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# RAPID DETERMINATION OF THE IMMOBILIZATION CONDITIONS FOR LEAD AND CADMIUM IN SOIL USING 2, 4, 6-TRIMERCAPTOTRIAZINE, TRISODIUM SALT, NONAHYDRATE

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**Abstract.** Chemical immobilization is widely used for remediation of heavy metal contaminated soils. The present study proposed a method for the immobilization of lead (Pb) and cadmium (Cd) in soil using 2, 4, 6-trimercaptotriazine, trisodium salt, nonahydrate (TMT). Simulation tests were performed in an aqueous solution to rapidly screen the operational conditions. The effects of TMT dosage, reaction pH, and the coordination ions ( $Al^{3+}$ ,  $Fe^{3+}$ ) on immobilization, and the thermodynamics for the TMT-DTPA-Zn-Pb-H<sub>2</sub>O system, were investigated. The results showed that the immobilization efficiencies of Pb and Cd were removed effectively via the addition of TMT and  $Fe^{3+}$  in the solution containing DTPA. Pb and Cd concentrations decreased from 50 mg/L to <3.9 mg/L and 1.4 mg/L, with a  $Fe^{3+}$ /DTPA molar ratio of 0.8 to 2.1, and a TMT dosage of 1.0 mol/mol (Pb and Cd). The screened results in the aqueous solution were used to immobilize Pb and Cd in soil. The extractable concentrations of Pb and Cd in the immobilized soil decreased to 19.6 mg/kg and 1.7 mg/kg, respectively, with a TMT dosage of 2.2 mol/mol (Pb and Cd), and a  $Fe^{3+}$ /DTPA molar ratio of 3.6. The bioavailability of Pb and Cd met the environmental quality standard for drylands in China (GB 15618-1995). The results demonstrated that remediation conditions could be rapidly screened in an aqueous solution rather than soil. The method using TMT and ferric sulfate was potentially effective in immobilizing Pb and Cd.

Keywords: chemical immobilization, screen, stability, simultaneous, coordination, thermodynamics.

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#### Introduction

Large amounts of heavy metals contained within wastewater and waste residual materials permeate into soil during mining and smelting processes (Pourret et al., 2016; Min, Wang, Chai, Yang, & Liao, 2017), causing serious health risks for humans and ecological risks for the environment (Yang et al., 2016; Li, Ma, van der Kuijp, Yuan, & Huang, 2014; Khan, Cao, Zheng, Huang, & Zhu, 2008). Thus, it is necessary to immobilize the metals such as lead (Pb) and cadmium (Cd) in soil.

Chemical immobilization has been widely studied as a potentially reliable and cost-effective remediation technique, and various chemical amendments have been screened (Ashrafi, Mohamad, Yusoff, & Hamid, 2014; Chiochetta et al., 2016; Lahori et al., 2017; Radziemska, Gusiatin, & Bilgin, 2017; Wu, Zhao, Liu, Fan, & Li, 2013; Yuan, Chai, Z. Yang, & W. Yang, 2017). Heavy metals are immobilized by solid-liquid reactions or solid-solid reactions,

including adsorption, precipitation, co-precipitation, and chelation (Basta & McGowen, 2004; Bolan et al., 2014; Zhang et al., 2014). A lengthy contact time is required for these reactions, due to the slow reaction rate between the amendments and soil. Therefore, the chemical immobilization process takes several months to screen the amendments and operational conditions.

2,4,6-trimercaptotriazine, trisodium salt, nonahydrate (TMT) is an organic sulfur compound, which can combine with heavy metals by chelate precipitation. TMT has been widely used in the treatment of wastewater containing heavy metals (Henke, Robertson, Krepps, & Atwood, 2000; Matlock, Henke, Atwood, Robertson, 2001; Blais, Djedidi, Cheikh, Tyagi, & Mercier, 2008). However, studies on the application of TMT as amendments for soil remediation have received little attention.

