results showed a significant reduction in Cd, Pb and Cu in the TCLP extracts from TPT-treated soils with higher application rates strengthening the reduction. Compared to the control, the TCLP extracts showed significant reduction of 26.96%-44.27%, 38.28%-60.23% and 21.08%-61.65% ($P < 0.05$) in Cd, Pb and Cu, respectively, in TPT treated soil. However, there was no significant difference among the addition rates in soil S1 ($P > 0.05$), unlike in soil S2, suggesting that immobilization efficacy may plateau beyond a threshold, which appears to be influenced by soil properties and amendment dosage.

Compared with materials reported in the literature (Table S6), which typically show immobilization efficiencies of 5%-58% for Cd, 7%-63% for Pb and 18%-63% for

Cu, TPT demonstrated a superior performance in simultaneously immobilizing metals with efficiencies of 27%-44%, 38%-60% and 21%-62%, respectively. Although not the most effective, the promising immobilization efficiency of TPT, coupled with its low cost and abundance as derived from recycled solid waste PT, underscores its potential as a sustainable remediation material that promotes phosphate resource reuse simultaneously. Furthermore, the thermal modification employed here, a one-step dry process, offers distinct advantages over conventional wet modification, including simplified operation, reduced processing time, and the elimination of washing or filtration steps (Wang et al., 2020). This method achieves the facile and rapid one-step mass preparation of TPT, enhancing its practical applicability in field-scale remediation. However, due to the complex and variable physicochemical properties of different soil (e.g., pH, OM, texture, and coexisting components) which affect the performance of amendment, further investigation is required to determine the optimal conditions for TPT application (Palansooriya et al., 2020; Tian et al., 2024; Wang et al., 2021).

