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Remediation of molybdenum(VI) contaminated soil by iron sulfide nanoparticles: mechanism and influencing factors

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ABSTRACT

Although iron sulfide (FeS) has been used to remove heavy metals from the environment, its capability for remediation of molybdenum (Mo) contaminated soil and some important influencing factors are still unclear. The purpose of this study was to investigate whether soil Mo(VI) contamination could be immobilized by using nano-FeS. The effects of FeS dosage, natural organic matter (NOM), and inorganic salts on soil Mo(VI) immobilization properties were compared and analyzed. The results showed that the addition of FeS significantly reduced the leaching of Mo in the soil. The amount of Mo leaching dropped from 87.66 to 2.20 mg/L when the molar ratio of FeS to Mo(VI) increased from 1:1 to 50:1. It was discovered that the major two mechanisms for the immobilization of soil Mo(VI) by FeS were adsorption and reduction. Soil Mo leaching was promoted with the existence of NOM, but the addition of SO_4^{2-} and $H_2PO_4^-$ prevented soil Mo(VI) leaching. Mo leaching from soil that was polluted with Mo(VI) and included humic acid, salicylic acid, SO_4^{2-}, or $H_2PO_4^-$ was reduced by 116.41–77.54 mg/L, 116.41–112.72 mg/L, 116.41–72.45 mg/L, and 116.41–84.39 mg/L, respectively, after FeS treatment. Meanwhile, the cabbage mustard growth experiments findings indicated that FeS particles have a significant field application potential for Mo(VI) contaminated soil remediation due to their high Mo(VI) immobilization efficiency.

Keywords: FeS particles; Mo(VI)-contaminated soil; Adsorption; Reduction; Phytotoxicity

1. Introduction

The rapid development of industry has led to the production and release of hazardous effluents into the environment. Heavy metal soil pollution is a severe environmental issue that affects industrialized countries [1]. Metal contaminants are concerning due to their toxicity, frequency, and presence in the environment. As heavy metals cannot be degraded and have physiological effects on living creatures, they are considered important even at trace concentrations [2]. Heavy metal molybdenum (Mo) is not only an essential nutrient for the survival of animals and plants but also a very

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important strategic resource. It also has been widely used in electronics, lighting, aerospace, machinery manufacturing, and other fields due to its good conductivity, thermal conductivity, wear resistance, and other characteristics [3]. The annual global usage of molybdenum is estimated to be about 230,000 metric tons [4]. It is worth noting that a large amount of Mo effluents from mining tailings without any pretreatment have caused serious pollution to some mining areas and farmland soils (Table 1). Previous studies revealed that, compared to the background content of 2.0 mg/kg for Mo in soils, the total Mo concentration of agricultural fields near a Mo mining site in China ranged from 3.3 to 325 mg/kg [5]. Besides, the Mo(VI) concentration in soil of other countries is also as high as 430 mg/kg [6]. Long-term intake of high concentrations of Mo will result in aquatic life mortality, hypothyroidism, liver and kidney problems, and growth retardation [7]. The development of efficient and cost-effective Mo(VI) contaminated soil immobilization technology has become a top priority to ensure human health and sustainable agricultural development in light of the rising reports of Mo pollution incidents, particularly in the farmland surrounding many Mo mining areas in China [8].

At present, the remediation methods of heavy metal pollution in soil mainly include leaching, electric remediation, adsorption, guest soil, phytoremediation, and immobilization remediation, among which the immobilization remediation method has attracted extensive attention because of its strong operability and low implementation cost [12–15]. Besides, Mo(VI) in the soil is mainly present in the form of positive hexavalent molybdenum acid ions (MoO_4^{2-}), which is between Zn(II) and Cr(III) compounds in toxicity and is relatively stable in the environment but easily ingested by living things [16]. Therefore, reducing Mo(VI) to low-cost state Mo and fixing it by adsorption or complexation is an ideal way to control soil Mo(VI) pollution. Natural reductants such as Fe(II)-bearing minerals can convert Mo(VI) into Mo(V) or Mo(IV) under an anoxic environment [17]. The slow reduction kinetics of these natural processes, however, fall short of the requirements for soil remediation [18].

Iron sulfide (FeS) is a natural reducing mineral that widely exists in soil, river sediment, underground water, and coastal waters [19]. Its unique molecular structure and surface chemical properties are crucial for the adsorption, immobilization, and transformation of various heavy metals (Se, Hg, As and etc.) and inorganic oxyanions in reducing environments [20–23]. For example, Han et al. [24] found that the mechanism of As(III) removed by FeS was chemical precipitation at pH 5, while surface adsorption was the main driving force when the pH value was higher than 6. Besides, compared with macroparticles, nano-FeS with stronger reducibility, higher activity, and the larger specific surface has greater application potential to reduce the heavy metal ions from aqueous solutions [19]. Lian et al. [25] found that nano-FeS played an important role in the migration and conversion behavior of Mo(VI) in water under anaerobic conditions, which indicated that the remediation of soil Mo(VI) pollution by nano-FeS is theoretically feasible. Additionally, a large number of natural organic matter (NOM) and inorganic anions that existed in the soil will interact with heavy metals, thus affecting the immobilization effect of heavy metals. Both salicylic acid, a small molecule phenol typically found in plants, and humic acid, a natural organic substance, are extensively distributed in nature and will react in different ways with heavy metals in the soil [26,27]. Besides, some competing anions such as $H_2PO_4^-$ and SO_4^{2-} are also common in soil. However, the influential mechanism of the above typical NOM and inorganic anions on soil Mo(VI) remediation remains unclear.

