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Complete stabilization of severely As-contaminated soil by a simple H_2O_2 pre-oxidation method combined with non-toxic TMT-15 and $FeCl_3·6H_2O$

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Abstract: The stabilization of severely As-polluted soil has been a challenge, especially for the extremely toxic As(III) contaminants. In this study, soil with a high As concentration (26084 mg/kg) was availably stabilized by a H_2O_2 pre-oxidation assisted TMT-15 ($Na_3S_3C_3N_3$ solution with a mass fraction of 15%) and $FeCl_3·6H_2O$ stabilization method. The results showed that the combination of the two stabilizers (i.e., TMT-15 and $FeCl_3·6H_2O$) presented a better stabilization behavior than either stabilizer used individually. The use of the H_2O_2 pre-oxidation assisted TMT-15 and $FeCl_3·6H_2O$ stabilization approach not only converted the As(III) to As(V) but also reduced the toxic leaching concentration of As to 1.61 mg/L, which is a safe level, when the additions of TMT-15 and $FeCl_3·6H_2O$ were 2 mL and 0.20 g, respectively. Thus, using only a simple H_2O_2 pre-oxidation to combine clean stabilization with non-toxic stabilizers TMT-15 and $FeCl_3·6H_2O$ could render the severely As-contaminated soil safe for disposal in a landfill.

Keywords: severely As-contaminated soil; non-toxic stabilizers; combining stabilization; pre-oxidation

1. Introduction

Arsenic (As) is a highly biotoxic and common metalloid element and it is specified as one of the top three priority substances listed by the Agency for Toxic Substances and Disease Registry (ATSDR) [1–3]. The biotoxicity of As compounds does not depend on the total amount of As but rather on its chemical species. Among As compounds, the toxicity of organic As compounds is lower than that of inorganic As ones, and As(III) compounds are more toxic than As(V) ones [4–5]. The International Agency for Research on Cancer identified As as a first-class carcinogen and found that human long-term exposure to environments, water or food containing inorganic As could significantly increase the incidence of skin and lung cancer [6–7].

Soil containing As at concentrations less than 50 mg/kg is generally considered safe for agricultural use; Unfortunately, with the development of the metallurgy industry and agriculture, the As content in some soils has become hundreds of times higher than recommended. The major contributors to this increase in As are nonferrous metallurgy, the mining industry, agricultural pesticides, and fertilizers [8–10]. Therefore, the remediation of As-contaminated soil, especially soils with high concentrations, plays an important role in protecting human health and the environment.

Currently, methods for the remediation of As-contaminated soils mainly include soil replacement, solidification/stabilization, phytoremediation, electrokinetic remediation, and soil washing [8,11]. Thus far, chemical stabilization has shown strong applicability, and it does little harm to the environment. Furthermore, it is widely used to reduce the mobility and bioavailability of As.

Fe(II) and Fe(III) salts are excellent stabilizers for As-contaminated water and soil. Li *et al*. [12] treated the red mud generated during alumina production with CO_2 and waste acid and found that adding $FeSO_4$ could reduce the As concentration in the red mud liquid phase from 6.1 to less than 0.05 mg/L. Xenidis *et al*. [13] investigated Pb- and

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As-contaminated soils and found that phosphate could remarkably immobilize Pb but enhance the phytoavailability of As; however, they also found that adding $FeSO_4$ could effectively retain the phytoavailability of As. Seidel *et al*. [14] reported that $FeSO_4$ could immobilize As-bearing tailings derived from a tin and tungsten mill tailings pond and reduce the concentration of water-extractable total As from 339 to less than 10 μg/L. Lin *et al*. [10] used $FeCl_2$-stabilized mine tailings and found that 96.22% of the acid-soluble As could be removed at pH = 7 when the Fe: As molar ratio was 1.0.