The extracting agents used for the bioavailability analysis of heavy metals generally involve DTPA (diethylenetriaminepentaacetic acid) and EDTA. The mobilized heavy

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metals in soils can be leached in the presence of extracting agents (Bolan et al., 2014). Therefore, immobilization efficiency is determined by the equilibrium between the amendments, the heavy metals, and the extracting agents.

In this paper, we used TMT as a chemical amendment to precipitate with Pb and Cd. We conducted a series of simulation immobilization tests in an aqueous solution, instead of in soil, to screen the operational conditions quicker. The effects of TMT dosage, reaction pH, and the coordination ions (Al<sup>3+</sup>, Fe<sup>3+</sup>) on immobilization were investigated. The thermodynamic equilibrium for the TMT-DTPA-Zn-Pb-H<sub>2</sub>O system was also studied. Then we conducted the immobilization tests in contaminated soil to validate the applicability of the results obtained in the aqueous solution.

Table 1. Thermodynamic Data for the TMT-DTPA-Pb-Cd-H<sub>2</sub>O System (25 °C)

Reaction numbers	Equilibrium reactions	log <i>K</i> (Sommers & Lindsay, 1979; Bailey et al., 2001)
(1)	$DTPA^{5-}+H^+ \rightleftharpoons HDTPA^{4-}$	10.45
(2)	$DTPA^{5-}+2H^+ \rightleftharpoons H_2DTPA^{3-}$	18.98
(3)	$DTPA^{5-}+3H^+ \rightleftharpoons H_3DTPA^{2-}$	23.26
(4)	$DTPA^{5-}+4H^+ \rightleftharpoons H_4DTPA^-$	25.91
(5)	$DTPA^{5-}+5H^+ \rightleftharpoons H_5DTPA$	27.73
(6)	$DTPA^{5-}+Cd^{2+} \rightleftharpoons CdDTPA^{3-}$	19.00
(7)	$DTPA^{5-} + Cd^{2+} + H^+ \rightleftharpoons$ $CdHDTPA^{2-}$	23.17
(8)	$DTPA^{5-} + 2Cd^{2+} \rightleftharpoons Cd_2DTPA^{-}$	21.30
(9)	$DTPA^{5-} + Pb^{2+} \rightleftharpoons PbDTPA^{3-}$	18.66
(10)	$DTPA^{5-} + Pb^{2+} + H^+ \rightleftharpoons PbHDTPA^{2-}$	23.18
(11)	$DTPA^{5-} + 2Pb^{2+} \rightleftharpoons Pb_2DTPA^{-}$	22.07
(12)	$DTPA^{5-} + Fe^{3+} \rightleftharpoons FeDTPA^{2-}$	27.30
(13)	$DTPA^{5-} + Fe^{3+} + H^+ \rightleftharpoons$ $FeHDTPA^-$	30.86
(14)	DTPA <sup>5-</sup> + Fe <sup>3+</sup> + H <sub>2</sub> O $\rightleftharpoons$ FeOHDTPA <sup>3-</sup> + H <sup>+</sup>	17.42
(15)	$DTPA^{5-} + Al^{3+} \rightleftharpoons AlDTPA^{2-}$	18.70
(16)	$DTPA^{5-} + Al^{3+} + H^+ \rightleftharpoons$ $AlHDTPA^-$	23.00
(17)	$DTPA^{5-} + Al^{3+} + H_2O \rightleftharpoons$ $AlOHDTPA^{3-} + H^+$	11.30
(18)	$TMT^{3-} + H^+ \rightleftharpoons HTMT^{2-}$	11.38
(19)	$HTMT^{2-} + H^+ \rightleftharpoons H_2TMT^-$	8.36
(20)	$H_2TMT^{2-} + H^+ \rightleftharpoons H_3TMT$	5.71

#### 1. Materials and methods

# 1.1. Simulating immobilization in an aqueous solution

The synthetic wastewater was prepared with lead nitrate and cadmium nitrate (analytical grade). The total concentrations of Pb and Cd in the synthetic wastewater were both 50 mg/L. The TMT solution (mass concentration 15%) was used as the immobilization agent. The synthetic wastewater (50 mL), DTPA, and TMT were mixed in a 100 mL plastic bottle and shaken for 2h at 25 °C. The reaction pH was adjusted by adding NaOH or HCl. The total concentrations of Pb and Cd were analyzed by ICP-AES (HJ804-2016).