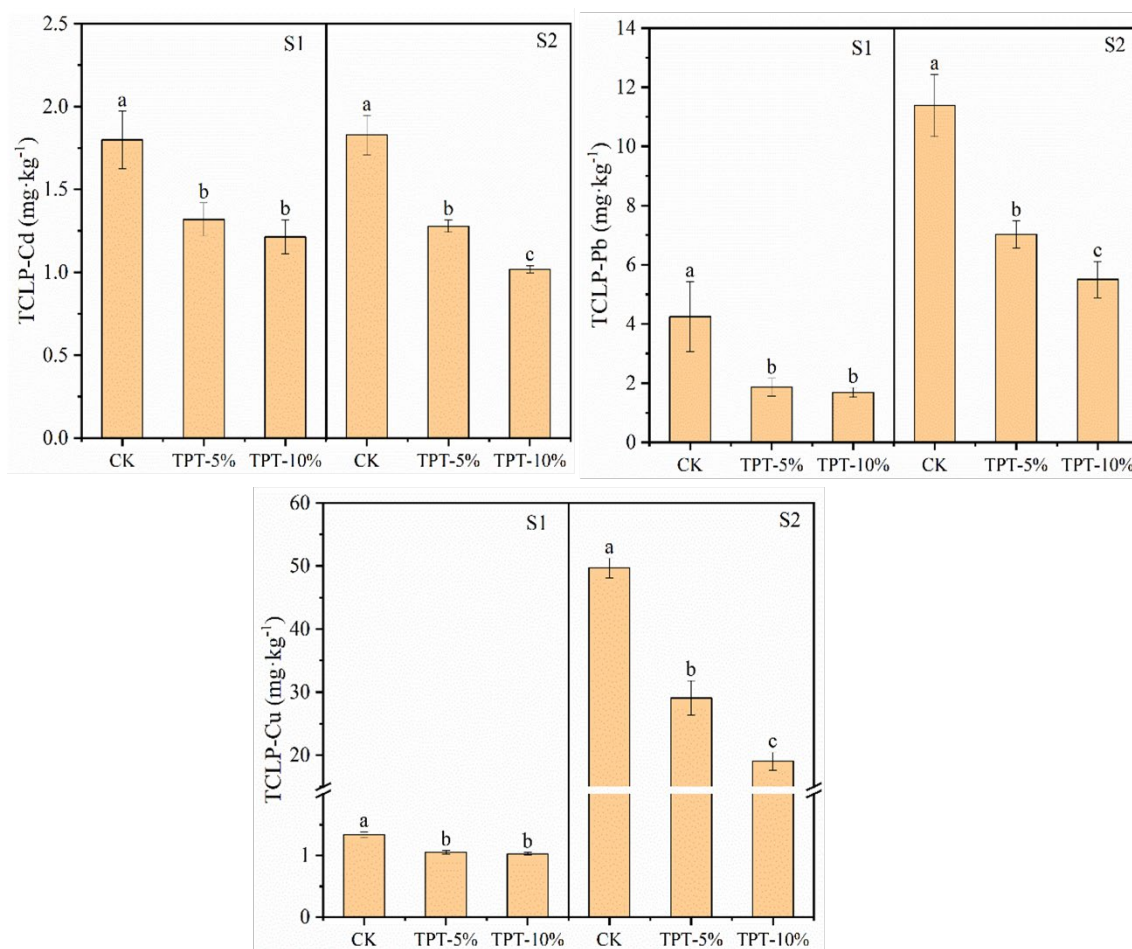


Fig. 6 Concentration of Cd, Pb and Cu in TCLP extraction from TPT treated soils

Different lowercase letters above the column indicate significant difference between treatments at $P < 0.05$.

3.3.3 Effects of amendments on fractions of heavy metals in soils

The BCR sequential extraction procedure was employed to determine the chemical speciation of heavy metals after TPT treatment (Fig. 7). In the control soils, Cd mainly existed in acid soluble and reducible fractions (89.11%-89.31%), while Pb was mainly bound to the reducible and residual forms (91.41%-96.93%). However, the speciation of Cu varied from soils: in soil S1, Cu mainly existed in reducible and residual fraction (89.29%), whereas in soil S2, it was distributed across acid soluble, reducible and

residual forms (89.05%).

TPT application reduced the proportion of acid soluble Cd, Pb and Cu in soil S1 by 7.81%-9.10%, 51.38%-52.17% and 19.64%-21.36%, respectively, while the effect was more pronounced in soil S2, with decreases of 10.67%-14.96%, 48.00%-61.83% and 50.30%-20.93%, respectively, with increasing rates. This difference may be attributed to the stronger pH increase in soil S2, as acid soluble fraction is notably sensitive to pH changes (Xia et al., 2017). The elevated pH promoted precipitation of metals with carbonates, phosphates, and hydroxides, transforming them into more stable forms (Jiang et al., 2012). Notably, TPT had a more significant effect on the acid soluble Pb, following the order Pb>Cu>Cd, consistent with the retention of metals in solution.

Concurrently, the residual fraction of Cd and Pb increased markedly by 30.17%-49.48% and 9.10%-50.94%, respectively, while Cu exhibited a smaller rise of 2.24%-13.32%, indicating a progressive transformation of metals into more stable forms with increasing TPT application rates.

Changes in reducible and oxidizable fractions were more complex. The reducible Cd increased in both tested soils, whereas the reducible Cu increased only in soil S2 but decrease in soil S1. Conversely, reducible Pb showed a consistent decrease after TPT application. Oxidizable fractions increased slightly for all metals, which might be limited by the inorganic nature of TPT and its scarcity of organic ligands, as oxidizable fractions associated with organic matters and sulfide (Zhao et al., 2021). In addition, the oxidizable fraction forms through a slower, specific process, while the reducible

fraction forms via a faster, non-specific process (Zhang et al., 2019), leading to temporary accumulation when acid soluble fraction are deplete under environmental changes.

Among all fractions, the residual form became the dominant transformation sink, particularly at the 10% TPT addition, highlighting the superior ability of TPT to reduce metal mobility. Compared to commonly used alkaline inorganic materials like lime and hydrated lime, which tend to transform metals into reducible forms after application (Guo et al., 2018; He et al., 2019; Inkham et al., 2019), TPT more effectively facilitated the formation of the residual fraction, the most stable form with minimal potential for re-release under environmental influences, thus offering greater long-term immobilization potential.