Although coprecipitation and adsorption between As and the hydroxide of Fe(II)/Fe(III) formed by hydrolysis of iron salts can enhance the stabilization, only Fe(III) salt could react with As compounds to generate crystalline $FeAsO_4{\cdot}2H_2O$, which is an important stable and safe material. Kim *et al*. [15] used $Fe_2(SO_4)_3$ to immobilize As-bearing tailings, decreasing the active As from 2090 to 428 mg/kg for Myoungbong tailings and reducing the mobile As from 1320 to 395 mg/kg for Daduck tailings. Lin *et al*. [10] used $FeCl_3$ to treat tailings and reduced the acid-soluble As by 93.42% and 96.22% at pH = 4 and pH = 7, respectively. Thus far, stabilization studies of Fe(III) salts have mostly involved the treatment of mine tailings; few investigators have focused on the immobilization of As-contaminated soil, especially those containing high levels of As.

For As-contaminated soils, inorganic iron salts and iron-containing minerals are the most important stabilizers that have been widely used, and some organic stabilizers are being implemented.

TMT ($C_3N_3S_3^{3-}$) has been used as an environmentally friendly stabilizer to treat industrial wastewater that contained heavy metals such as Cu^{2+}, Hg^{2+}, and Pb^{2+} [16]. Moreover, previous research has reported that heavy-metal ions (e.g., Ag^+, Hg^+, Zn^{2+}, Pb^{2+}, Cd^{2+}, and Hg^{2+}) in sewage can be transformed into an insoluble and highly stable chelate by reaction with Na_3TMT [17–18]. Therefore, the possibility of using Na_3TMT as a stabilizer to immobilize As-contaminated soil, especially soil with high levels of As, needs further exploration.

Among the stabilizers, hydrolysis of Fe(III) causes the acidification of soil during the stabilization process and alkaline TMT-15 also damages the soil; we therefore investigated whether the combination of these two stabilizers would result in a mild and effective method for treating severely As-contaminated soil. In this paper, the non-toxic stabilizers Na_3TMT and $FeCl_3{\cdot}6H_2O$ were used to stabilize severely As-contaminated soil, and H_2O_2 pre-oxidation assisted Na_3TMT and $FeCl_3{\cdot}6H_2O$ stabilization was also investigated in detail.

2. Experimental

2.1. Samples and equipment

The sample soil was collected from a region near a tailings pond and was dried in a shaded area for two weeks. The soil was sieved with a 10-mesh sieve (2 mm) and then ground to fit through a 100-mesh screen (0.149 mm). The As content of the original soil was measured according to Chinese national standard GB/T 22105.1—2008. All of the chemical agents used in this work were analytical-reagent grade; deionized water was used throughout the experiments. The non-toxic organic sulfur stabilizer TMT-15 used in the experiment was an aqueous solution of Na_3TMT ($Na_3S_3C_3N_3$) with a mass fraction of 15%.

Energy dispersive spectroscopy (EDS, Supra-55, Zeiss Corp., Germany) was used to analyze the composition of contaminated soil. X-ray diffraction (XRD, D/max-2500, Rigaku Corp., Japan) was employed to analyze the phases in the soil samples. Inductively coupled plasma mass spectrometry (ICP-MS, ICAP RQ, Thermo Fisher Scientific Co., Ltd., US) was used to quantify the As concentration of solutions. Analysis by X-ray photoelectron spectroscopy (XPS, Axis Ultra, Kratos Analytical, Ltd., United Kingdom) was carried out to judge the valence state of As in the original soil and after the oxidation pre-treatment.

2.2. Stabilization methods of As-polluted soil

The severely As-contaminated soil was treated by TMT-15 stabilization, $FeCl_3{\cdot}6H_2O$ stabilization, TMT-15 and $FeCl_3{\cdot}6H_2O$ stabilization, and H_2O_2 pre-oxidation assisted TMT-15 and $FeCl_3{\cdot}6H_2O$ stabilization, respectively. Generally, the stabilization effect of the soil was quantified on the basis of the toxic leaching concentration of As in the soil. The safe disposal of As-polluted soil requires the toxic leaching concentration of As to be less than 5 mg/L. For evaluating the stabilization effect, the stabilization efficiency K was calculated according to the following equation:

$$K = \left(1 - \frac{C_1}{C_0}\right) \times 100\% \quad (1)$$

where K is the stabilization efficiency of As in the soil; C_1 is the toxic leaching concentration of As in the soil after it had been stabilized by the toxicity characteristic leaching procedure (TCLP), mg/L; C_0 is the TCLP toxic leaching concentration of As in the original soil samples, mg/L.

