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Removal of arsenic from contaminated soil by washing with amino acid-derived ionic liquids: Remediation effects and potential mechanisms

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ABSTRACT

It is a challenging task to find an environmentally friendly and effective washing agent for the remediation of contaminated soil. In this study, the remediation effect of 15 amino acid-derived ionic liquids (AA-ILs) on arsenic (As)-contaminated soil was evaluated, and the best washing agent was selected to optimize the washing conditions. The results showed that 1.0 mol/L [Ala][H₂PO₄] (Ala represents alanine) exhibited the highest As removal efficiency of 90.1 % at a liquid-soil ratio of 4:1 and a washing time of 480 min. The results of kinetic studies showed that the As removal process by [Ala][H₂PO₄] washing followed a second-order kinetic model. After washing, residual As was the main form of As in soil, which inhibited the bioavailability and toxicity of As. In addition, the soil type remained unaltered, the content of nutrient elements increased, but the soil pH and mineral content decreased. The potential mechanisms of As removal by [Ala][H₂PO₄] included acid dissolution, ion exchange and coordination reactions. In conclusion, [Ala][H₂PO₄] can be used as a green washing agent for efficient remediation of As-contaminated soil.

1. Introduction

The contamination of soil with heavy metals resulting from industrial activities represents a significant global environmental issue (Chen and Costa, 2021; Yang et al., 2022). Arsenic (As) has drawn widespread public attention due to its high toxicity, carcinogenicity, and the wide range of pollution (Shi et al., 2023; Rehman et al., 2021). A national soil contamination survey conducted in 2014 showed that 2.7 % of soil samples in China exceeded the limits of As (Zhao et al., 2015). Therefore, it is urgent to develop green, efficient and sustainable technologies to remediate As-contaminated soils.

A variety of techniques have been reported for the removal of As from contaminated soil, such as replacement, solidification/

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stabilization, soil washing, electrical remediation, phytoremediation, and microbial remediation (Wan et al., 2019; Vareda et al., 2019; Liao et al., 2022; Arteaga et al., 2022). Among the techniques available for soil remediation, soil washing is a particularly effective method due to its straightforward, rapid operation and consistent remediation effect (Gu et al., 2022). Soil washing is a process whereby heavy metals are transferred from the solid phase of soil to the liquid phase of the washing agent through a series of chemical reactions, including dissolution, chelation, ion exchange and desorption, to achieve the purpose of removing heavy metals from soil (Azhar et al., 2022; Song et al., 2022).

Washing agents are considered to be the key factor influencing the soil washing process as they largely determine the As removal efficiency (Liao et al., 2022). Inorganic washing agents, including acids, bases and inorganic salts, are mainly used to remove heavy metals from soil through acid dissolution, ion exchange or complexation (Marzi et al., 2022; Resmi et al., 2023). However, this may result in the mobility of As and damage to the soil structure, which may lead to a loss of soil nutrients and soil acidification or salinization (Liu et al., 2022). Chelating agents can form stable complexes with heavy metals in the soil, thus promoting heavy metal desorption (Lestan et al., 2008). For instance, ethylenediaminetetraacetic acid (EDTA) is an effective chelating agent but it is little biodegradable and may affect soil structure, inhibit plant growth and, in some cases, lead to secondary pollution (Bloem et al., 2017). Moreover, the use of natural organic acids as washing agents for the removal of heavy metals is not an effective method (Xu et al., 2022). Surfactants can reduce the adsorption of heavy metals on soil colloids by modifying soil surface tension (Zheng et al., 2022). Nevertheless, surfactants are often toxic and contribute to secondary pollution, resulting in a relatively low frequency of use (Yan et al., 2021). Furthermore, the process of soil washing has the potential to influence the soil properties such as soil texture, organic matter content, total nitrogen content, and even the mobility and bioavailability of heavy metals in the soil (Ko et al., 2005). Therefore, it is of great importance to develop an environmentally friendly washing agent for the effective remediation of contaminated soil.

In addition to the type of washing agent, its concentration, the liquid-soil ratio and the washing time are all important factors that affect the removal efficiency of heavy metals (Zhu et al., 2021; He et al., 2023). Furthermore, in the process of optimizing washing conditions it is essential to consider not only the removal efficiency, but also the economic cost and energy consumption (Wang et al., 2020).

Ionic liquid (IL) is an ionic compound with melting point below 100 °C that typically consists of an organic cation associated with an inorganic or organic anion (Sadjadi, 2021). ILs offer several advantageous properties, including low vapor pressure, high stability, and tunable properties (Gujjala et al., 2024, Roy and Ahmaruzzaman, 2022). Therefore, ILs have potential applications in a variety of fields, including chemical synthesis, electrochemistry, extraction, and environmental remediation (Goutham et al., 2022). However, the widely used ILs, such as imidazolium- and pyridinium-based ILs, are somehow toxic and resistant to biodegradation (Deng et al., 2015).

Since the toxicity and poor biodegradability of traditional ILs are typically attributable to the cations (Deng et al., 2015), Tao's group embarked on the synthesis of a new generation of "fully green" IL, by facilely mixing amino acids, serving as the cationic precursor, with a relatively strong acid (Tao et al., 2005, 2006). The amino acids utilized are bio-renewable natural compounds, and the synthesis protocol is a streamlined one-step process, representing a quintessential atom-economic reaction that yields no toxic by-products. Given that the cation in these amino acids-derived ILs (AA-ILs) is derived from amino acids, it exhibits comparable biodegradability to its amino acid precursor. Our previous research findings indicated that the AA-IL, glycine hydrochloride ([Gly][Cl]), that is synthesized from glycine and hydrochloric acid, removed 82.2 % of the total Cd under optimized conditions. Notably, the washing process exerted no significant alteration on the soil morphology. After the pH was adjusted by Ca(OH)₂, the germination index of the rice witnessed a 7.5 % increment. Moreover, the growth of the rice was conspicuously promoted, with the lengths and weights of the rice plants registering increases of 56 % and 32 % two weeks later, respectively (Deng et al., 2023). However, the application of AA-ILs in the remediation of As-contaminated soil has not been reported. We inferred that other AA-ILs could possibly remove As from

Table 1

Effect of physical and chemical properties of soil before and after washing with [Ala][H₂PO₄] at a concentration of 1.0 mol/L, a liquid-soil ratio of 4:1 and a washing time of 480 min.