To determine the influence of TMT dosage, the experiment was conducted at a DTPA to Me (Zn and Pb) molar ratio of 0.0–1.0, and a reaction pH of 6.0±0.2. To determine the influence of reaction pH, the experiment was conducted at a DTPA to Me molar ratio of 1.0, and a TMT dosage of 1.0 mol/mol (Me). To determine the influence of coordination ions, the experiment was conducted at a DTPA to Me molar ratio of 1.0, a reaction pH of 6.0±0.2, and a TMT dosage of 1.0 mol/mol (Me). Aluminium chloride and ferric sulfate was added to supply the coordination ions (Al $^{3+}$ ,  $^{Fe3+}$ ).

## 1.2. Thermodynamic modeling

The equilibrium relations between the possible species for the TMT–DTPA–Pb–Cd– $H_2O$  system are listed in Table 1, where log K is the logarithm of the equilibrium constant (K).

Equations (1)–(20) correlated the thermodynamic equilibrium constants to the molar concentrations of different complexes according to reactions (1)–(20).

$$c(DTPA^{5-}) \times c(H^+) \times 10^{10.45} = c(HDTPA^{4-});$$
 (1)

$$c(DTPA^{5-}) \times c(H^+)^2 \times 10^{18.98} = c(H_2DTPA^{3-});$$
 (2)

$$c(DTPA^{5-}) \times c(H^+)^3 \times 10^{23.26} = c(H_3DTPA^{2-});$$
 (3)

$$c(DTPA^{5-}) \times c(H^+)^4 \times 10^{25.91} = c(H_4DTPA^-);$$
 (4)

$$c(DTPA^{5-}) \times c(H^+)^5 \times 10^{27.73} = c(H_5DTPA);$$
 (5)

$$c(DTPA^{5-}) \times c(Cd^{2+}) \times 10^{19.00} = c(CdDTPA^{3-});$$
 (6)

$$c(DTPA^{5-}) \times c(Cd^{2+}) \times c(H^+) \times 10^{23.17} = c(CdHDTPA^{2-});$$
(7)

$$c(DTPA^{5-}) \times c(Cd^{2+})^2 \times 10^{21.30} = c(Cd_2DTPA^{-});$$
 (8)

$$c(DTPA^{5-}) \times c(Pb^{2+}) \times 10^{18.66} = c(PbDTPA^{3-});$$
 (9)

$$c(DTPA^{5-}) \times c(Pb^{2+}) \times c(H^+) \times 10^{23.18} = c(PbHDTPA^{2-});$$
(10)

$$c(DTPA^{5-}) \times c(Pb^{2+})^2 \times 10^{22.07} = c(Pb_2DTPA^-);$$
 (11)

$$c(DTPA^{5-}) \times c(Fe^{3+}) \times 10^{27.30} = c(FeDTPA^{2-});$$
 (12)

$$c(\text{DTPA}^{5-}) \times c(\text{Fe}^{3+}) \times c(\text{H}^+) \times 10^{30.86} = c(\text{FeHDTPA}^-);$$
(13)

$$c(\text{DTPA}^{5-}) \times c(\text{Fe}^{3+}) \times 10^{17.42} = c(\text{FeOHDTPA}^{2-}) \times c(\text{H}^+);$$
(14)

$$c(DTPA^{5-}) \times c(Al^{3+}) \times 10^{18.70} = c(AlDTPA^{2-});$$
 (15)

$$c(\text{DTPA}^{5-}) \times c(\text{Al}^{3+}) \times c(\text{H}^+) \times 10^{23.00} = c(\text{AlHDTPA}^-);$$
(16)

$$c(DTPA^{5-}) \times c(Al^{3+}) \times 10^{11.30} = c(AlOHDTPA^{2-}) \times c(H^+);$$
(17)

$$c(TMT^{3-}) \times c(H^+) \times 10^{11.38} = c(HTMT^{2-});$$
 (18)

$$c(HTMT^{2-}) \times c(H^+) \times 10^{8.36} = c(H_2TMT^-);$$
 (19)

$$c(H_2TMT^-) \times c(H^+) \times 10^{5.71} = c(H_3TMT)$$
 (20)