2.2.1. As-contaminated soil stabilized by TMT-15

Five soil samples (1.00 g each) were placed in five different vessels and then 0, 0.1, 0.2, 2.0, and 4.0 mL TMT-15 were added, respectively. The appropriate amount of deio-

nized water was added to keep the soil/liquid ratio at 1/4 g/mL. The soils and stabilizers were mixed and stirred at 25°C for 4 h and then dried at 130°C for 24 h. Finally, the toxic leaching concentration of As was tested using ICP-MS. The toxic leaching concentration of As was measured by the TCLP method [19], as follows: The leaching liquor was first prepared by diluting 5.7 mL of glacial acetic acid (98wt%) to 1 L with deionized water (the pH was maintained at 2.88 ± 0.05). The particle size of the stabilized soils was then decreased to less than 9.5 mm. The stabilized samples (1.00 g each) were placed into a 50-mL centrifuge tube, and then 20 mL of leaching liquor was added. The acquired mixtures were further revolved at 30 r/min at 25°C for 18 h and then centrifuged. Finally, the supernatant was collected and analyzed by ICP-MS.

2.2.2. As-contaminated soil stabilized by $FeCl_3 \cdot 6H_2O$

Five (1.00 g each) samples were placed in five different vessels. Similarly, 0, 0.02, 0.06, 0.20, and 0.60 g $FeCl_3 \cdot 6H_2O$ were also added to the vessels, respectively, and sufficient deionized water was added to bring the volume to 4 mL. The mixture was stirred at 25°C for 4 h and then dried at 130°C for 24 h. The toxic leaching concentration of As was tested by ICP-MS after TCLP processing.

2.2.3. As-contaminated soil stabilized by TMT-15 and $FeCl_3 \cdot 6H_2O$

The five soils (1.00 g each) were placed in five different vessels, and 2.0 mL of TMT-15 was added to each sample. The obtained mixtures were stirred at 25°C for 4 h. Then, 0, 0.02, 0.06, 0.20, and 0.60 g $FeCl_3 \cdot 6H_2O$ were successively added to the vessels and sufficient deionized water was added to bring the volume to 4 mL. The obtained mixtures were also stirred at 25°C for 4 h and dried at 130°C for 24 h. The toxic leaching concentration of As was determined after TCLP treatment.

2.2.4. As-contaminated soil treated by pre-oxidation assisted TMT-15 and $FeCl_3 \cdot 6H_2O$ stabilization

Five soil samples (1.00 g each) were added to five different 100-mL beakers and then separately oxidized by 10 mL of H_2O_2 for 24 h. The oxidized soil was cleaned with deionized water and then immobilized by TMT-15 and $FeCl_3 \cdot 6H_2O$ following the same steps described in the previous paragraph.

3. Results and discussion

To effectively stabilize the severely As-contaminated soil and investigate the reaction mechanism, we analyzed As species in the soil and then investigated the stabilization of the non-toxic stabilizers TMT-15 and $FeCl_3 \cdot 6H_2O$.

3.1. As content detection and species analysis

The total As content in the soil samples was measured according to Chinese national standard GB/T 22105.1—2008, and the As content was determined as 26084 mg/kg, which is more than 180 times the pollution control value (140 mg/kg) stipulated in Chinese national standard GB36600—2018. This level of As pollution poses a serious threat to the security of the soil environment and to human health.

To further investigate As species in the soil sample, EDS was used to observe the distribution of As. The results are shown in Fig. 1. The EDS images clearly show that As co-occurred with O in the soil matrix. As in soils is usually composed of As-oxides, arsenate, or arsenite. Moreover, XRD phase analysis (Fig. 2) shows that a certain amount of $CaSO_4 \cdot 2H_2O$ was present in the soil.