In view of the above, a group of experiments using nano-FeS was conducted to remediate Mo(VI)-contaminated soils. Firstly, the influence of FeS dosage on Mo leaching in soil was analyzed. Secondly, the effect of NOM and inorganic anions on the immobilization of Mo in soil by nano-FeS was investigated. Thirdly, the toxic effect of nano-FeS remediated Mo(VI)-contaminated soil on cabbage mustard was evaluated.

2. Materials and methods

2.1. Materials

Sodium molybdate 2-hydrate ($Na_2MoO_4·2H_2O$) was used to prepare 1,000 mg/L Mo(VI) stock solution, which would be further diluted to the required concentration. Sodium sulfide ($Na_2S·9H_2O$) was purchased from Aladdin Reagent Co., Ltd., (Shanghai, China). Ferrous chloride ($FeCl_2$) was provided by Alfa Aesar-A Johnson Matthey Company (MA, USA). Other chemicals such as sodium hydroxide and hydrochloric acid were of analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China). The deionized water (18.2 MΩ·cm) was autoclaved at 394 K for 20 min, and then purged with high purity N_2 (99.999%) for at least 30 min to remove the oxygen before use. Reagents were stored under nitrogen and used as purchased.

Table 1
Soil pollution condition of Mo(VI) in different parts of the world

Region	Soil properties	Mo content (mg/kg)		Literature source
		Mean	Maximum	
Luanchuan County, Henan	Mining soil	28.19	343	[9]
Lake Baikal	Residential areas	223	420	[6]
	Relaxation area	293	430	
Yerevan	Urban soil	2.6	421	[10]
Hulunbuir	Natural pasture soil	1.53	3.77	[11]

The raw soil samples were collected from a farm in Maanshan City, China. The Mo(VI)-contaminated soil was prepared by adding $Na_2MoO_4·2H_2O$ into raw soil samples following the procedure reported by Wang et al. [28]. The concentrations of Mo(VI) in soil were 500 mg/kg. The soil was sieved with a standard 2 mm sieve after air drying and then characterized for physicochemical properties. Raw soil had a pH of 6.35 and a water content of 25.62%. The raw soil contains 0.57% of organic carbon and was initially free of Mo(VI). The soil was a yellow-brown earth with 69.9 wt.% SiO_2, 16.76 wt.% Al_2O_3, 5.51 wt.% Fe_2O_3, 2.34 wt.% K_2O, 1.47 wt.% Na_2O, 1.39 wt.% MgO and 1.06 wt.% CaO. Cabbage mustard seeds were obtained from the Jiangyang Ecological Agriculture Co., Ltd., (Yangzhou, China).

2.2. Synthesis and characterization of FeS

FeS was synthesized by mixing $FeCl_2$ and Na_2S under N_2 (99.99%) protection in a three-necked flask according to the method described by Li et al. [29] with minor adjustments. In brief, 250 mL of 0.2 M Na_2S was slowly added into 250 mL of 0.2 M $FeCl_2$ in a container equipped with a magnetic stir plate. After aging for 3 d, black nanoparticles were collected and washed three times with nano pure water. The freshly prepared FeS was stored in ethanol at 277 K to prevent its oxidation. The particles were dried in a vacuum oven for 1 d prior to their further use and characterizations. The surface composition and morphology were investigated by transmission electron microscopy with an energy-dispersive X-ray (TEM-EDS) system at 15 kV (FEI Talos F200S). The specific surface area, pore size, and pore volume distribution of the specimens were measured by N_2 adsorption–desorption isotherms using Brunauer–Emmett–Teller (BET, 3H-2000PS2, Bershide Instrument, China).

2.3. Effect of remediation conditions: FeS dosage, NOM and inorganic salts

A series of shake flask tests were conducted to investigate the effects of remediation conditions according to the method described by Gao et al. [30]: the dosage of FeS particles, NOM, and inorganic salts in soil samples. 5 g of Mo(VI)-laden soil samples were placed in 20 mL brown glass bottles and then mixed with 15 mL of FeS solution with corresponding concentrations. To test the effect of FeS dosage on Mo(VI) immobilization effectiveness, a range of FeS:Mo(VI) molar ratios (1:1, 5:1, 10:1, 20:1, 30:1, 40:1 and 50:1) were tested. The mixtures were rotated (150 rpm) at 23°C ± 2°C for 1, 3, and 6 d, respectively. Ather centrifugation for 10 min at 3,000 r/min, the supernatant was filtered through a 0.45 mm filter membrane. The filtrates were preserved with HNO_3 for further Mo(VI) analysis. The reacted soil samples were freeze-dried and then stored for Mo morphology testing. A control test was conducted without FeS particles added in the system. Three parallel tests were conducted for all tests.

To assess the effect of soil NOM and inorganic salts, experiments were carried out at the molar ratios of salicylic acid, NaH_2PO_4, and Na_2SO_4 to Mo(VI) were 0.5:1, 1:1, 3:1, 5:1, 10:1, respectively. The mass ratios of humic acid to Mo(VI) were 0.5%, 1.0%, 2.0%, 3.0%, and 5.0%, respectively. The above tests were conducted with 5 g soil containing 500 mg/kg Mo(VI). The experimental procedures were similar to the effect of FeS dosage except for the fixed treatment period of 7 d and the desired remediation conditions. Three parallel tests were conducted for all experiments.