Characteristics		Before washing	After washing
Basic properties of soil	Sand (%)	61.0 ± 0.1	70.6 ± 5.7
	Silt (%)	33.1 ± 0.1	25.9 ± 5.2
	Clay (%)	5.9 ± 0.0	3.6 ± 0.5
	pH	6.7 ± 0.2	3.0 ± 0.0
	EC (ms/cm)	1.6 ± 0.1	1.8 ± 0.1
	OM (g/kg)	11.2 ± 0.2	11.5 ± 0.3
Exchange performance in soil	CEC (cmol/kg)	18.6 ± 0.0	18.3 ± 0.1
	Ex-Ca (g/kg)	6.8 ± 0.4	3.3 ± 0.1
	Ex-Mg (g/kg)	0.4 ± 0.0	0.1 ± 0.0
Nutrient in soil	TN (g/kg)	0.8 ± 0.2	1.3 ± 0.1
	TP (g/kg)	1.9 ± 0.0	3.9 ± 0.1
	TK (g/kg)	11.6 ± 0.2	8.9 ± 0.7
	AP (g/kg)	70.9 ± 0.4	285.5 ± 7.1
	AK (g/kg)	179.2 ± 0.5	141.4 ± 2.7
Mineral element in soil	Ca (g/kg)	86.0 ± 3.6	34.3 ± 2.5
	Mg (g/kg)	40.3 ± 2.1	36.6 ± 3.1
	Mn (g/kg)	0.8 ± 0.1	0.4 ± 0.0
	Fe (g/kg)	33.7 ± 1.0	26.6 ± 0.9

soil efficiently, through dissolution, ion exchange and complexation with As. Therefore, studies into the effect and mechanism of AA-ILs in the remediation of As-contaminated soil would fill an important knowledge gap.

In this study, a series of washing experiments were conducted to investigate the effect of AA-ILs. The main objectives were (1) to explore the feasibility of using AA-IL for soil washing to remove As; (2) to evaluate the effect of the AA-IL on the physicochemical properties of soil; and (3) to reveal the mechanism of the AA-IL as a washing agent for the removal of As from soil. This study could provide a green and sustainable solution for the remediation of As-contaminated soil.

2. Materials and methods

2.1. Soil samples

As-contaminated soil was collected from the surface soil (0–20 cm) in a chemical plant in Shanghai. After natural air drying and removal of impurities, the soil samples were completely ground for sorting through a 10-mesh screen and finally stored in sealed bags. The soil sample was typified by a sandy loam composition, exhibiting pH value of 6.7 ± 0.2 , organic matter (OM) content of 11.2 ± 0.2 g/kg, cation exchange capacity (CEC) of 18.6 ± 0.0 cmol/kg, and As concentration of 1396.0 ± 21.5 mg/kg. A comprehensive overview of the basic physical and chemical properties of soils is provided in Table 1.

2.2. Preparation of AA-ILs

The preparation of AA-ILs was carried out according to a previous report (Tao et al., 2005). The amino acid and inorganic acid were evenly mixed in water with a molar ratio of 1:1, and stirred at 60 °C for 6 h to generate the AA-ILs (Fig. 1).

AA-ILs were named in the form of [AA][X], where [AA] stands for the amino acid and [X] represents the acid anion. In this study, the amino acids employed were alanine (Ala), cysteine (Cys), methionine (Met), glycine (Gly), and threonine (Thr), while the inorganic acids used were HCl, HNO₃, and H₃PO₄. The structural formulas of AA-ILs are shown in Table S1.

2.3. Design of washing experiment

2.3.1. Screening of washing agent

The soil sample (5.0 g) was accurately weighed and transferred into a 50 mL plastic centrifuge tube, before addition of a 20.0 mL [AA][X] solution with a concentration of 0.3 mol/L. The mixture was oscillated at 150 r/min for 480 min, after which it was centrifuged at 4000 r/min for 10 min. The resulting supernatant was subsequently discarded. The concentration of As in the soil was determined following air-drying of the washed soil sample. In this experiment, deionized water was used as washing agent in the control group.

2.3.2. Optimization of washing conditions

The most efficient washing agent from the above experiments was selected to explore the optimal washing conditions. To investigate the effect of washing agent concentration on As removal efficiency, the concentration of the washing agent was set at 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.8, 1.0, and 1.5 mol/L, with a washing agent volume of 20 mL and washing time of 480 min.

To investigate the effect of liquid-soil ratio on As removal efficiency, the volume of the washing agent was set at 10, 15, 20, 25, 30, 35, and 40 mL, with a washing agent concentration of 1.0 mol/L and washing time of 480 min.

To investigate the effect of washing time on As removal efficiency, the washing time was set at 30, 60, 120, 240, 480, 720, and 1440 min, with a washing agent concentration and volume of 1.0 mol/L and 20 mL, respectively.

2.3.3. Exploration of As removal mechanism

Based on the above experimental results, a soil washing experiment was carried out with the best agent under the optimal washing conditions. The soil samples before and after washing were used for the analysis of As morphology and soil physicochemical properties. Meanwhile, the microscopic morphology and structural composition of soil samples were analyzed by various characterization methods.

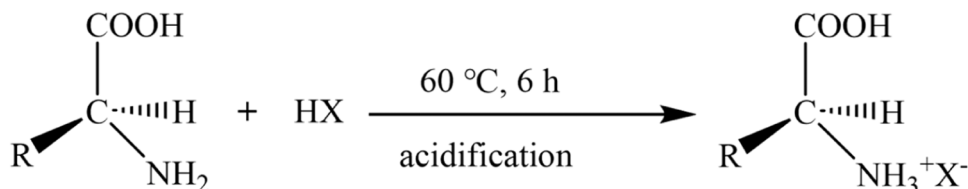


Fig. 1. Schematic diagram of synthesis of AA-ILs.

2.4. Determination of As content and As form

The soil samples were digested by $\text{HNO}_3\text{-HCl-HF}$ with a microwave digestion instrument SHB-III (AntonPaar, Graz, Austria), as detailed in Table S2. Following digestion, the digestion solution was transferred to a crucible of polytetrafluoroethylene and heated to 200 °C on an electric furnace to drive the acid away. The digestion solution was then brought to 50 mL with deionized water and filtered through a 0.45 μm filter membrane to obtain the As detection solution. The concentration of As was measured by an atomic fluorescence spectrometer (AFS, AFS-930, Jitian Com., China). The detection limit and the lower limit of quantification of this method are 0.4 mg/L and 1.6 mg/L, respectively (National Environmental Protection Standards of the People's Republic of China HJ 803–2016).

A sequential extraction procedure (SEP) was used to extract different forms of As in soil samples (Table S3), and the concentrations of As in the different forms were determined by AFS.

2.5. Determination of physical and chemical properties of soil

The physical and chemical properties to be determined included basic properties, exchange performance, nutrient element, and mineral element of soils. The details are described in Supplementary Material 1.1.