To identify the As species in the original soil, the XPS analysis method was used to determine the valence state of As in the original soil; the results are shown in Fig. 3. The peaks of As(III) and As(V) in the XPS spectra were fitted, and their peak positions were located at 43.5 eV [20] and 44.7 eV [21], respectively. Therefore, the XPS analysis demonstrated that As in the original soil mainly existed in two forms: As(III) and As(V). This result is consistent with the conclusion that the main forms of As in the soil are likely As-oxides, arsenate, and arsenite.

The As(III)/As(V) mass ratio in the soil before and after the oxidation was determined quantitatively by XPS analysis because XPS analysis is more accurate than chemical analysis for quantifying these species. The chemical analysis requires sequential chemical extraction, the results of which depend on the extractant, pH, and temperature during the As-species transformation process [22]. The peak areas of As(III) and As(V) in the spectrum of the original soil (Fig. 3) were calculated by XPS peak-fitting software; they were 536.0 and 555.5, respectively. Therefore, the As(III)/As(V) mass ratio equals area ratio (0.97:1), as shown in Fig. 3.

3.2. TMT-15 stabilization of As-contaminated soil

Considering environmental friendliness and outstanding performance in the treatment of heavy metals polluted wastewater treatment, the non-toxic stabilizer TMT-15 was used to stabilize the As-contaminated soil. The results are shown in Fig. 4.

The toxic leaching concentration of As decreased with increasing amount of TMT-15. When the volume of TMT-15 was increased to 2.0 mL, the stabilization efficiency of As increased to 62.6% and the toxic leaching concentration of As was reduced to 167.5 mg/L. With the addition of 4.0 mL of TMT-15, the stabilization efficiency of As in-

creased slowly to 67.1% and the toxic leaching concentration of As reached 147.2 mg/L. These results were mainly attributed to the chelation of As by TMT-15. Many studies have shown that TMT strongly chelates most heavy metals; the related reaction equations are shown in Eqs. (2) and (3) [16]:

$$3Me^{+}_{(aq)} + (C_3N_3S_3)^{3-}_{(aq)} \longrightarrow Me_3(C_3N_3S_3)_{(S)} \quad (2)$$

$$3Me^{2+}_{(aq)} + 2(C_3N_3S_3)^{3-}_{(aq)} \longrightarrow Me_3(C_3N_3S_3)_{2(S)} \quad (3)$$