2.4. Cabbage mustard growth

The cabbage mustard growth experiments were conducted to estimate the effects of FeS on the growth of cabbage mustard seedlings and the accumulation of Mo. Three soil samples Mo-free soil (C0), Mo-contaminated soil (C1), and FeS-treated soil (C2) were used for the experiments as a comparison. The specific procedure of cabbage mustard growth experiments was as follows: 2 kg of Mo(VI)-contaminated soil (500 mg/kg) was packed into nine plastic flower pots (diameter 20 cm, depth 25 cm). 15 cabbage mustard seeds were sown in each flower pot. The flower pots were then placed in a growth chamber. Three parallels were conducted in the above tests. The germination of seeds was recorded during plant growth. After 20 d of growth, the seedlings were harvested and washed with deionized water. The leaves, stems, and roots were separated, measured, oven dried, and weighed for further use. The length and dry weight of each part was recorded. The total Mo content of dried roots, stems, and leaves was analyzed. The seedlings were raised and prepared using the techniques described by Wang et al. [31].

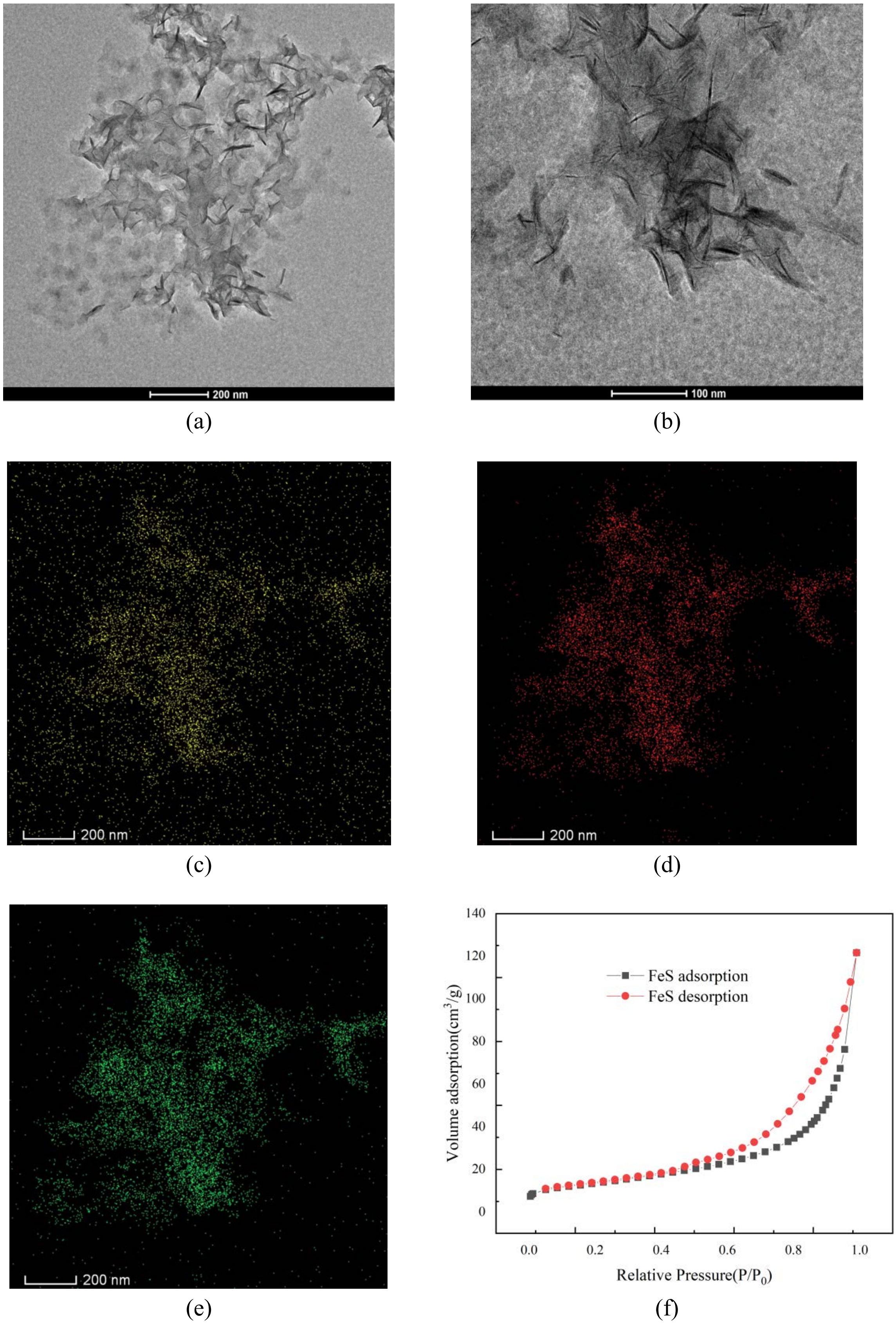
2.5. Analyses

To selectively separate Mo(V) from Mo(VI), the tartrate solution was added into the samples to complex with Mo(V). Mo(V)-containing complexes were removed by passing the solutions through poly-prep columns with Amberlite XAD 7HP resins [32] followed by elution with acidic acetone. Mo(V) in the elute and remaining Mo(VI) in the samples were analyzed using a flame atomic absorption spectrometer (PinAAcle 900T, PerkinElmer, USA). Molybdenum morphology in soil was tested using sequential extraction procedures developed by Tessier et al. [33]. All data were expressed as means plus or minus one standard deviation. Data were analyzed using Microsoft Excel 2010, and figures were plotted using Origin 2016, version 9.3. The mean values in all treatment groups were compared using one-way analysis of variance (ANOVA) of the SPSS version 19.0.