The total concentration of DTPA, Pb, Zn, and TMT, denoting  $c_{\text{T,DTPA}}$ ,  $c_{\text{T,Pb}}$ ,  $c_{\text{T,Cd}}$  and  $c_{\text{T,TMT}}$ , was the sum of the concentrations of their complexes and free ions, as illustrated in Equations (21)–(24).

$$\begin{split} c_{\text{T,DTPA}} &= c(\text{DTPA}^{5-}) + c(\text{HDTPA}^{4-}) + c(\text{H}_2\text{DTPA}^{3-}) + \\ c(\text{H}_3\text{DTPA}^{2-}) + c(\text{H}_4\text{DTPA}^-) + c(\text{H}_5\text{DTPA}) + \\ c(\text{CdDTPA}^{3-}) + c[\text{CdHDTPA}^{2-}] + c[\text{Cd}_2\text{DTPA}^-] + \\ c(\text{PbDTPA}^{3-}) + c[\text{PbHDTPA2}] + c[\text{Pb}_2\text{DTPA}^-] + \\ c(\text{FeDTPA}^{2-}) + c(\text{FeHDTPA}^-) + c(\text{FeOHDTPA}^{3-}) + \\ c(\text{AlDTPA}^{2-}) + c(\text{AlHDTPA}^-) + c(\text{AlOHDTPA}^{3-}); \end{split} \tag{21}$$

$$c_{\mathrm{T,Pb}} = c(\mathrm{Pb^{2+}}) + c(\mathrm{PbDTPA^{3-}}) + c[\mathrm{PbHDTPA^{2-}}] + 2c[\mathrm{Pb_2DTPA^{-}}]; \tag{22}$$

$$\begin{split} c_{T,\mathrm{Cd}} &= c(\mathrm{Cd^{2+}}) + c(\mathrm{CdDTPA^{3-}}) + c[\mathrm{CdHDTPA^{2-}}] + \\ 2c[\mathrm{Cd_2DTPA^{-}}]; \end{split} \tag{23}$$

$$c_{T,TMT} = c(TMT_{3-}) + c(HTMT_{2-}) + c(H_2TMT^-) + c(H_3TMT).$$
 (24)

The distribution of TMT<sup>3-</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup>, denoting  $\alpha$ (TMT<sup>3-</sup>),  $\alpha$ (Pb<sup>2+</sup>), and  $\alpha$ (Zn<sup>2+</sup>), was defined by Equations (25)–(27).

$$\alpha(\text{TMT}^{3-}) = \frac{c(\text{TMT}^{3-})}{c_{\text{T.TMT}}};$$
(25)

$$\alpha(Pb^{2+}) = \frac{c(Pb^{2+})}{c_{T,Pb}}; \tag{26}$$

$$\alpha(\mathrm{Cd}^{2+}) = \frac{c(\mathrm{Cd}^{2+})}{c_{\mathrm{T,Cd}}}.$$
 (27)

Distribution of the TMT complexes in solution was determined by Equations (18)–(20) and Equations (24)–(25).