2.6. Characterization of soil

The soil samples were characterized by scanning electron microscope (SEM), Fourier transform infrared spectrometer (FT-IR), X-ray diffractometer (XRD), and X-ray electron spectrometer (XPS). The details are shown in Supplementary Material 1.2.

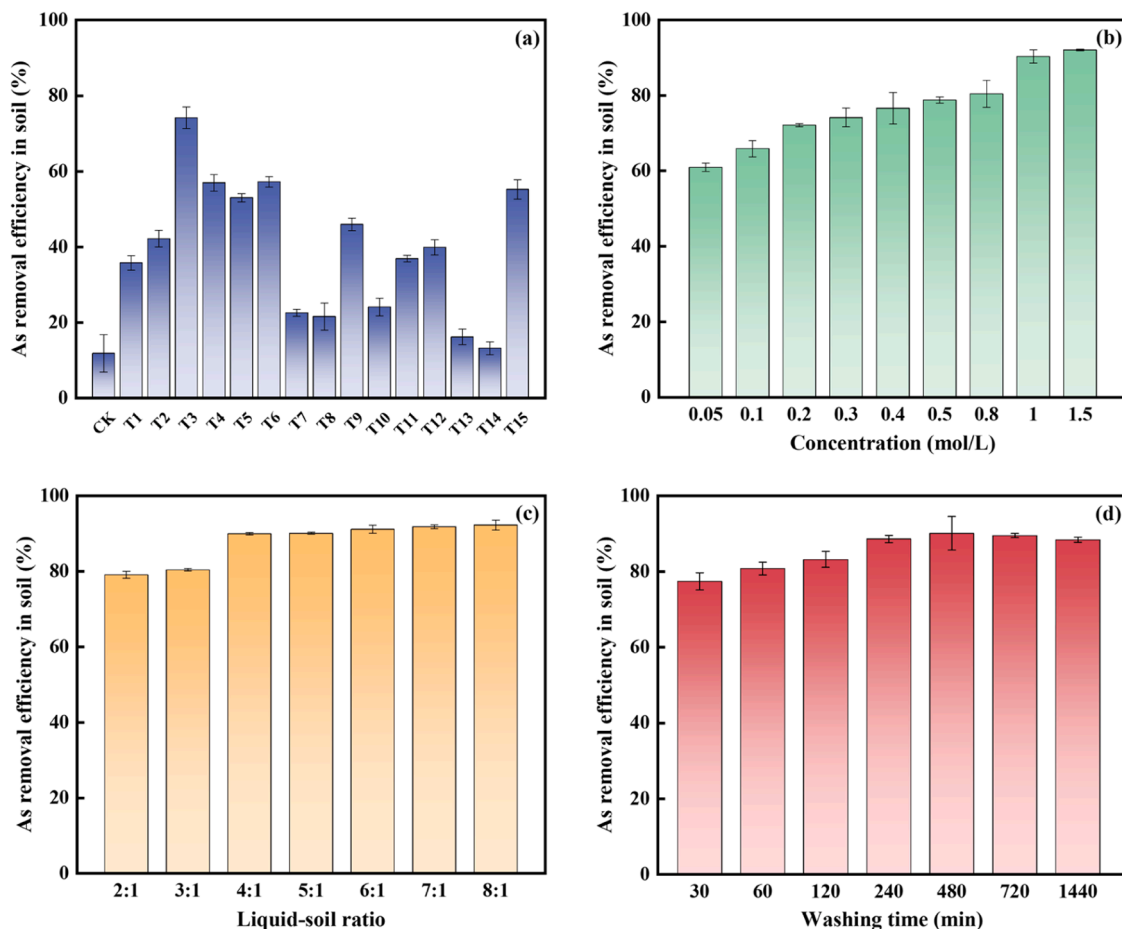


Fig. 2. Removal efficiency of As from soil by different AA-ILs (a), and the effects of concentration (b), liquid-soil ratio (c) and washing time (d) with [Ala][H_2PO_4] as the washing agent on the removal efficiency of As from soil. CK represents the control group, and T1-T15 represent [Ala][Cl], [Ala][NO_3], [Ala][H_2PO_4], [Cys][Cl], [Cys][NO_3], [Cys][H_2PO_4], [Met][Cl], [Met][NO_3], [Met][H_2PO_4], [Gly][Cl], [Gly][NO_3], [Gly][H_2PO_4], [Thr][Cl], [Thr][NO_3], and [Thr][H_2PO_4], respectively.

2.7. Quality control and data analysis

Certified reference material of soil (GBW07405a, Institute of Geophysical and Geochemical Exploration) and blank digestion samples were performed to confirm the quality assurance and quality control. The recovery rate ranged from 90 % to 105 % to ensure the accuracy and trustworthiness of data. Additionally, the standard sample was incorporated at the 15-sample interval during the detection process, with the objective of maintaining the stability of the analysis process.

The removal efficiency of As (RE%) was calculated using the following formula:

$$RE(\%) = \frac{C_{As} - Q_{As}}{C_{As}} \times 100\%$$

where C_{As} (mg/kg) represents the total amount of As in soil before washing, and Q_{As} (mg/kg) represents the total amount of As in soil after washing.

The experimental data were obtained based on three repetitions and subsequently processed and analyzed by Excel 2021. The peak detection of the XRD data was conducted using MDI Jade (Version 6). XPSPEAK 41 was used to analyze the XPS data. The figures were generated by Origin 2018.

3. Results and discussion

3.1. As removal efficiency of various AA-ILs

Fig. 2a shows the removal efficiency of As from soil by washing with 0.3 mol/L of different AA-ILs solutions, whose pH range mainly in 1.4 ~ 1.8. When using deionized water as control, the removal efficiency of As in soil was 11.8 %. In comparison to the control, different AA-ILs demonstrated higher capacity to remove As from soil through washing. In particular, the washing effect of [Ala][H₂PO₄] was the best, with an As removal efficiency of 74.2 %. Huang et al. (2021) used various organic acids to wash the As-contaminated soil (3.3 g/kg). Their highest removal efficiency was 55.9 % when they used 0.8 mol/L oxalic acid (pH=0.77) for 4 h at a solid-liquid ratio 1:10. They also adjusted the pH to 2–12, and the highest removal efficiency is 56.2 % when pH was 2. The lowest removal efficiency of As by [Thr][NO₃] was only 13.2 %, which is only 1.4 % than water. These results indicated that the pH effects of the washing agent are limited. The removal efficiency of [Ala][H₂PO₄] was significantly higher than that of other AA-ILs with the same H₂PO₄⁻ anion. In the pH range of 3–9, the predominant chemical forms of As are H₃AsO₃, H₂AsO₄⁻, and HAsO₄²⁻ (Smedley and Kiniburgh, 2002). Ala can be employed as a substitute for As(III) or used for the adsorption of As(V) with the objective of removing As (Hong et al., 2014). At the same time, the removal efficiency of As by [Ala][H₂PO₄] was significantly higher than that of other AA-ILs with Ala as cation. As previously reported, acids containing oxygen anions demonstrate superior efficacy compared to their oxygen-deficient counterparts when acid-base solutions are employed as soil washing agents for the removal of As (Im et al., 2015). Due to the similarity in the properties of P and As, PO₄³⁻ may reduce the resorption of anionic As on the active surface of the soil (Tan et al., 2023; Zheng et al., 2022). [Ala][H₂PO₄] was more efficient in removing As from soil compared with organic acids and phosphates as washing agents (Wei et al., 2022). In conclusion, [Ala][H₂PO₄] can be considered a promising washing agent for the remediation of As-contaminated soil.