3. Results and discussion

3.1. Study on passivation of Mo(VI) by FeS in soil

As shown in Fig. 1a and b, FeS has a needle cluster-like amorphous structure, which is relatively scattered. The particle size of FeS is very small. The elemental surface scan analysis showed that the contents of O, S, and Fe elements in nano-FeS were 36.52%, 32.97%, and 30.51%, respectively (Fig. 1c–e). Fig. 1f showed that the adsorption isotherm conforms to the second type model in the Brunauer, Deming, Deming and Teller categories [34,35], that is, the surface of the large porous solid is reversibly adsorbed by



(a) (b)

(c) (d)

(e) (f)

Fig. 1. TEM images (a) 200 nm scale, (b) 100 nm scale, elemental maps (c) O, (d) S and (e) Fe, and N_2 adsorption–desorption isotherms images (f) of FeS.

multiple layers. The specific surface area of FeS was calculated as 47.92 m^2/g. The average pore size of FeS was 92.60 Å, and the total void volume was 0.19 cm^2/g.

The amount of Mo that leached at different molar ratios of FeS and Mo(VI) steadily reduced as reaction time increased (Fig. 2). The higher FeS concentration, the smaller Mo was leached. After the reaction for 6 d, the concentration of Mo in the aqueous phase was 117.60 mg/L, and the concentration of Mo(VI) in the aqueous phase corresponding to FeS and Mo molar ratios of 1:1 and 50:1 was 87.66 and 2.20 mg/L. Statistical analysis results showed that there was no significant difference between the leaching amount of Mo and the control group without the addition of ferrous sulfide, and the ratio of ferrous sulfide to molars was 1:1 ($P > 0.05$). There was also no significant difference in Mo leaching when the molar ratio of FeS and Mo was 30:1–50:1 ($P > 0.05$). These showed that either an excessively low or excessively high FeS dosage has no discernible impact on soil Mo leaching. In this study, the average partition coefficient K_d is used to reflect the relative affinity of FeS for Mo, which refers to the ratio of the concentration of components in the solid and liquid phases at a certain temperature when the reaction reaches equilibrium. The values of K_d reflect the migration capacity and separation efficiency of the solute in the two phases, and it is an important characteristic parameter to describe the behavior of the substance in the two phases [21,36]. As shown in Eq. (1):

$$K_d = \frac{q}{C} \tag{1}$$

where q and C are the concentration of Mo in the solid-phase (mg/kg) and the concentration of Mo in the mobile phase (mg/L), respectively.

Table 2 shows that K_d increases as FeS concentration rises, and in the reaction system the K_d value of the FeS to Mo molar ratio of 50:1 is roughly 54 times that of the FeS-free group. It is evident that the immobilization of Mo(VI) in the soil is greatly improved by the addition of FeS.

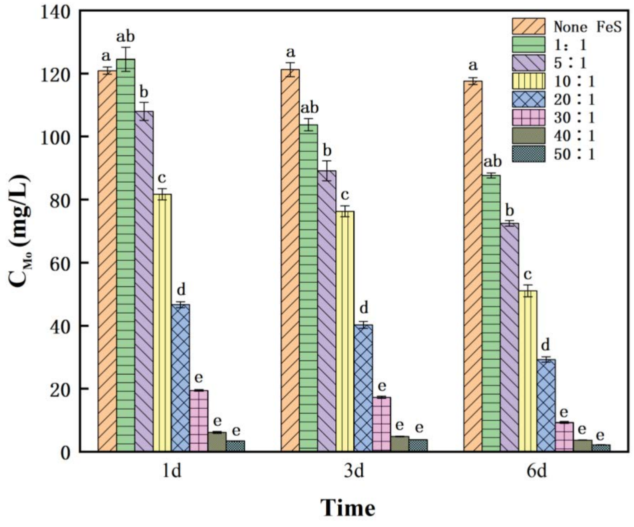


Fig. 2. Influence of FeS dosage on Mo leaching in soil (different lowercase letters indicate that different FeS dosing amounts differ significantly in Mo leaching ($P < 0.05$)).

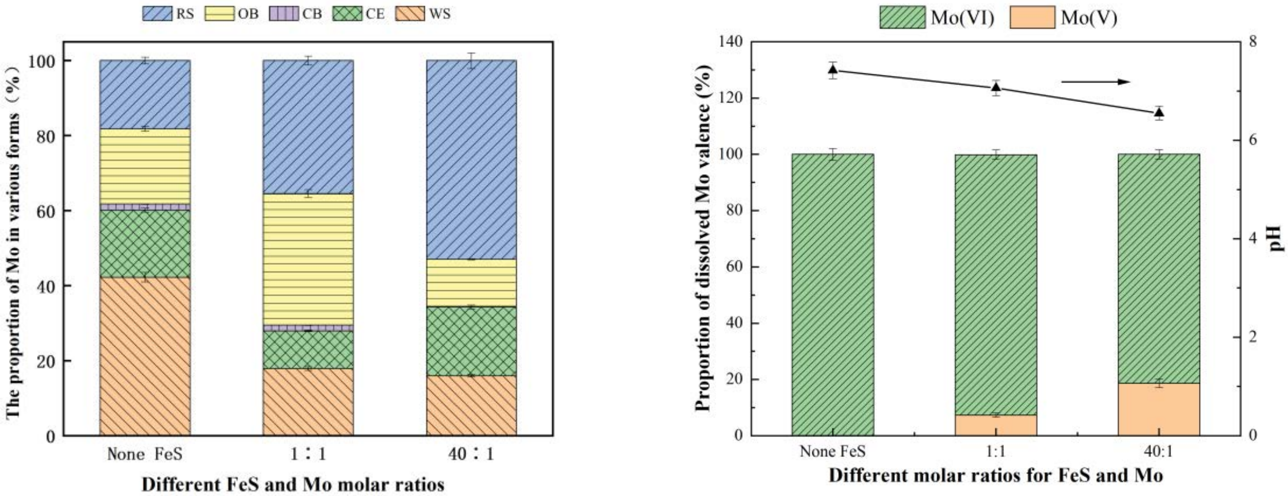
3.2. Immobilization mechanism of Mo(VI) by FeS in soil