This immobilization effect can be attributed to several pathways. TPT application significantly increased soil pH to around 8.5-9.0, creating an alkaline environment facilitating the precipitation of metals and enhancing the negative surface charge of soil particles and amendment, improving electrostatic attraction for cationic metals (Ali et al., 2020; Zhang et al., 2020). Beyond pH-mediated effects, TPT provides abundant oxygen functional groups like Si-OH with high affinity for metals, as shown in batch sorption experiment, resulting in heavy metals retention on material (Wang et al., 2018; Zhang et al., 2020). Mineral components within TPT also played a vital role: PO_4^{3-} generated from fluorapatite might react with metals to form low-solubility metal-phosphate precipitates, thereby enhancing the conversion of residual fractions (Dong et al., 2016; Xu et al., 2016). Furthermore, ion exchange might occur between divalent

metal ions and $\text{Ca}^{2+}/\text{Mg}^{2+}$ sites on mineral like MgO , fluorapatite and calcite, further stabilizing metals within the matrix (Sanderson et al., 2015; Wang et al., 2019; Zeng et al., 2017).

Overall, the decrease in acid soluble fraction and corresponding increase in residue fraction following TPT treatment demonstrated its significant efficacy in immobilizing heavy metal by converting labile metals into more stable form, highlighting its potential as a long-term, sustainable amendment for soil remediation.

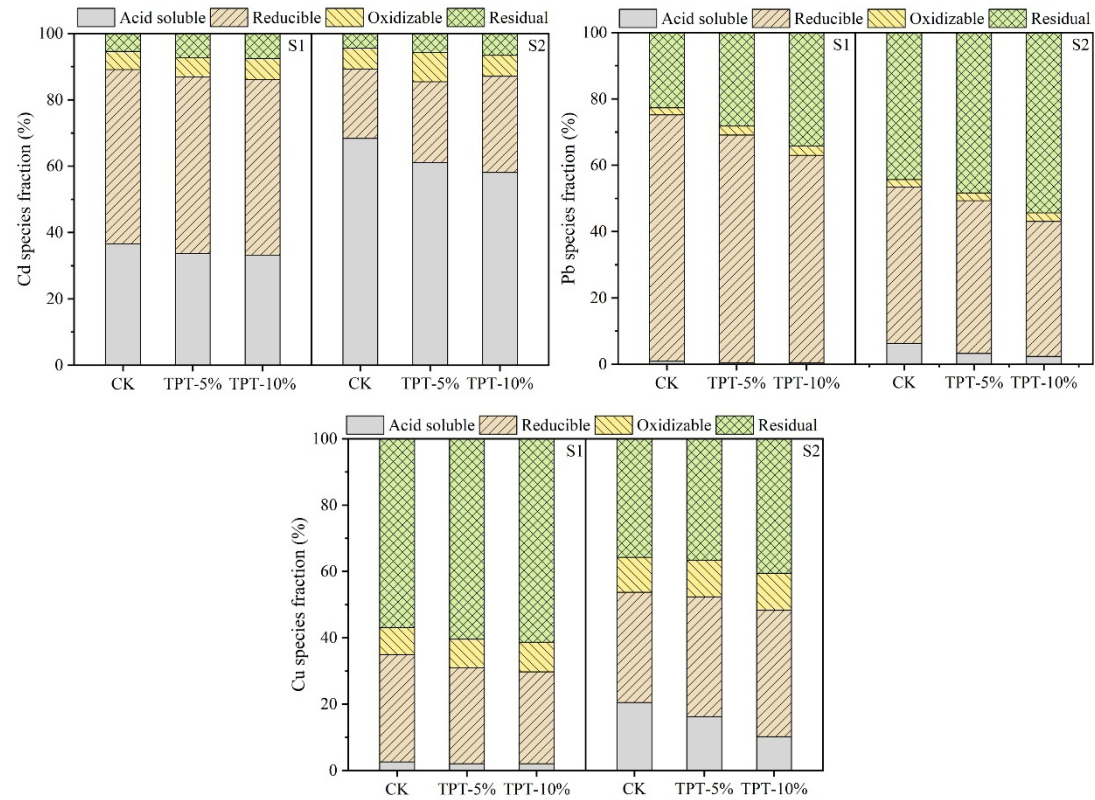


Fig. 7 Influence of TPT on chemical fractions of Cd, Pb and Cu

4 Conclusion

The findings of this study highlight the significant potential of thermally modified phosphate tailings (TPT) as a novel and effective material for heavy metal remediation