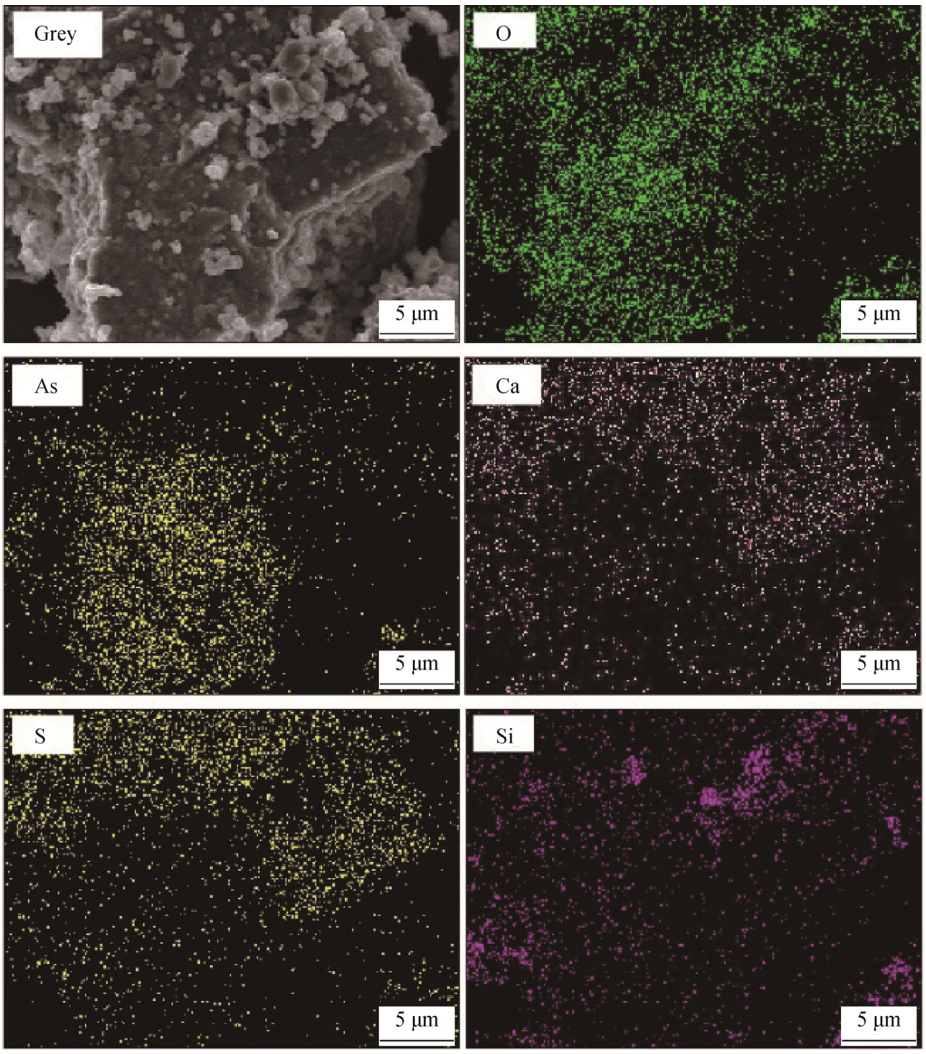

Fig. 1. Distribution of elements in EDS analysis of the original soil.

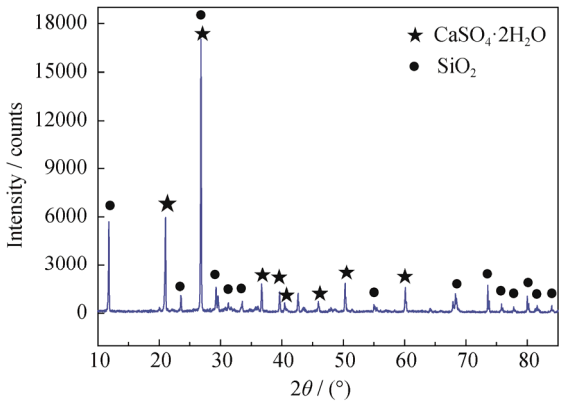

Fig. 2. XRD analysis of the original soil.

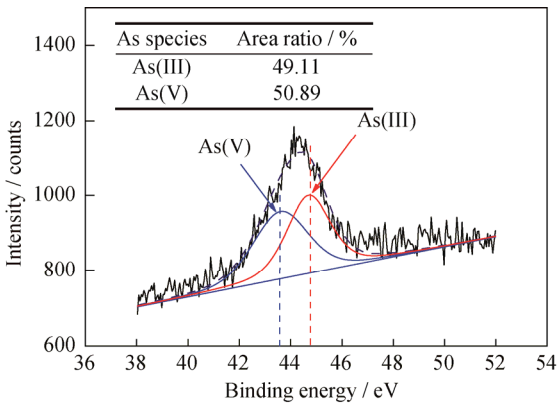

Fig. 3. XPS analysis of As in the original soil.

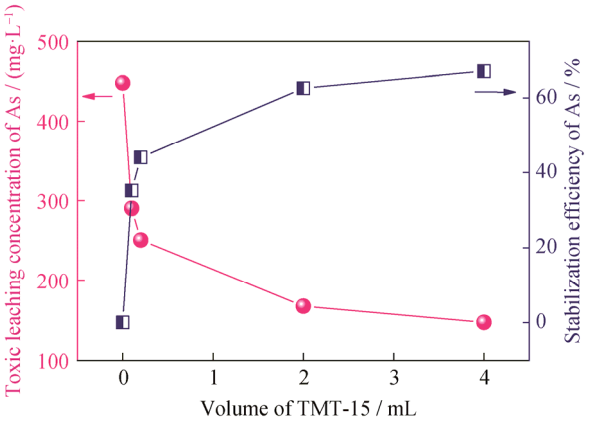

Fig. 4. Effect of TMT-15 on As stabilization.