Distribution of  $Pb^{2+}$  and  $Cd^{2+}$  in solution was determined by Equations (1)–(17), Equations (21)–(23), and Equations (26)–(27), according to the following assumptions:

(a) No coordination ion exists,  $c_{T,DTPA} = c(Pb^{2+}) = c(Cd^{2+}) = 1 \text{mol/L};$ 

- (b) Coordination ion of Al<sup>3+</sup>,  $c_{T,DTPA} = c(Pb^{2+}) = c(Cd^{2+}) = c(Al^{3+}) = 1 \text{mol/L};$
- (c) Coordination ion of Fe<sup>3+</sup>,  $c_{T,DTPA} = c(Pb^{2+}) = c(Cd^{2+}) = c(Fe^{3+}) = 1 \text{mol/L}.$

#### 1.3. Immobilization of the contaminated soil

The soil was collected from a site contaminated by Pb milling and smelting operations in Chenzhou City, Hunan Province, China (113°17′17.76″E–13°17′36.07″E, 25°45′39.29″N-25°46′1.13″N). The soil samples were collected from the surface layer (0–15 cm depth), and air-dried at room temperature, and then sieved through 20 mesh (0.9 mm). The sieved soils were digested with aqua regia for total concentration analysis of Pb and Cd. The bioavailability of Pb and Cd in soil was evaluated using the extracting agent DTPA (w/w of 0.01:1 DTPAsoil). Pb and Cd concentrations were analyzed by ICPAES (HJ804-2016). Soil pH was measured by a pH meter (FE20K) with a glass electrode in water (v/w of 1:2.5 H<sub>2</sub>O-soil). Table 2 shows the chemical properties of the initial soils.

Table 2. Chemical properties of the initial soils

Properties	Value±SD	
Soil pH	7.9±0.1	
Total concentration of Pb (mg·kg <sup>-1</sup> )	1372.0±8.7	
Total concentration of Cd (mg·kg <sup>-1</sup> )	25.2±0.3	
DTPA-extractable concentration of Pb (mg·kg <sup>-1</sup> )	547.1±5.4	
DTPA-extractable concentration of Cd (mg·kg <sup>-1</sup> )	17.4±0.1	
Values are means $\pm$ SEM ( $n = 3$ ) per group. SD: standard deviation.		

The sieved 20-mesh soils were used for immobilization treatment. The TMT solution (mass concentration 15%) and the ferric sulfate solid were used as the remediation agents. Soil samples (200 g) were added to a 250 mL plastic bottle and mixed with the remediation agent at room temperature.

The experiment was carried out at a ferric sulfate dosage of 35.7g·kg<sup>-1</sup>, a reaction time of 60 d, a percentage of the field capacity of 70%, and a soil pH of 7.6±0.2. Soil pH was adjusted by adding HCl or NaOH. The immobilized soil was air-dried at room temperature, and sieved through 20 mesh (0.9 mm). Then the bioavailability of Pb and Cd was measured.

# 2. Results and discussion

# 2.1. Simulating immobilization in an aqueous solution

# 2.1.1. Influence of the TMT dosage

Figure 1 shows the influence of TMT dosage on Pb and Cd concentrations in an aqueous solution. Pb and Cd

concentrations decreased with increasing TMT dosage. In the absence of DTPA, Pb and Cd concentrations decreased to levels <6.4 mg/L and 4.7 mg/L, respectively, with a TMT dosage between 0.48-1.44 mol/mol Me (Zn and Pb). The TMT was effective for the removal of Pb and Cd in an aqueous solution. Pb and Cd concentrations decreased to levels <34.6 mg/L and 28.6 mg/L when the DTPA to Me molar ratio was 1.0. This indicated that the mobilized Pb and Cd in the aqueous solution were leached in the presence of DTPA.

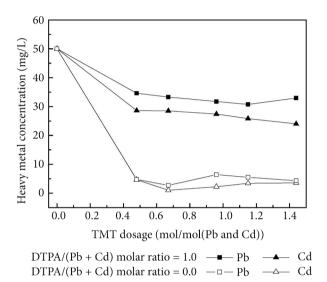


Figure 1. Influence of TMT dosage on Pb and Cd concentrations in an aqueous solution

# 2.1.2. Influence of the reaction pH

Figure 2 shows the influence of reaction pH on Pb and Cd concentrations in an aqueous solution. Pb and Cd concentrations decreased with increasing reaction pH. Pb and Cd concentrations decreased to 22.3 mg/L and 27.1 mg/L, respectively, at pH 9.0. This was caused by the distribution of the TMT complexes in solution. The possible