in contaminated soils. Through a rapid one-step mass preparation process, thermal modification transformed the dolomite in PT into MgO and CaCO₃, markedly enhancing the adsorption capacity of TPT by 28-fold for Cd²⁺ and Cu²⁺ and 7-fold for Pb²⁺, compared to the non-modified PT, with surface precipitation regarded as the dominant mechanism for heavy metal removal. After applying to soil, TPT reduced the extractable fractions of Cd, Pb, and Cu by 27%-44%, 38%-60%, and 21%-62%, respectively, and transformed acid-soluble metal fractions into more stable residual forms, thereby minimizing the environmental risks associated with heavy metal contamination. Our study pioneered the systematic enhancement of PT via thermal modification, providing a novel contribution to the soil remediation field, offering both a performance breakthrough in soil remediation and a scalable pathway for recycling industrial by-products in line with circular economy principles. These findings pave the way for broader applications of modified phosphate tailings in environmental management and contribute to advancing sustainable remediation technologies. However, this study was conducted under controlled laboratory conditions. Therefore, long-term field experiments should be conducted in the future to verify the effectiveness and stability of TPT under natural environmental conditions, especially under varying moisture levels, temperature fluctuations, microbial activity, and leaching dynamics over extended periods. Such investigations are essential to comprehensively assess not only its applicability and long-term resilience across diverse environmental scenarios, but also its potential impacts on soil physical and chemical properties, ensuring the preservation of soil functionality.

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CRediT authorship contribution statement

Shengning Deng: Investigation, Formal analysis, Writing- original draft. **Yanwei Hou:** Conceptualization, Data curation, Writing - Review & Editing. **Zhao Liu:** Investigation, Writing - Review & Editing. **Youchi Zhang:** Conceptualization, Writing - Review & Editing. **Frederic Coulon:** Writing - Review & Editing. **Yuting Tang:** Writing - Review & Editing. **Chao Cai:** Conceptualization, Supervision, Writing - Review & Editing

Appendix A. Supplementary data

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Supplementary material

Novel Thermal Modification of Phosphate Tailings for Enhanced Heavy Metals
Immobilization in Soil

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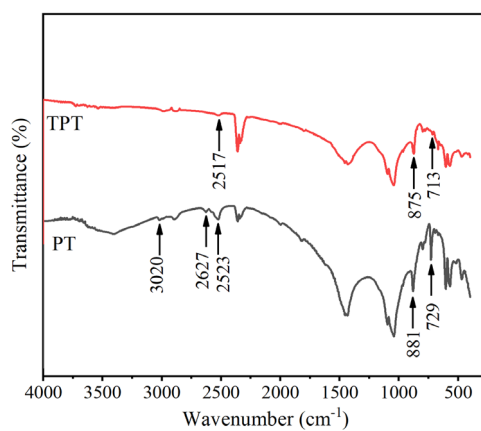
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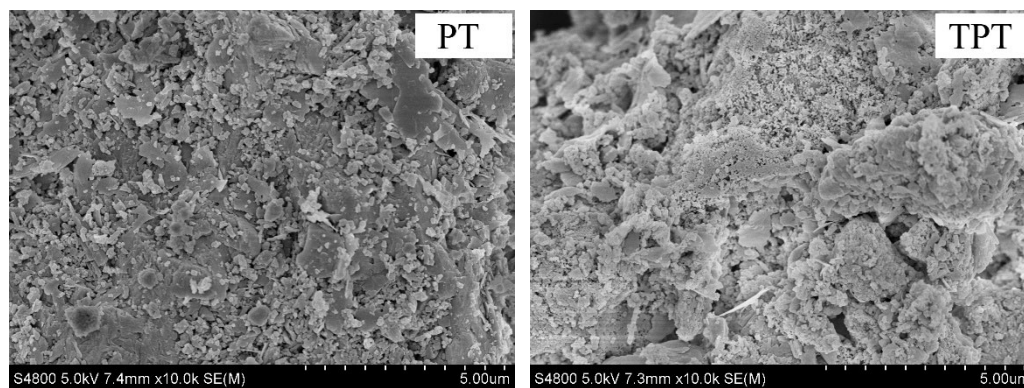


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Fig. S1 FTIR of PT and TPT

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Fig. S2 SEM micrographs of PT and TPT