3.2. As removal efficiency with [Ala][H₂PO₄]

3.2.1. Effect of [Ala][H₂PO₄] concentration

The concentration of washing agent is one of the significant factors influencing the efficacy of the washing process for contaminated soil. The results of Fig. 2b show that the washing effect of [Ala][H₂PO₄] at different concentrations on As-contaminated soil at different concentrations. When the concentration of [Ala][H₂PO₄] was lower than 1.0 mol/L, the removal efficiency of As in soil increased rapidly with increasing [Ala][H₂PO₄] concentration: 0.05 mol/L [Ala][H₂PO₄] gave 61.0 % As removal, increasing to 90.4 % with 1.0 mol/L [Ala][H₂PO₄]. An increased concentration of washing agent provides more functional groups and phosphates, thereby enhancing the removal efficiency of As in soil washing (Jho et al., 2015; Zhu et al., 2021). However, when the concentration of [Ala][H₂PO₄] exceeded 1.0 mol/L, the removal efficiency increased slowly. This indicates that the removal efficiency of As in soil may tend to a plateau. It may be attributed to the occurrence in soil of loosely bound As that is easy to extract with the washing agent; in contrast, As that is tightly bound to the soil is challenging to remove, even with an increased concentration of the washing agent (Im et al., 2015). Furthermore, the presence of multiple ions in the soil matrix may also lead to competitive or reactive interactions with As ions, which could potentially influence the efficiency of the removal (Jho et al., 2015; Marzi et al., 2022; Yang et al., 2024). Therefore, in light of the economic cost and removal effect, 1.0 mol/L was selected as the optimal concentration of [Ala][H₂PO₄] for washing As-contaminated soil.

3.2.2. Effect of the liquid-soil ratio

Liquid-soil ratio is also an important process parameter of soil washing remediation technology. The effect of different liquid-solid ratios on As removal efficiency was thus investigated, as shown in Fig. 2c. When the liquid-soil ratio increased from 2:1–4:1, the As removal efficiency in the presence of [Ala][H₂PO₄] increased from 79.1 % to 90.0 %. A low liquid-soil ratio limits the volume of washing agent, which prevents the complete dispersion of soil particles. Consequently, the As present in the soil is unable to fully come

in contact with the leaching agent, which limits the effectiveness of As removal (Son and Jung, 2011). A higher liquid-solid ratio usually means that more ligand material is available, while simultaneously increasing the contact area and mass transfer time between the soil and the washing solution. This, in turn, enhances the efficiency of the removal process (Wei et al., 2016; He et al., 2023). However, when the liquid-to-soil ratio increased from 4:1–8:1, the removal efficiency of As by [Ala][H₂PO₄] increased only from 90.0 % to 92.3 %. In addition, a high liquid-soil ratio can increase the cost of soil remediation. In comparison to literature liquid-solid ratios of 20:1 (1-hydroxyethylidene-1,1-diphosphonic acid + lactic acid + FeCl₃), 10:1 (Na₂S₂O₄ + tartaric acid) or 5:1 (iron-based compounds) employed in soil washing for the removal of As (Xu et al., 2022; He et al., 2023; Zhu et al., 2021), a liquid-solid ratio of 4:1 exhibits a distinct advantage. The lower the liquid-soil ratio is, the less water will be required, and consequently, the less wastewater will need to be treated. Meanwhile, the volume of the reactor that requires design will also be reduced correspondingly, thereby cutting down the costs. Therefore, 4:1 is our recommended liquid-solid ratio for the washing of As-contaminated soil with [Ala][H₂PO₄].

3.2.3. Effect of the washing time

The washing time is another crucial process parameter of the soil washing technology. Appropriate washing time can not only improve the washing efficiency, but also reduce the damage to the soil. The removal efficiency of As in soil by [Ala][H₂PO₄] varied with the washing time, as shown in Fig. 2d. In the initial stage of washing (0–240 min), the removal efficiency of As from soil by [Ala][H₂PO₄] increased rapidly with time, reaching 77.4 % at 30 min and 88.6 % at 240 min. During the intermediate phase of the washing process (240–480 min), the efficiency of As removal exhibited a gradual increase with time and reached a maximum (90.1 %) at 480 min. When the washing time exceeded 480 min, there was a slight decrease in the removal efficiency of As. In the rapid reaction stage, the As fractions showing strong migration in the soil will be removed easily. In the slow reaction stage, the As that is closely bound to the soil particles will be gradually removed, resulting in a gradual increase in washing efficiency and a plateau trend (Rahman et al., 2022; Wang et al., 2020). If the washing time is excessive, the As present in the washing solution after it has been released from the soil may be adsorbed onto the soil surface once more (Cao et al., 2017; Yan et al., 2021). Therefore, 480 min was selected as the optimal washing time for As-contaminated soil with [Ala][H₂PO₄].