The sequential extraction procedures developed by Tessier et al. [33] were used to quantify the fraction of the various Mo species. According to the relative availability of soil-bound heavy metals, Mo species can be divided into five fractions which have been defined as water-soluble (WS), cation-exchanged (CE), carbonate-bound (CB), organically bound (OB), and residual (RS). The degree of difficulty of water dissolution in molybdenum form ranges from easy to difficult: WS > CE > CB > OB > RS. Among them, the immobilization of WS, CE, and CB are relatively poor, while the immobilization of OB, especially the RS, is stronger. Mo species in none FeS were water-soluble (WS, 42.26%), cation-exchanged (CE, 17.86%), carbonate-bound (CB, 1.63%), organically bound (OB, 20.08%) and residual (RS, 18.17%). Compared with that none FeS, in the soil samples with a molar ratio of 1:1 and 40:1 between FeS and Mo(VI), the proportion of RS increased with the increase of FeS concentration, while WS was the opposite. In the soil sample with FeS to Mo(VI) molar ratio of 40:1, the proportion of residual Mo was 52.93%, and the proportion of water soluble state was decreased to 15.94%. As can be seen from Fig. 3b, the valence state of soil supernatant Mo(VI) without FeS has not changed, and the addition of FeS is conducive to the reduction of soil Mo salt. When the molar ratio of FeS and Mo(VI) increased from 1:1 to 40:1, the relative content of Mo(V) in the soil supernatant after the reaction increased from 7.43% to 18.65%, and since the valence states of Mo(V) were ineffective for plants [7], the addition of FeS could significantly reduce the content of soil available Mo, thereby alleviating the biotoxicity of soil Mo.

To further analyze the valence changes of residual Mo, the concentrations of Mo with different valences were tested. The results showed that the relative content of Mo(VI) decreased with the increase of FeS dosage, which indicated that the removal of Mo(VI) by FeS was mainly through adsorption and reduction. This may be related to the change of pH in the reaction system. It is reported that the reaction process of Mo(VI) and FeS under different pH conditions is different [25]. Under acidic conditions, Mo(VI) is rapidly adsorbed on the surface of FeS and reduced to Mo(V)

Table 2
Average partition coefficient of Mo(VI) in solid-phase and aqueous phase under different molar ratio of nano-FeS to Mo(VI)

FeS to Mo(VI) molar ratio	C (mg/L)	K_d (L/kg)
0 (None FeS)	117.60	4.24
1:1	87.66	5.69
5:1	72.44	6.89
10:1	51.07	9.77
20:1	29.27	17.07
30:1	9.25	54.01
40:1	3.69	135.33
50:1	2.20	227.54



(a) (b)

Fig. 3. Morphology analysis of Mo in soil (a) and the valence analysis of Mo in soil supernatant (b).

and Mo(IV)-related species. Wang et al. [37] also reported that Mo(VI) is retained in anoxic deposits by reduction to $Mo^VO_xS_y$ and MoS_2 in an acidic environment [Eq. (2)]. Under neutral conditions, the increase of OH^- concentration reduces the reducing ability of FeS, so it is not conducive to the transformation of Mo(VI) to MoS_2 [Eq. (3)]. However, the reductive transformation extent of Mo(VI) into Mo(V) decreased as the pH increased, which may be due to partial deactivation of active sites resulting from precipitation of iron oxy-hydroxide on the surface of FeS [Eqs. (4) and (5)] [38]. It can be seen from Fig. 3b that with the increase of FeS dosage, the pH of the reaction system gradually decreases, which is more conducive to the reductive removal of Mo(VI).

$$\mathrm{Mo}\left(\mathrm{VI}\right)+\mathrm{Fe}^{2+}+\mathrm{HS}^{-}+\mathrm{H}^{+}\rightarrow\mathrm{MoS}_2+\mathrm{Mo}^{V}\mathrm{O}_X\mathrm{S}_Y+ \\ \mathrm{Fe}^{3+}+\mathrm{S}_2^{2-}+\mathrm{H}_2\mathrm{O} \tag{2}$$

$$\mathrm{MoO}_4^{2-}+\mathrm{FeS}\rightarrow\mathrm{Mo}^{V}\mathrm{O}_X\mathrm{S}+\mathrm{Fe}^{3+}+\mathrm{S}_2^{2-} \tag{3}$$