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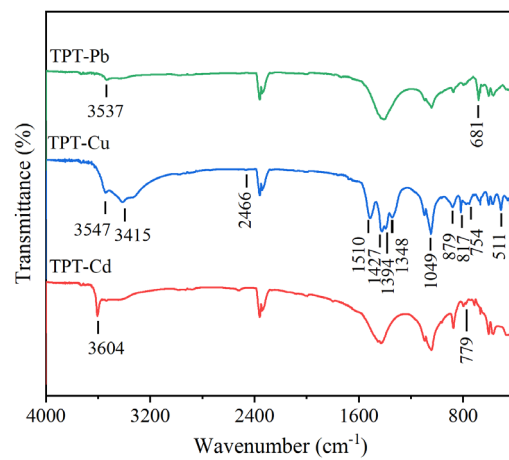


Fig. S3 FTIR of TPT after adsorbed Cd^{2+} , Pb^{2+} and Cu^{2+}

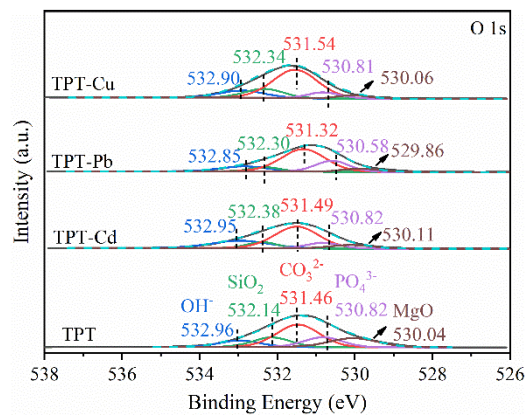
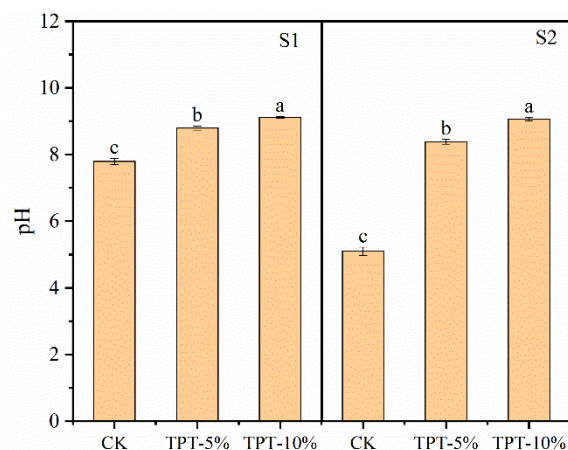


Fig. S4 XPS spectra of O1s in TPT after adsorbed Cd^{2+} , Pb^{2+} and Cu^{2+}



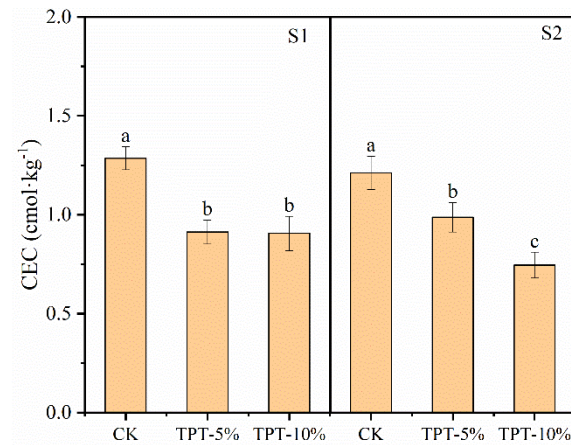
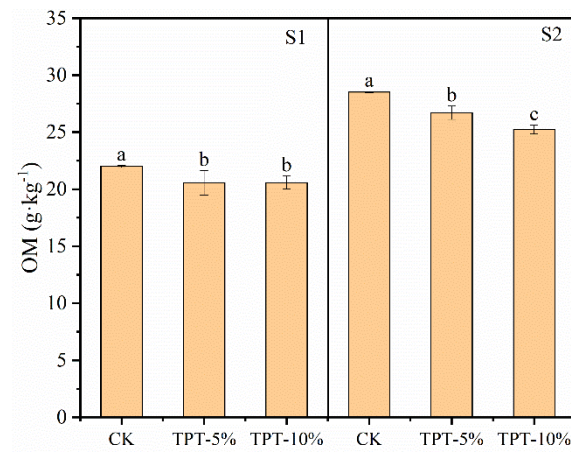


Fig. S5 Effect of TPT on soil pH, CEC and OM content.