In order to study the kinetic characteristics of As removal in soil, several models (second order kinetic model, Elovich model, double constant model and diffusion model) were applied to fit the washing experimental data. The expressions of the models are shown in

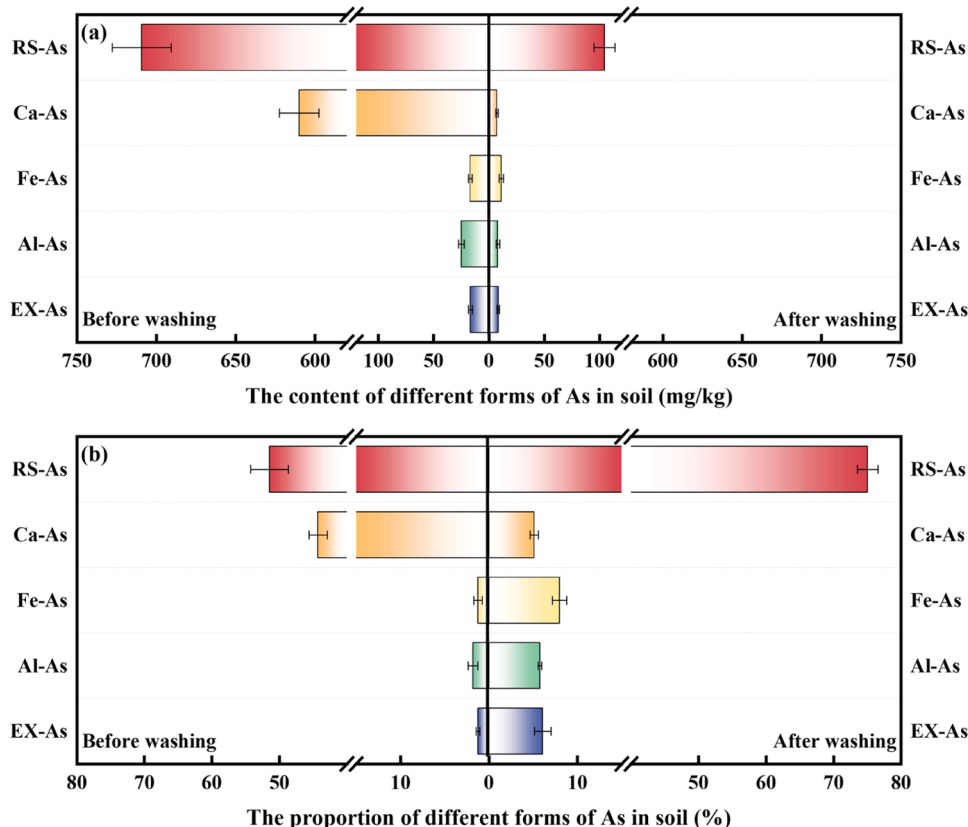


Fig. 3. Effect on the content (a) and proportion (b) of As forms in the soil before and after washing with [Ala][H₂PO₄] at a concentration of 1.0 mol/L, a liquid-soil ratio of 4:1 and a washing time of 480 min. EX-As represents exchangeable As, Al-As represents Al-bound As, Fe-As represents Fe-bound As, Ca-As represents Ca-bound As, and RS-As represents residual As.

Supplementary Material. Fig. S1 shows the fitting results of the above four kinetics models. A further comparison of the correlation coefficient (R^2) and standard error (SE) from Table S4 reveals that the second-order kinetic equation ($R^2=0.9999$, $SE=0.0017$) is an appropriate model to describe As removal from soil by $[Ala][H_2PO_4]$. These results suggest that the mechanism of action of $[Ala][H_2PO_4]$ in soil washing was mainly chemical washing. The washing agent $[Ala][H_2PO_4]$ contains hydrophilic groups, including H^+ , the carboxyl group, and the amino group, which react with heavy metal ions in the soil through ion exchange and complexation during the washing process.

3.3. Effect of soil washing with $[Ala][H_2PO_4]$ on As forms in soil

The soil washing process can affect the form of heavy metals, which determines the migration capacity and bioavailability of heavy metals in contaminated soil (Wei et al., 2016). As shown in Fig. 3, the use of $[Ala][H_2PO_4]$ had a great influence on the form of As in soil. The main forms of As in soil before washing were residual As (RS-As) and Ca-bound As (Ca-As), with respective concentrations of 727.3 and 610.1 mg/kg, accounting for 52.1 % and 43.7 % of total soil As, respectively. This was followed by comparable amounts of Al-bound As (Al-As), Fe-bound As (Fe-As) and exchangeable As (EX-As), which accounted for 1.8 %, 1.2 % and 1.2 % of total As, respectively. It is important to note that EX-As is exchangeable As, which is highly active and highly toxic. Fixed As species include Fe-As, Ca-As, Al-As, and RS-As, which are stable and, therefore, less toxic (Xu et al., 2022; Wei et al., 2016). Our data suggest that As occurred predominantly in a fixed form within the soil before washing, with its biological availability being constrained. The content of all As forms, and, most notably, of EX-As in soil decreased significantly after washing, which effectively reduced the potential harm of soil As.

The soil washing removal efficiencies of EX-As, Al-As, Fe-As, Ca-As, and RS-As were 49.5 %, 67.8 %, 34.2 %, 98.8 % and 85.3 %, respectively. In general, the residual components of the heavy metals in contaminated soil are very difficult to remove. In the present study, more than 80 % of Ca-As and RS-As were removed, which may be due to the facile extraction of Ca-As and RS-As under acidic conditions of the washing agent (the pH value of 0.3 mol/L $[Ala][H_2PO_4]$ is 2.41). Interestingly, similar results on residual As were obtained with contaminated soil using ethylenediaminetetraacetic acid disodium salt, oxalic acid, and phosphoric acid (Wei et al., 2016).

3.4. Effect of soil washing with $[Ala][H_2PO_4]$ on soil properties

3.4.1. Microscopic morphology of soil

The microscopic morphology of the soil surface before and after washing was observed by SEM, as shown in Fig. 4. Before washing the As-contaminated soil exhibited a lamellar structure, predominantly comprising large particles that were relatively dispersed. The erosion effect of $[Ala][H_2PO_4]$ washing on soil surface was not obvious. Due to the hydrodynamic scouring effect, the microscopic morphology of the soil surface after drenching had a slight change, yet it remained discernible. The soil flake particles became smaller, more dispersed, and coarser after washing. This may be due to the fact that the washing agent promoted the dissolution of soil surface materials, which would help to remove As in bound state on the soil surface (Tang et al., 2017; He et al., 2023). Additionally, it generated a multidimensional layered structure, and the increase in specific surface area provides more contact points between the IL and soil particles, thus improving the removal efficiency. (He et al., 2023; Tang et al., 2017).