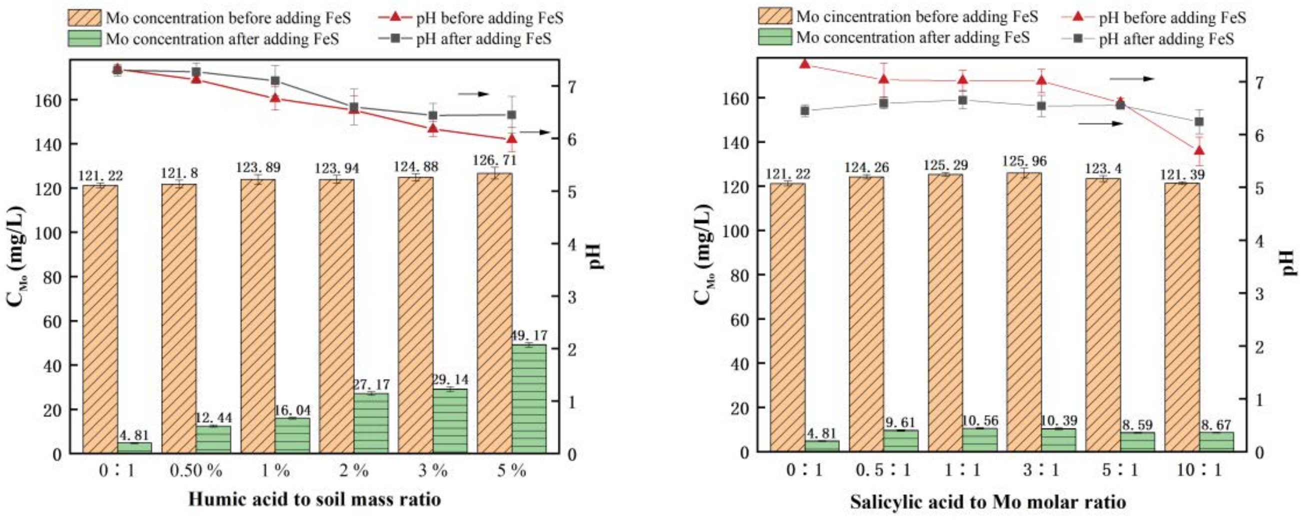
$$2\equiv\mathrm{Fe}-\mathrm{OH}+\mathrm{MoO}_4^{2}\leftrightarrow\left(\equiv\mathrm{Fe}\right)_2\mathrm{MoO}_4+\mathrm{H}_2\mathrm{O}+2\mathrm{OH}^{-} \tag{4}$$

$$\mathrm{MoO}_4^{2-}+\mathrm{FeS}+\mathrm{OH}^{-}\rightarrow\mathrm{Mo}^{V}\mathrm{O}_X\mathrm{S}_Y+\mathrm{FeOOH}+\mathrm{FeS}_2+\mathrm{H}_2\mathrm{O} \tag{5}$$

3.3. Effect of NOM on soil Mo(VI) immobilization

Heavy metals extensively exist in soil environments, and NOM plays a significant role in facilitating their migration and circulation [39]. As shown in Fig. 4a, both before and after FeS treatment, the Mo concentration in soil leachate increased along with the increase in humic acid content. When no FeS was added into the system, the Mo leaching amount of the treatment group with a humic acid specific gravity of 5% was significantly different from that of the control group ($P < 0.05$). Humic acid reduced the soil's pH, indicating that acidity may be a significant factor impacting Mo leaching. When FeS treated Mo-contaminated soil with humic acid, the Mo concentration in the leachate was significantly reduced, which further proved that FeS had a strong immobilization effect on Mo(VI) in the soil. However, under the same FeS addition, the Mo concentration of soil leaching solution was increased with the increase of humic acid concentration, and there are significant differences between the treatment group and the control group ($P < 0.05$), indicating that humic acid significantly inhibited the immobilization of Mo in the soil by FeS. From Fig. 4b, it can be seen that before and after FeS treatment, the Mo concentration of soil leaching solution was firstly increased with the increase of salicylic acid content and then decreased. Before FeS treatment, the Mo concentration of the leachable solution was significantly different from the control group at the ratio of salicylic acid to Mo molars from 0.5:1 to 3:1 ($P < 0.05$). The Mo concentration of the leachate after FeS treatment was significantly reduced, and the difference between the treatment groups and the control group was significant ($P < 0.05$). The presence of salicylic acid also reduces the soil pH, but the change of Mo concentration in the leachate is not consistent with humic acid, suggesting that the pH value is not only one of the effects of organic acids, and it may also be related to the complexation of organic acids on Mo, or the masking or activation of other adsorption sites [40,41].

The effect of FeS on soil Mo speciation in the presence of NOM was further investigated (Fig. 5). Compared with the FeS-free treatment, the WS was reduced from 42.26% to 15.94% after FeS treatment, and the RS was increased from 18.17% to 52.93%. FeS increased the content of steady-state Mo, which proved the immobilization effect of FeS on Mo in soil. Compared with the original soil, the addition of humic acid increased the WS from 42.26% to 49.90%, while salicylic acid increased CE from 17.86% to 27.17% and OB from 20.08% to 30.77%. In the FeS treatment group, the addition of NOM increased the proportion of WS and OB content in the soil and decreased the proportion of RS. This indicated that



(a) (b)

Fig. 4. Effect of humic acid (a) and salicylic acid (b) on the immobilization of Mo in soil by nano-FeS (different lowercase letters indicate that different organic acid dosages differ significantly in Mo leaching ($P < 0.05$)).

the organic acid may compete with Mo for the active site on FeS, or formed a film with less conductive conductivity on the surface of FeS, thereby weakening the reduction effect of FeS on Mo [42].