Different lower case letters indicate significant difference between treatments at tested soils. ($P < 0.05$).

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Table S1 Properties of experimental soils

Soil	pH	CEC ($\text{cmol}\cdot\text{kg}^{-1}$)	OM ($\text{g}\cdot\text{kg}^{-1}$)	Content of heavy metal ($\text{mg}\cdot\text{kg}^{-1}$)		
				Cd	Pb	Cu
S1	7.55 $\pm$ 0.02	13.69 $\pm$ 0.09	25.91 $\pm$ 0.65	6.29 $\pm$ 0.04	1091.56 $\pm$ 61.09	103.40 $\pm$ 8.93
S2	4.56 $\pm$ 0.01	11.39 $\pm$ 0.01	32.24 $\pm$ 0.98	3.09 $\pm$ 0.06	644.00 $\pm$ 31.34	657.16 $\pm$ 43.22

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Table S2 Physical-chemical properties of PT and TPT

Sample	pH	Chemical composition (%)							
		Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	P ₂ O ₅	SiO ₂
PT	7.19	1.50	43.94	1.05	0.32	9.80	0.14	17.74	10.60
TPT	12.14	1.80	45.46	1.14	0.32	12.34	0.20	18.49	11.52

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Table S3 Adsorption kinetic parameters of Cd²⁺, Pb²⁺ and Cu²⁺ on PT and TPT

Ions	Adsorbents	pseudo-first-order kinetic model			pseudo-second-order kinetic model		
		q _{e1} ($\text{mg}\cdot\text{g}^{-1}$)	k ₁ (h ⁻¹)	R ²	q _{e2} ($\text{mg}\cdot\text{g}^{-1}$)	k ₂ ($\text{g}\cdot\text{mg}\cdot\text{h}^{-1}$)	R ²
Cd ²⁺	PT	3.39	0.2978	0.943	3.68	0.1034	0.981
	TPT	230.51	0.0831	0.918	267.87	0.0004	0.945
Pb ²⁺	PT	68.67	0.0446	0.929	89.10	0.0005	0.938
	TPT	538.51	0.0859	0.852	605.27	0.0002	0.900
Cu ²⁺	PT	3.40	1.6926	0.860	3.56	0.7373	0.966
	TPT	417.80	0.0210	0.995	639.71	0.0000	0.996

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Table S4 Isotherm parameters of Langmuir and Freundlich for the adsorption of Cd^{2+} , Pb^{2+} and Cu^{2+} on PT and TPT

Ions	Adsorbents	Langmuir			Freundlich		
		$Q_{\max}(\text{mg}\cdot\text{g}^{-1})$	$K_L(\text{L}\cdot\text{mg}^{-1})$	R^2	$K_F(\text{mg}\cdot\text{g}^{-1})$	$1/n$	R^2
Cd^{2+}	PT	8.82	0.028	0.605	2.30	0.193	0.961
	TPT	248.27	0.018	0.904	69.58	0.180	0.990
Pb^{2+}	PT	78.88	0.112	0.775	37.55	0.121	0.967
	TPT	531.45	0.006	0.882	60.01	0.296	0.965
Cu^{2+}	PT	15.57	0.005	0.968	0.62	0.464	0.977
	TPT	433.30	0.003	0.988	17.46	0.430	0.939

Table S5 Adsorption capacity of amendments reported in literature

Heavy metal	Adsorbent	Capacity($\text{mg}\cdot\text{g}^{-1}$)	Reference
Cd	DSBS/Absep (sodium dodecylbenzene sulfonate composites acid-base modified sepiolite)	240	(Gao et al., 2022)
	HA-3HPB (Hydroxyapatite tailored hierarchical porous biochar composite)	88	(Wu et al., 2022)
	Nano-scale sugar beet waste	33	(Lashen et al., 2022)
	Nano-scale brick factory waste	10	
	HyFe/Absep(Hydroxy ferric combined acid-base modified sepiolite)	221	(Xie et al., 2020)
	$\text{MgFe}_2\text{O}_4\text{-NH}_2\text{@sRHB}$ (Amine- functionalized MgFe_2O_4 -biochar)	200	(Li et al., 2022)
	ATBS (Amine- and thiol- bifunctionalized mesoporous silica material)	38	(Tang et al., 2022)
	Thermal-activated sepiolite	21	(Zhou et al., 2022)
	Goethite-loaded montmorillonite	44	(Zhao et al., 2023)