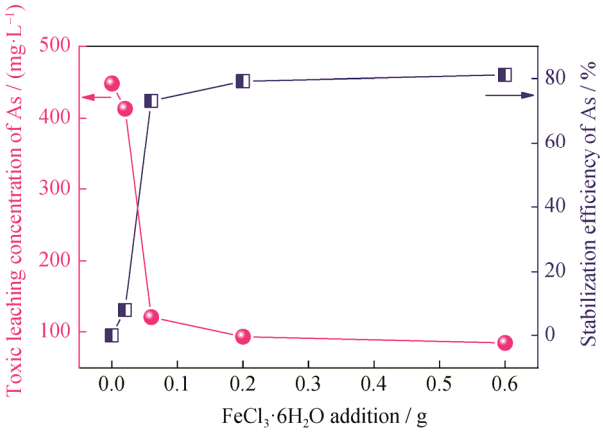

Fig. 5. Effect of $FeCl_3·6H_2O$ on As stabilization.

Norwood III and Kohler [23] also demonstrated experimentally that TMT has a certain removal effect on As. Hence, the toxic leaching concentration of As could be reduced effectively by TMT; however, the toxic leaching concentration of As was much higher than the hazardous waste leaching concentration limit stipulated by the US Environmental Protection Agency (EPA) (<5 mg/L). Thus, Further stabilization was required to be investigated for the severely As-polluted soil.

3.3. $FeCl_3·6H_2O$ stabilization of As-contaminated soil

Iron salts are the most widely used in As stabilization. $FeCl_3·6H_2O$ was used in this study, and the stabilization results are shown in Fig. 5. With increasing $FeCl_3·6H_2O$ content, the stabilization efficiency of As gradually increased. When the addition of $FeCl_3·6H_2O$ was increased to 0.02 g, the stabilization efficiency of As increased slowly to 7.8% and the toxic leaching concentration of As decreased from 448.1 to 413.0 mg/L. With further addition of $FeCl_3·6H_2O$ to 0.20 g (i.e., when the Fe/As mole ratio was increased to 10.0), the stabilization efficiency of As reached 79.2% and the toxic leaching concentration of As decreased to 93.3 mg/L. With the addition of 0.60 g of $FeCl_3·6H_2O$, the stabilization efficiency of As increased to 81.1% and the toxic leaching concentration of As reached 84.6 mg/L.

With this process, As contamination was effectively stabilized, mainly because of the adsorption and coprecipitation of $Fe(OH)_3$ as a result of the hydrolysis and stabilization caused by $FeCl_3·6H_2O$.

When the addition of $FeCl_3·6H_2O$ was less than 0.02 g, the lower concentration of Fe^{3+} facilitated the generation of $Fe(OH)_3$ by hydrolysis, as shown in Eq. (4), and the adsorption and coprecipitation was dominant compared with the stabilization of $FeAsO_4·2H_2O$, which was formed by reaction of Fe^{3+} and the As(V) pollutants.

$$Fe^{3+} + H_2O = Fe(OH)_3 + 3H^+ \quad (4)$$

When more than 0.06 g of $FeCl_3·6H_2O$ was added, the resultant high concentration of Fe^{3+} contributed to the formation of $FeAsO_4·2H_2O$, as shown in Eq. (5) [24]:

$$AsO_4^{3-} + Fe^{3+} + 2H_2O = FeAsO_4·2H_2O \quad (5)$$

The stabilization of $FeAsO_4·2H_2O$ played a major role at this time. When the additive amount of $FeCl_3·6H_2O$ increased to 0.60 g, the increasing trend of stabilization efficiency of As became stable.