3.4. Effect of inorganic anions on soil Mo(VI) immobilization

Inorganic anions in the soil also play an important role in promoting the migration and circulation of heavy metals in soil. As can be seen from Fig. 6 that the addition of SO_4^{2-} or $H_2PO_4^-$ significantly reduced soil Mo leaching before FeS treatment ($P < 0.05$), which may be due to the formation of a complex between two anions and molybdate ion [43]. Besides, the Mo concentration of leachate in soil was significantly reduced after FeS treatment, which also indicated that FeS had a significant immobilization effect on Mo(VI) in soil. In addition, the soil pH decreased after the addition of FeS, which was beneficial to the immobilization of Mo(VI) in soil. However, pH is obviously not the only factor for immobilization of Mo(VI) in soil by FeS in the complex system with the addition of inorganic anions. The immobilization effect of FeS on Mo(VI) in soil decreased with the increase of SO_4^{2-} or $H_2PO_4^-$ concentration. This may be due to the internal complexes such as iron sulfate or iron phosphate precipitation may form on the surface of iron oxides with the increase of SO_4^{2-} or $H_2PO_4^-$ concentration [44], thus hindering the immobilization of Mo in the soil by FeS.

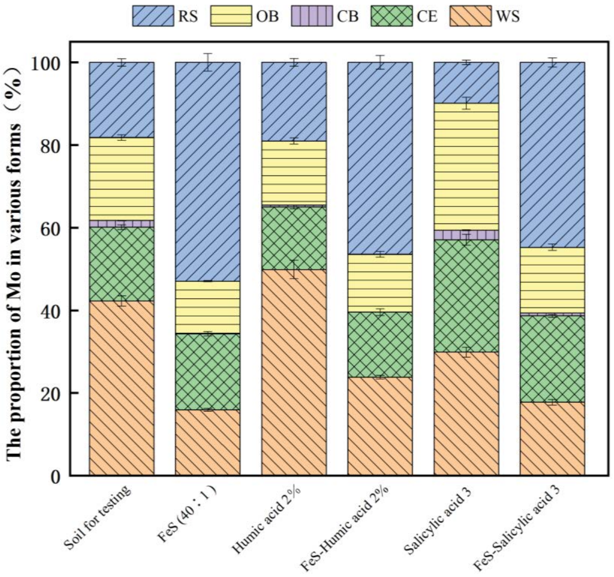
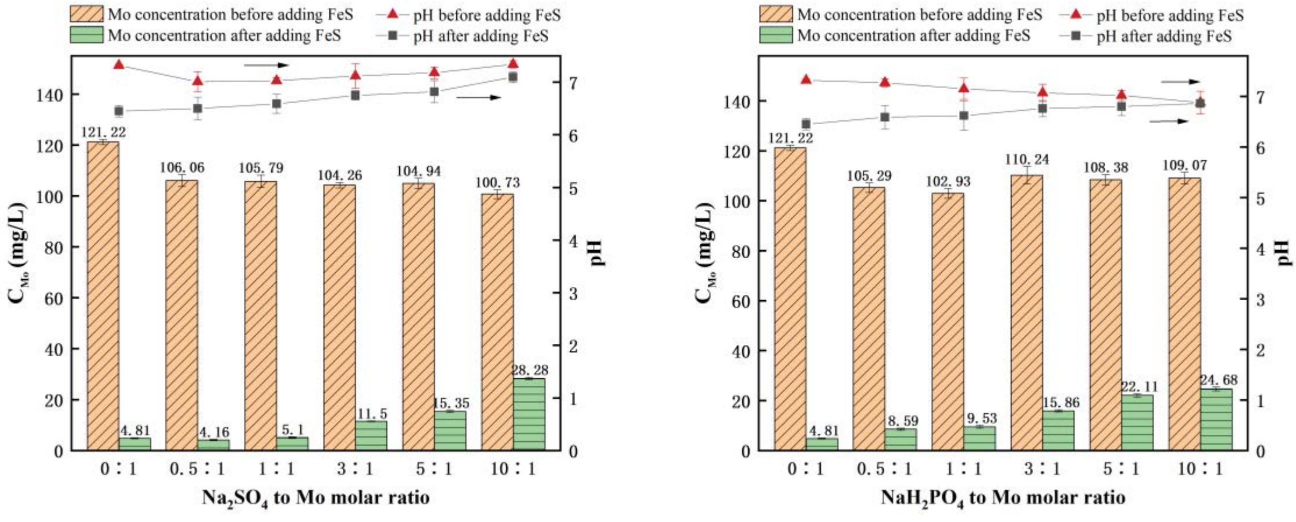


Fig. 5. Morphology analysis of Mo in soil (soil for testing means Mo-contaminated soil without FeS; FeS (40:1) means that the mole ratio of FeS to Mo(VI) is 40:1; 2% refers the mass ratio of humic acid to soil; 3 refers the molar ratio of salicylic acid to Mo(VI)).

The effects of two inorganic anions on Mo speciation were further investigated (Fig. 7). Compared to the original soil, the addition of SO_4^{2-} decreased the Mo content of both the WS and CE before the FeS treatment, while the Mo content of OB and RS increased, indicating that SO_4^{2-} inhibited the leaching of soil Mo. After the FeS treatment, the immobilization effect of Mo was further improved, and the residual Mo was increased from 25.0% to 50.52%. The effect of $H_2PO_4^-$ on soil Mo speciation was similar to that of SO_4^{2-}, $H_2PO_4^-$ reduced the Mo content of WS from 42.26% to 35.68%, indicating that $H_2PO_4^-$ can reduce the available Mo content. After FeS treatment, the residual Mo was increased from 19.22% to 34.74%. Compared with the FeS (40:1) treatment group, $H_2PO_4^-$ more than SO_4^{2-} inhibits the immobilization of FeS on soil Mo. Chen et al. [43] have shown that PO_4^{3-} was similar in structure to $HMo_7O_{24}^{5-}$, making it easy to compete with Mo for FeS surface sites. Therefore, HPO_4^{2-} and PO_4^{3-} formed by ionization of $H_2PO_4^-$ have strong ionic competitiveness, thereby inhibiting the adsorption and reduction of FeS on Mo [Eqs. (6) and (7)].