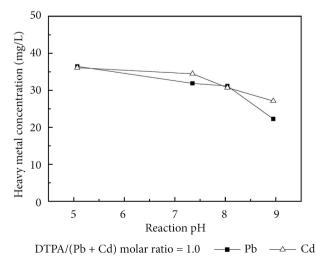


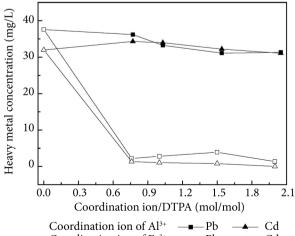
Figure 2. Influence of reaction pH on Pb and Cd concentrations in an aqueous solution

TMT complexes included H<sub>3</sub>TMT, H<sub>2</sub>TMT<sup>-</sup>, HTMT<sup>2-</sup>, and TMT<sup>3-</sup>. The last three complexes could combine with heavy metals (Dongmei, Yunbai, Ping, & Zhigang, 2006). As shown in Figure S1 (See supplemental material), H<sub>3</sub>T-MT was the dominating complex at pH values <4.0. The distribution ratio of H<sub>2</sub>TMT<sup>-</sup>, HTMT<sup>2-</sup> and TMT<sup>3-</sup>, increased from 1.91-99.99% at a pH range of 4.0-9.0. Therefore, Pb-TMT and Cd-TMT precipitates were more stable at higher pH, which was consistent with previous results (Matlock et al., 2001).

# 2.1.3. Influence of the coordination ions

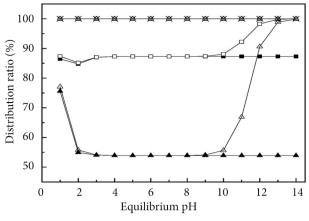
Figure 3 shows the influence of coordination ions on Pb and Cd concentrations in an aqueous solution. Figure 4 shows the distribution of Pb2+ and Cd2+ in solution as a function of pH. The concentrations of Pb and Cd remained stable with increasing Al<sup>3+</sup> dosage in Figure 3. In contrast, Pb and Cd concentrations decreased to <3.9 mg/L and 1.4 mg/L, respectively, with a Fe<sup>3+</sup>/DTPA molar ratio of 0.8 to 2.1. The immobilization efficiencies of Pb and Cd were determined by the equilibrium competition among TMT, Pb, Cd, and DTPA. The free ions of Pb<sup>2+</sup> and Cd<sup>2+</sup> favored the formation of Pb-TMT and Cd-TMT precipitates, while the Pb-DTPA and Cd-DTPA complexes had the opposite effect. As shown in Figure 4, 46.1% of Pb2+ transformed into Pb-DTPA complexes, and 12.7% of Cd<sup>2+</sup> transformed into Cd-DTPA complexes at a pH range of 2.0-9.0 for the DTPA-Zn-Pb-H<sub>2</sub>O system. Therefore, TMT-Pb and TMT-Cd precipitates became unstable, and Pb and Cd concentrations increased in the presence of DTPA. Furthermore, the addition of Al3+ had little influence on the distribution ratio at a pH range of 2.0-9.0, while the distributions of Pb2+ and Cd2+ increased close to 100% in the presence of Fe<sup>3+</sup>. This indicated that the precipitates of Pb-TMT and Cd-TMT were stable via the addition of Fe<sup>3+</sup>, which decreased Pb and Cd concentrations.