3.4. TMT-15 and $FeCl_3·6H_2O$ stabilization of As-contaminated soil

Because safe disposal could not be achieved with TMT-15 and $FeCl_3·6H_2O$ separately, the combination of the two stabilizers was further investigated. The alkaline stabilizer TMT-15 was acted synergistically with $FeCl_3·6H_2O$. The experimental results are shown in Fig. 6.

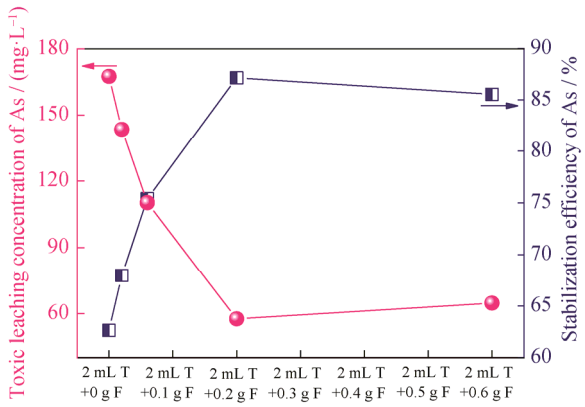

Fig. 6. Effect of combination of 2 mL TMT-15 and different additions of $FeCl_3·6H_2O$ on As stabilization (T—TMT-15; F—$FeCl_3·6H_2O$).

The stabilization efficiency of As was remarkably improved by the addition of TMT-15 and $FeCl_3·6H_2O$. When 2

mL of TMT-15 and 0.20 g of $FeCl_3·6H_2O$ were added, the stabilization efficiency of As reached a maximum of 87.2%. The toxic leaching concentration of As was 57.6 mg/L, which was still higher than the level of safe disposal regulated by the US EPA.

This high As stabilization efficiency results mainly from the stabilization induced by the superposition of TMT-15 and $FeCl_3·6H_2O$, which significantly stabilized As. The addition of $FeCl_3·6H_2O$ resulted in a large decrease in the pH of the soil mixed with TMT-15 while substantially enhancing the chelation of TMT [25].

3.5. H_2O_2 pre-oxidation assisted TMT-15 and $FeCl_3·6H_2O$ stabilization of As-contaminated soil

The toxicity and mobility of the As-bearing soil depended on the valence state of As. The toxicity and mobility of As(III) is stronger than that of As(V); thus, further oxidation of As(III) to As(V) was necessary. To adequately oxidize As(III) pollutants (Fig. 3), non-toxic H_2O_2 was selected as the oxidant. The XPS analysis of the As in soil after H_2O_2 oxidation is shown in Fig. 7. The two peaks of As(V) in the XPS spectrum were fitted, and their peak positions were 44.57 eV [26] and 45.7 eV [27]. Furthermore, the mass fraction of As(V) increased from 50.89% in the original soil to 100.00% in the H_2O_2-oxidized soil (Figs. 3 and 7). The As(V) contaminants easily formed the stable $FeAsO_4·2H_2O$ and dramatically improved the stabilization efficiency.

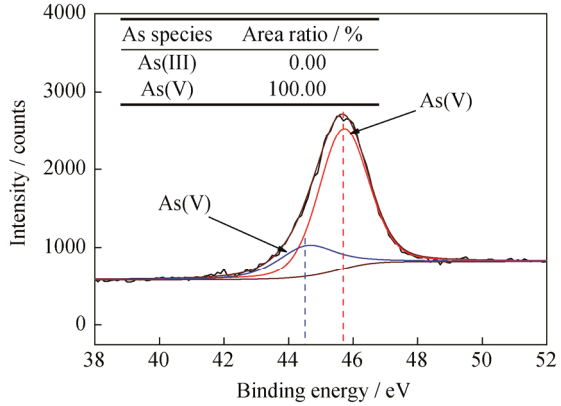

Fig. 7. XPS analysis of As in the soil after oxidation with H_2O_2.