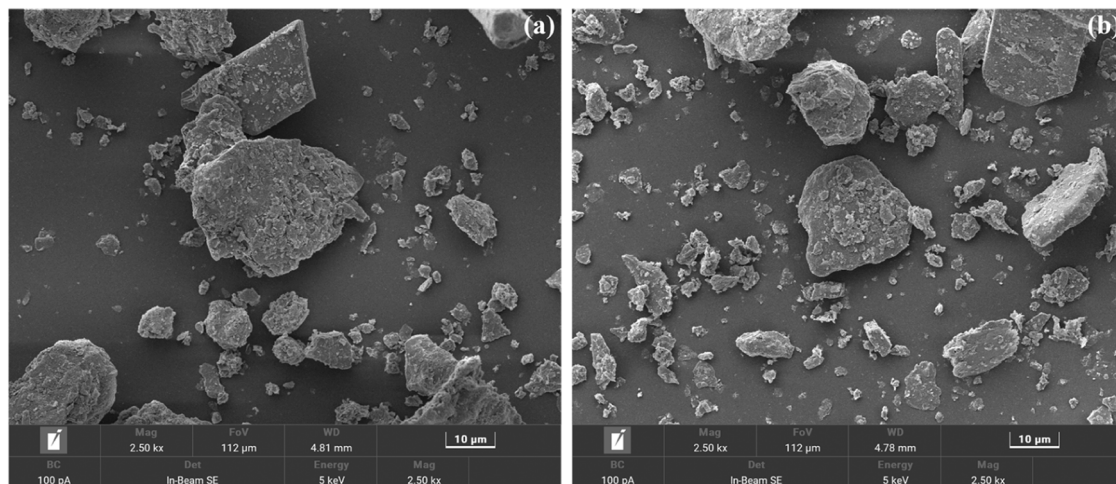


Fig. 4. SEM images of soil before (a) and after washing (b) with $[Ala][H_2PO_4]$ at a concentration of 1.0 mol/L, a liquid-soil ratio of 4:1 and a washing time of 480 min.

3.4.2. Physical and chemical properties of soil

The physical and chemical properties of soil before and after washing are shown in Table 1. Soil washing has influence on the basic properties of soil. The As-contaminated soil before washing belonged to sandy loam, in which the proportion of clay was 5.9 % and the proportion of sand was 61.0 %. After washing by [Ala][H₂PO₄], the proportion of clay particles in the soil decreased to 3.6 %, and the sand particles increased to 70.6 %, but the soil composition was still predominantly sandy and the overall soil texture remained unaltered. The pH of soil can impact the growth of plants and the activity of microbes, as well as the presence, availability, migration and transformation of heavy metals within the soil (Li et al., 2019). A decrease in soil pH was observed after washing, with a reduction from 6.7 to 3.0. This may be due to the low pH of the washing agent, which resulted in a significant concentration of H⁺ remaining in the soil after washing, thereby causing soil acidification. The Electric conductivity (EC) of soil exhibited a slight increase after washing, which may be attributed to the residual presence of a portion of the AA-ILs in the soil. This residual ionic compound would result in an elevated salt content in the soil. The OM in soil plays key role in soil formation and function, which serves as a vital indicator of soil fertility (Chen et al., 2020). The washing with [Ala][H₂PO₄] resulted in a small (2.7 %) increase in the OM content of the soil.

In addition, soil washing has effect on soil exchange properties. CEC, exchangeable calcium (Ex-Ca), and exchangeable magnesium (Ex-Mg) in soil are a significant indicator of soil fertility, enabling the assessment of the buffering capacity and fertilizer retention capacity of the soil. [Ala][H₂PO₄] washing had little effect on CEC in soil that decreased by 1.6 %, from 18.6 to 18.3 cmol/kg. This may be due to the low proportion of organic matter and clay particles present in the soil after washing. However, Ex-Ca content in the soil decreased from 6.8 to 3.3 g/kg (52.0 % reduction), and Ex-Mg content decreased from 0.4 to 0.1 g/kg (80.1 % reduction) after washing. The significant depletion of Ex-Ca and Ex-Mg in soil after washing may be attributed to the ability of H⁺ present in the washing agent to displace Ca²⁺ and Mg²⁺ from soil colloids.

Nitrogen (N), phosphorus (P) and potassium (K) in soil are important sources of nutrients for plant growth. In general, our soil washing resulted in an increase in the content of essential nutrients, with a notable rise in the levels of N and P. Conversely, the K content exhibited a slight decline. In detail, after washing with [Ala][H₂PO₄], Total nitrogen (TN) content in soil increased from 0.8 to 1.3 g/kg (63.6 % increase). Total phosphorus (TP) content in soil nearly doubled, from 1.9 to 3.9 g/kg. Available phosphorus (AP) content in soil increased by nearly three times, from 70.9 to 285.5 mg/kg. This is likely a consequence of the fact that [Ala][H₂PO₄] residuals provide N and AP to the soil. In contrast, after washing with [Ala][H₂PO₄], the content of total potassium (TK) and available potassium (AK) in soil decreased by 23.5 % and 21.1 %, respectively. Potassium predominantly occurs in soil in inorganic forms, including insoluble K and readily extractable substitutable K (adsorbed by soil colloids). The latter forms can be readily extracted by washing agents and, additionally, acidic [Ala][H₂PO₄] may facilitate the dissolution of some insoluble K forms.

Mineral elements such as Ca, Mg, Mn, and Fe were partially lost from the soil after washing with [Ala][H₂PO₄]. Their respective concentrations decreased from 86.0 to 34.3 g/kg, from 40.3 to 36.6 g/kg, from 0.8 to 0.4 g/kg, and from 33.7 to 26.6 g/kg. This may be attributed to the complexation of [Ala][H₂PO₄]. During the washing process, both target element (As) and the non-target elements (Ca, Mg, Mn, Fe) will complex with IL, resulting in the loss of the Ca, Mg, Mn, and Fe along with As. In addition, the massive loss of Ca may be due to the acidic nature of [Ala][H₂PO₄], which dissolve soil CaCO₃ and extract Ca²⁺ in the water phase. The loss of Mn and Fe may be due to a combination of acidic dissolution and complexation, the latter typically involving carboxyl, amino, and sulfhydryl groups in the washing agents (Rahman et al., 2022).

In general, the soil type remained unaltered after washing, with an increase in nutrient and organic matter content. However, a decrease in pH and loss of mineral elements were observed. This has no obvious impact on the remediation of contaminated sites. Nevertheless, when the washing agent is applied to the remediation of contaminated soil in farmland, alkaline substances can be added to adjust the pH value to neutral in order to facilitate plant growth (Wang et al., 2020). Additionally, the incorporation of mineral fertilizer may be beneficial to improve the performance of soil washing (Wang et al., 2016).