	Mn/Al-layered double oxide-loaded biochar	73	(Lin et al., 2023)
	Alkali-modified biomass ash	56	(Cui et al., 2024)
	The thermal adsorption residue	323	(Zhang et al., 2022)
	Core-shell structured nanoscale zero-valent iron@mesoporous hydrated silica	105	(Ma et al., 2022)
	TPT (Thermally modified phosphate tailings)	248	This work
Pb	HA-3HPB (Hydroxyapatite tailored hierarchical porous biochar composite)	110	(Wu et al., 2022)
	MgFe ₂ O ₄ -NH ₂ @sRHB (Amine-functionalized MgFe ₂ O ₄ -biochar)	200	(Li et al., 2022)
	ATBS (Amine- and thiol-bifunctionalized mesoporous silica material)	117	(Tang et al., 2022)
	Alkali-modified biomass ash	255	(Cui et al., 2024)
	Montmorillonite modified by ferrihydrite	2	(Jiang et al., 2023)
	Tourmaline-biochar composites	480	(Liu et al., 2024)
	Core-shell structured nanoscale zero-valent iron@mesoporous hydrated silica	372	(Ma et al., 2022)
	TPT (Thermally modified phosphate tailings)	531	This work
Cu	Nano-scale sugar beet waste	1111	(Lashen et al., 2022)
	Nano-scale brick factory waste	33	
	HAP/C-S-H	138	(Liu et al., 2021)
	MCSB (Magnetic biochar)	372	(Ma et al., 2024)
	Biochar supported layered double hydroxide	92	(Shao et al., 2023)
	Mn/Al-layered double oxide-loaded biochar	66	(Lin et al., 2023)
	Alkali-modified biomass ash	108	(Cui et al., 2024)
	The thermal adsorption residue	340	(Zhang et al., 2022)
	TPT (Thermally modified phosphate tailings)	433	This work

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54 **Table S6** Comparison of various materials for immobilization effects on Cd, Pb and

55 Cu.

Amendments	Heavy Metal	Effect on immobilization efficiency	Reference
Bone Meal	Cd	35% reduction in TCLP-extractable Cd	(Huang et al., 2016)
	Pb	An Increase in TCLP extractable Pb	
	Cu	43% reduction in TCLP-extractable Cu	
Phosphate Rock	Cd	23% reduction in TCLP-extractable Cd	
	Pb	54% reduction in TCLP-extractable Pb	
	Cu	18% reduction in TCLP-extractable Cu	
Oxalic Acid-activated Phosphate Rock	Cd	24% reduction in TCLP-extractable Cd	
	Pb	63% reduction in TCLP-extractable Pb	
	Cu	28% reduction in TCLP-extractable Cu	
Nanoparticle Hydroxyapatite	Cu	28%-63% reduction in TCLP-extractable Cu	(Sun et al., 2018)
Sechura Phosphate Rock	Cd	36% reduction in NH ₄ NO ₃ -extractable Cd	(Seshadri et al., 2017)
	Pb	47% reduction in NH ₄ NO ₃ -extractable Pb	
Christmas Island Phosphate Rock	Cd	5% reduction in NH ₄ NO ₃ -extractable Cd	
	Pb	7% reduction in NH ₄ NO ₃ -extractable Pb	

Lignosulfonate-activated Low-grade Phosphate Rock	Cd	58% reduction in soil available Cd	(Shao et al., 2021)
Humic Acid-activated Low-grade Phosphate Rock	Cd	29% reduction in soil available Cd	
Attapulgite-hydrochar composite	Cd	32% reduction in TCLP extractable Cd	(Xia et al., 2021)
Layered double hydroxides prepared from dolomite	Cd	20% reduction in TCLP extractable Cd	(Zhang and Liu, 2022)
Phosphate solubilizing fungi associated with tricalcium phosphate	Pb	43% reduction in TCLP extractable Pb	(Hao et al., 2022)
Thermally Modified Phosphate Tailing	Cd	27%-44% reduction in TCLP-extractable Cd	This study
	Pb	38%-60% reduction in TCLP-extractable Pb	
	Cu	21%-62% reduction in TCLP-extractable Cu	

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