The stabilization of As by both TMT-15 and $FeCl_3·6H_2O$ was further carried out after H_2O_2 pre-treatment; the results are shown in Fig. 8. The stabilization efficiency of As was significantly increased with increasing additions of both TMT-15 and $FeCl_3·6H_2O$. When the additions of TMT-15 and $FeCl_3·6H_2O$ were 2 mL and 0.20 g, respectively, the stabilization efficiency of As reached 99.6% and the toxic leaching concentration of As was 1.61 mg/L, which reached the level of safe disposal (<5 mg/L). When the addition of $FeCl_3·6H_2O$ was further increased to 0.60 g, the toxic leaching concentration of As in the soil remained at 1.66 mg/L, indicating that it had achieved the ideal stabilizing effect.

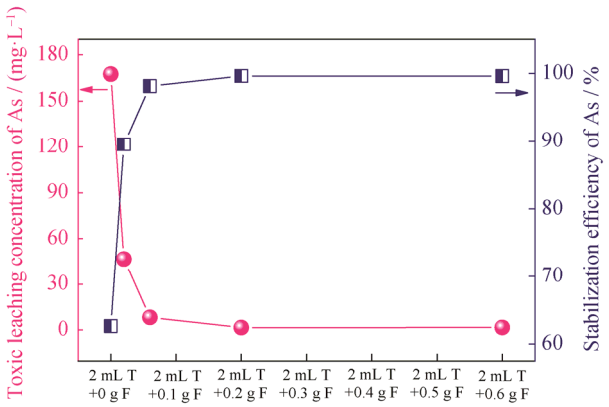

Fig. 8. Effect of H_2O_2 pre-oxidation assisted combination of 2 mL TMT-15 and different additions of $FeCl_3·6H_2O$ on As stabilization (T—TMT-15; F—$FeCl_3·6H_2O$).

On the basis of the aforementioned experiments, the effective combination of H_2O_2 pre-oxidation and stabilization is explained as follows: The H_2O_2 pre-oxidation availably realized the transformation of As from As(III), which is highly toxic, to As(V), which is less toxic. After the oxidation treatment, more As(V) contaminants were further converted to crystalline $FeAsO_4·2H_2O$. The superposition of the two stabilizers (TMT-15 and $FeCl_3·6H_2O$) also substantially improved stabilization. The $CaSO_4·2H_2O$ present in the soil (shown in Fig. 2) could significantly reduce the solubility of scorodite (crystalline $FeAsO_4·2H_2O$) [28].

Hence, a simple H_2O_2 pre-oxidation assisted non-toxic TMT-15 and $FeCl_3·6H_2O$ stabilization could successfully reduce the toxic leaching concentration of As in severely As-polluted soil (originally containing 26084 mg/kg As) from 448.1 to 1.61 mg/L, which is a level that can be safely landfilled.

4. Conclusions

In this study, As-contaminated soil that contained 26084 mg/kg of toxic As, which far exceeded the concentrations in previous studies and posed a severe hazard to human health, was successfully remediated by a simple H_2O_2 pre-oxidation assisted non-toxic TMT-15 and $FeCl_3·6H_2O$ stabilization method. The results indicated that the stabilization effects of the two stabilizers (TMT-15 and $FeCl_3·6H_2O$) for As in soil

was clearly better than either of their individual stabilization effects, and the toxic leaching concentration of As could be decreased from 448.1 to 57.6 mg/L. Surprisingly, using the simple H_2O_2 pre-oxidation to assist non-toxic TMT-15 and $FeCl_3·6H_2O$ stabilization enabled the safe disposal of the As-polluted soil and decreased the toxic leaching concentration of As from 448.1 to 1.61 mg/L. This effect was mainly attributed to the extremely toxic As(III) being converted into As(V), which is less toxic than As(III) and easily forms the stable compound $FeAsO_4·2H_2O$ after H_2O_2 pre-oxidation. Furthermore, the superposition of the two stabilizers (TMT-15 and $FeCl_3·6H_2O$) promoted the stabilization and $CaSO_4·2H_2O$ present in the soil inhibited decomposition of the crystalline $FeAsO_4·2H_2O$. Therefore, this study provides a useful reference for the remediation of severely As-contaminated soil.

Acknowledgements

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