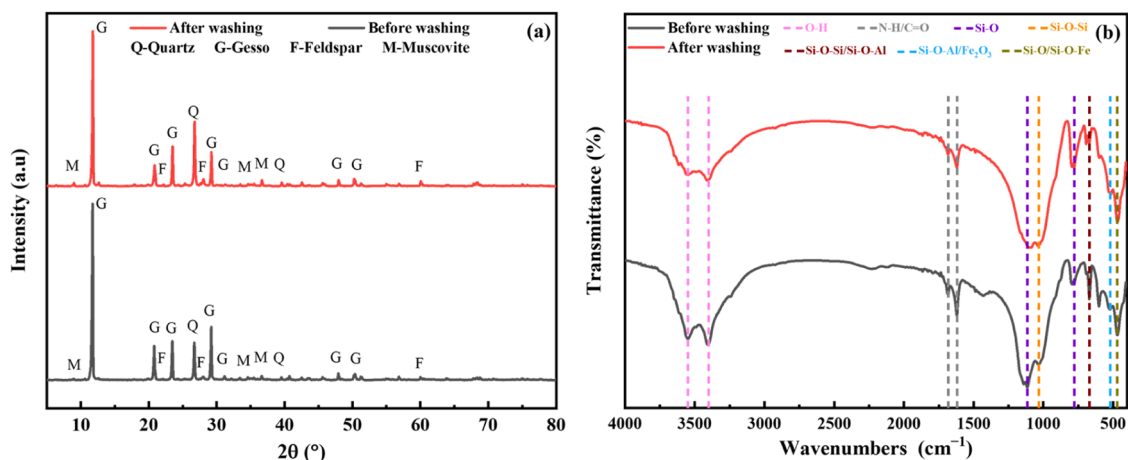


Fig. 5. XRD spectra (a) and FT-IR spectra (b) of soil before and after washing with [Ala][H₂PO₄] at a concentration of 1.0 mol/L, a liquid-soil ratio of 4:1 and a washing time of 480 min.

3.4.3. Mineral composition of soil

The use of commonly employed washing agents, such as EDTA, can result in the dissolution of soil minerals, which in turn affects their composition (Jelusic and Lestan, 2014). Therefore, XRD was used to analyze the effect of soil washing with $[\text{Ala}][\text{H}_2\text{PO}_4]$ on

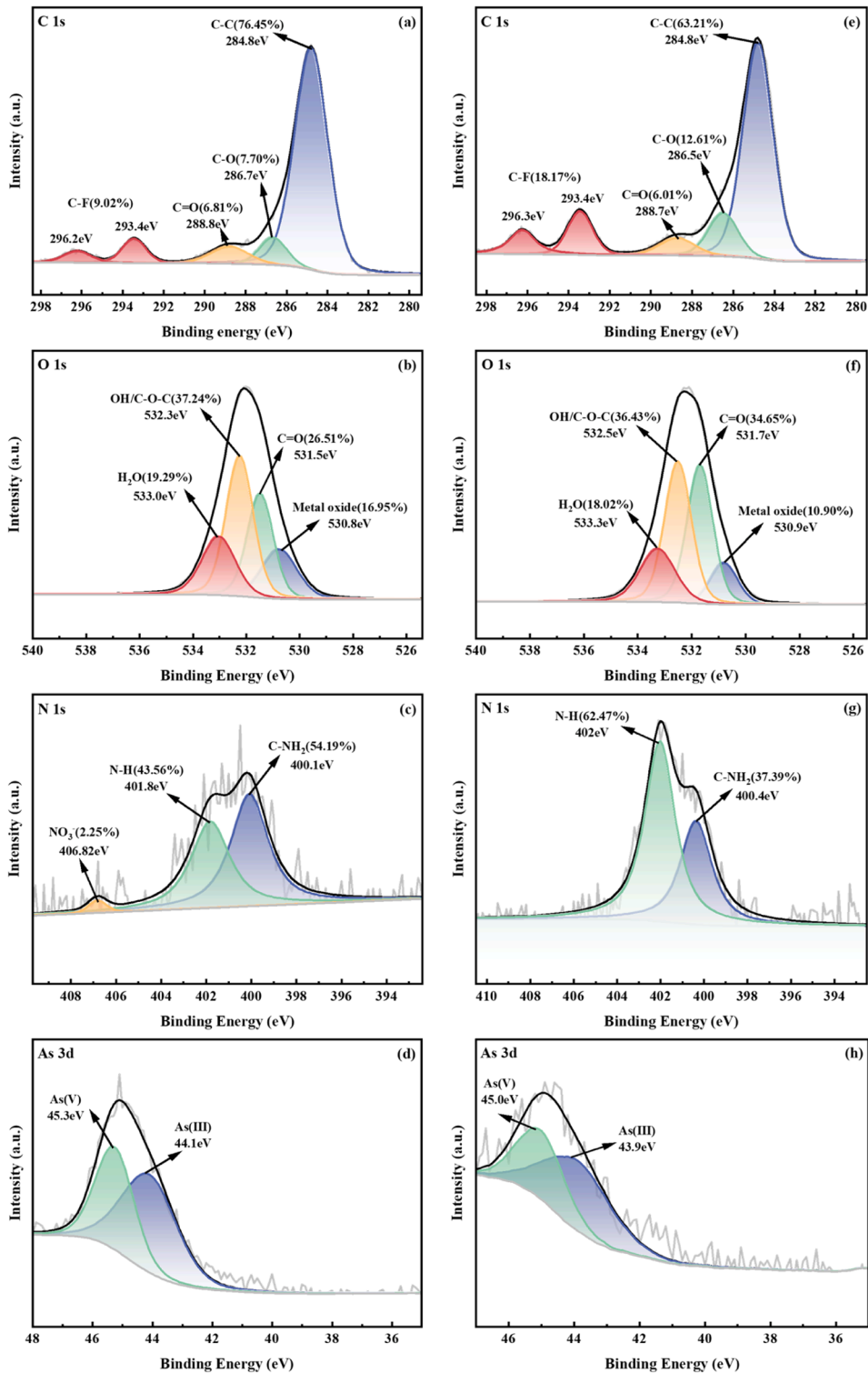


Fig. 6. High-resolution XPS spectra of the C 1s, O 1s, N 1s, and As 3d for soil before (a-d) and after washing (e-h) with $[\text{Ala}][\text{H}_2\text{PO}_4]$ at a concentration of 1.0 mol/L, a liquid-soil ratio of 4:1, and a washing time of 480 min.

mineral composition of soil, as shown in Fig. 5a. The characteristic peak at 11.72° and the accessory peaks at 20.80° , 23.48° , 29.20° , and 47.92° of As-contaminated soil before washing indicate the presence of gypsum. Moreover, the characteristic peak of 26.72° and the accessory peak at 40.38° indicates the presence of quartz. In addition, there were small amounts of muscovite (8.92° , 35.06° , 36.64°) and feldspar (22.20° , 27.89° , 60.04°). The positions of the corresponding peaks in the soil after washing did not undergo a notable change in comparison to those observed before washing. Additionally, no new minerals were identified, suggesting that the mineral composition of the soil remained largely unaltered by washing (Tang et al., 2017). However, a decrease in the peak intensity of gypsum was detected in the soil after washing, suggesting that gypsum was partially dissolved during the washing process (He et al., 2023; Wei et al., 2016).