The simulation tests for the TMT-DTPA-Zn-Pb-H<sub>2</sub>O system showed that TMT was effective for removal of Pb and Cd. The Pb-TMT and Cd-TMT precipitates were



Coordination ion of Fe<sup>3+</sup>  $-\Box - Pb$ 

Figure 3. Influence of coordination ions on Pb and Cd concentrations in an aqueous solution



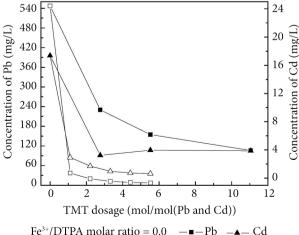
$$\begin{split} c_{_{\text{T,DTPA}}} &= c(\text{Pb}^{2+}) = c(\text{Cd}^{2+}) = 1 \text{ mol/L} \\ c_{_{\text{T,DTPA}}} &= c(\text{Pb}^{2+}) = c(\text{Cd}^{2+}) = c(\text{Al}^{3+}) = 1 \text{ mol/L} \\ c_{_{\text{T,DTPA}}} &= c(\text{Pb}^{2+}) = c(\text{Cd}^{2+}) = c(\text{Fe}^{3+}) = 1 \text{ mol/L} \\ \end{split} \\ - \bigcirc - \alpha(\text{Pb}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ - \bigcirc - \alpha(\text{Cd}^{2+}) - \triangle - \alpha(\text{Cd}^{2+}) \\ -$$

Figure 4. Distribution of  $Pb^{2+}$  and  $Cd^{2+}$  in solution as a function of pH

more stable when Fe<sup>3+</sup> was added in the solution containing DTPA. The operational conditions were determined rapidly by the solution tests and thermodynamic modeling, which were used to guide the immobilization of heavy metals in contaminated soils.

#### 2.2. Immobilization of the contaminated soil

Figure 5 shows the bioavailability of Pb and Cd in the immobilized soils. The extractable concentrations of Pb and Cd were <19.6 mg/kg and 1.7 mg/kg, respectively, with a TMT dosage of 2.2 mol/mol (Pb and Cd), and a Fe<sup>3+</sup>/DTPA molar ratio of 3.6. The extractable concentrations of Pb and Cd decreased markedly via the addition of Fe<sup>3+</sup>, which was consistent with the results obtained in the aqueous solution (Figure 3). Moreover, the extractable concentrations of Pb and Cd met the environmental quality standard for drylands in China (GB 15618-1995, State Environmental Protection Administration of China



Fe<sup>3+</sup>/DTPA molar ratio = 0.0  $-\blacksquare$  - Pb  $-\blacktriangle$  - Cd Fe<sup>3+</sup>/DTPA molar ratio = 3.6  $-\Box$  - Pb  $-\blacktriangle$  - Cd

Figure 5. The bioavailability of Pb and Cd in immobilized soils

(1995)). As shown in Table S1 (See supplemental material), the approximate cost including TMT,  $Fe_2(SO_4)_3$ , and  $Ca(OH)_2$  was \$80 US/t of soil, which was relatively inexpensive compared to other traditional amendments (Guo, Zhou, & Ma, 2006; Rampley & Ogden, 1998). These results demonstrated that the method using TMT and ferric sulfate was effective and financially viable in immobilizing Pb and Cd in contaminated soils.

#### Conclusions

TMT is used as the chemical amendments for immobilization of Pb and Cd in soil. To screen the operational conditions rapidly, the simulating tests in an aqueous solution and the thermodynamics for the TMT-DTPA-Zn-Pb-H<sub>2</sub>O system were investigated. The results show that Pb and Cd can be removed effectively via the addition of TMT and Fe<sup>3+</sup> in the solution containing DTPA. Pb and Cd concentrations decrease to <3.9 mg/L and 1.4 mg/L, respectively, with a Fe<sup>3+</sup>/DTPA molar ratio of 0.8 to 2.1, and a TMT dosage of 1.0 mol/mol (Pb and Cd).

The contaminated soil was treated at a TMT dosage of 2.2 mol/mol (Pb and Cd), and a Fe<sup>3+</sup>/DTPA molar ratio of 3.6. The extractable concentrations of Pb and Cd decrease to 19.6 mg/kg and 1.7 mg/kg, respectively, which meet the environmental quality standard for drylands in China (GB 15618-1995). The method using TMT and ferric sulfate is effective for immobilization of Pb and Cd in soil. The operational conditions screened in the aqueous solution can be used to guide the immobilization of contaminated soil.

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