3.4.4. Functional groups in soil

To further investigate the changes in soil functional groups during washing, FT-IR analysis was carried out on the soil before and after washing by [Ala][H₂PO₄], as shown in Fig. 5b. The analysis of As-contaminated soil revealed significant absorption peaks at the following wavenumbers (cm⁻¹): 3549, 3406, 1684, 1620, 1115, 1034, 780, 671, 522, and 470. The absorption peaks at 3549 and 3406 cm⁻¹ were indicative of O-H stretching vibrations in adsorbed water, hydroxyl, and carboxyl groups (Parolo et al., 2017). The change in peak shape after washing indicates the possibility of ion exchange between As-O and H⁺, or the formation of coordination bonds between O-H and As (Xu et al., 2024). The absorption peaks at 1115–470 cm⁻¹ were attributed to the Si-O, Si-O/Si-O-Fe, Si-O-Si, and Si-OAl/Si-O minerals in soil. Variations in the location and intensity of these peaks may indicate the dissolution of metal-silicon oxides (Kim and Baek, 2015). The vibrational peak of Si-O at 1115 cm⁻¹ shifted to 1089 cm⁻¹ and the peak intensity of Si-O-Al/Si-O-Si at 671 cm⁻¹ weakened after washing, indicating that partial dissolution of minerals in soil caused by [Ala][H₂PO₄] washing may be associated with As removal. However, the XRD results showed that there was no significant change in soil mineral composition after the washing process. This may be attributed to the fact that [Ala][H₂PO₄] solely dissolved amorphous minerals, whereas the dissolution of crystals was meager.

3.4.5. Elements chemical form and content in soil

XPS analysis was performed on the soil before and after washing, as shown in Fig. S2. The full spectrum analysis revealed the presence of C 1 s, O 1 s, N 1 s, Mg 1 s, Na 1 s, Fe 2p, K 2p, Ca 2p, Al 2p and Si 2p in the soil samples, both before and after washing. In particular, the As-contaminated soil exhibited the presence of S 2p before washing. However, the S-2p signal was no longer detected after washing, although P 2 s was appeared. This may be due to S loss during the washing process, while P would be contributed by residual [Ala][H₂PO₄] on the soil surface.

As shown in Fig. 6, the fitting results of C 1 s and O 1 s suggest that the soil contained C-C, C-O, C=O, C-F, Al(Si)-OH, C-O-C and other bonds, as well as metal oxides. This finding would suggest the presence of significant amounts of carbonates in the soil (Khan et al., 2019). The increase in C-C and C-O content in the soil after washing may be due to the fact that [Ala][H₂PO₄] contains a considerable amount of C-C and C-O bonds, some of which remained on the soil surface after washing. In addition, the proportion of metal oxides in the soil after washing with [Ala][H₂PO₄] decreased as consequence of acid dissolution.

The fitting results of N 1 s showed that the soil before washing contained C-NH₂, N-, and NO₃⁻. The content of N-H in the soil after washing by [Ala][H₂PO₄] increased from 43.6 % to 62.5 %, indicating that the amino group of [Ala] remained in the soil. Conversely, the content of C-NH₂ decreased from 54.2 % to 37.4 %, which may be attributed to the formation of chemical bonds between -NH₂ and the soil metals. Moreover, the soil NO₃⁻ content decreased significantly, suggesting that a large amount of water-soluble NO₃⁻ entered the washing solution, coherently with the FT-IR results. According to the data of soil physicochemical properties, the total nitrogen content in the soil increased after washing, indicating that the residual [Ala][H₂PO₄] did more than offset the NO₃⁻ loss. The As 3d fitting peaks were identified as As (III) (43.9–44.1 eV) and As (V) (45.0–45.3 eV), respectively, indicating that the soil contained As (III)-O and As (V)-O (Fan et al., 2014). The reduction in As 3d binding energy observed in the soil after washing may be due to the deviation of the lone pair electrons of -COOH and -NH₂ to the metal orbit, resulting in an increase in the electron cloud density (Wang et al., 2020). This observation suggests the occurrence of interactions between As and the -COOH and -NH₂ groups of [Ala].

4. Conclusions and perspectives

This study investigated the potential of AA-ILs as washing agent in the remediation of As-contaminated soil. The main conclusions are as follows:

- (1) Among the tested AA-ILs, [Ala][H₂PO₄] exhibited the highest As removal efficiency. Specifically, a 90.1 % removal efficiency was achieved when using a 1.0 mol/L solution of it at a liquid-soil ratio of 4:1 and after a washing time of 480 minutes. And the content of all forms of As was significantly reduced.
- (2) After washing, the soil type remained unaltered. The pH value and the contents of metal oxides and amorphous minerals decreased, whilst the content of organic matter and nutrient elements increased.
- (3) The removal of As by [Ala][H₂PO₄] washing was consistent with a second-order kinetic model, with the main mechanisms identified as acid dissolution, ion exchange, and coordination.

This study tentatively proved that AA-ILs show considerable potential to be used as a green washing agent to remove heavy metals from contaminated soils with high efficiency. However, substantial efforts are still required before their practical application in the future. Firstly, it is necessary to optimize the operating conditions and washing methods tailored to specific soil types. Secondly, the

recyclability and reusability of the IL need to be explored. Additionally, appropriate treatment measures should be devised for both the post-washing water and the generated sludge.

From an economic perspective, although the required concentration of AA-ILs as well as solid-liquid ratio is lower than the conventional washing agents, which implies a smaller reactor size and diminished wastewater generation, thus conferring certain cost advantages in these respects, it remains an irrefutable fact that the price of AA-ILs still eclipses that of conventional washing agents with an equivalent weight. Consequently, procuring amino acids of relatively inferior purity via the hydrolysis of organic waste might potentially present a viable remedy to alleviate the problem of exorbitant costs.

CRedit authorship contribution statement

Fu Lin: Writing – original draft, Methodology, Investigation. **Wang Sheng:** Writing – original draft, Methodology, Investigation. **Deng Yun:** Writing – review & editing, Supervision, Resources, Project administration, Conceptualization. **Zhang Changbo:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Xue Weijie:** Resources, Methodology, Conceptualization. **Deng Jiawei:** Investigation. **Luo Xin:** Investigation. **Liu Yuyao:** Investigation. **Mailhot Gilles:** Writing – review & editing. **Vione Davide:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.eti.2025.104060](https://doi.org/10.1016/j.eti.2025.104060).

Data availability

Data will be made available on request.

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