(a) (b)

Fig. 6. Effect of Na_2SO_4 (a) and NaH_2PO_4 (b) on the immobilization of Mo(VI) in soil by nano-FeS (different lowercase letters indicate that different inorganic anion dosing amounts differ significantly in molybdenum leaching ($P < 0.05$)).

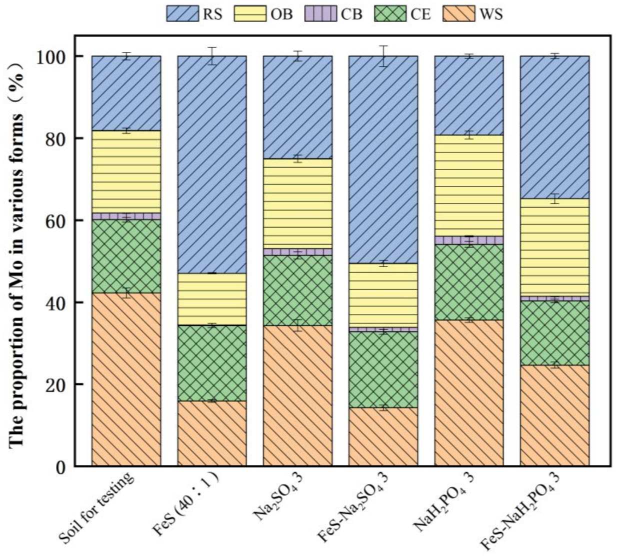


Fig. 7. Morphology analysis of Mo(VI) in soil (soil for testing refers to Mo(VI)-contaminated soil without FeS; FeS (40:1) refers to the mole ratio of FeS to Mo(VI); 3 refers to the molar ratio of inorganic anions to Mo(VI)).

$$H_2PO_4^- \leftrightarrow H^+ + HPo_4^{2-} \quad (6)$$

$$HPO_4^- \leftrightarrow H^+ + Po_4^{3-} \quad (7)$$

3.5. Plant growth and metal bioavailability

3.5.1. Effects on plant seedling growth

To determine the effect of the different treatments on plant growth, seedling growth and biomass production were measured. As shown in Fig. 8, the length of the root and stem of cabbage mustard grown in C0 were 38.52 and 34.93 mm, respectively. The growth of cabbage mustard in C1 (22.84 mm for the root and 27.15 mm for the stem) was obviously suppressed compared to that in C0. The length of the root and stem of cabbage mustard grown in C2 were 32.08 and 33.75 mm, respectively, which showed accelerated growth of the cabbage mustard compared to that in C1. The biomass of the root, stem, and leaf of cabbage mustard grown in C0 were 10.53, 21.53, and 37.92 mg, respectively. Compared with that in C0, the biomass of the root, stem and leaf in C1 decreased by 5.18, 6.59, and 9.83 mg, respectively. The biomass of the cabbage mustard plant grown in C0 was 10.53 mg for the root, 21.53 mg for the stem, and 37.92 mg for the leaf.

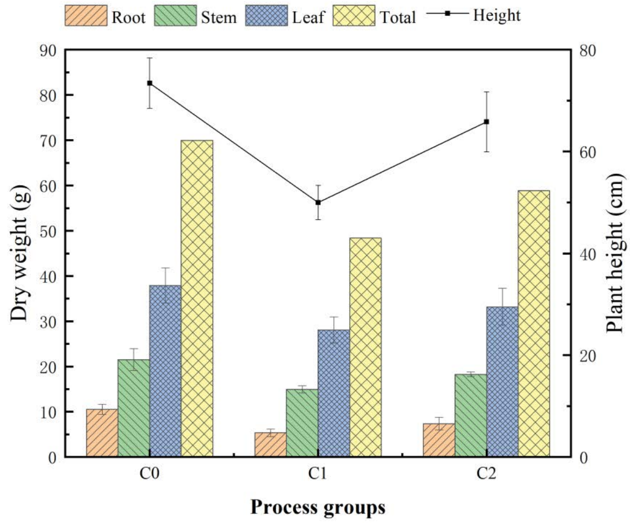


Fig. 8. Effects of different treatments on cabbage mustard biomass (C0: Mo-free soil; C1: Mo-contaminated soil; C2: FeS-treated soil).

3.5.2. Accumulation and translocation of Mo(VI)

The remediation of Mo(VI)-contaminated soil was aimed at reducing Mo uptake and migration in plants. To further validate the immobilization efficiency of FeS on Mo(VI) in soil, the accumulation and translocation of Mo in the plants grown in different soils were compared. The root, stem, and leaf of the cabbage mustard grown in C1 contained, respectively, 5.15, 2.95, and 0.82 mg/g of Mo(VI), as shown in Fig. 9. The root's, stem's, and leaf's respective Mo contents in C2 were 3.08, 0.85, and 0.27 mg/g, indicating that Mo contents in plants were all decreased compared with that in C1. This indicated that the addition of FeS to Mo(VI)-contaminated soil significantly decreased the content of Mo in the cabbage mustard tissues.

The enrichment ability of heavy metals is an important basis for the selection of remedial plants, and the relative ratio of heavy metal content in plants to soil and their distribution characteristics in plants are important indicators for the study of plant enrichment of heavy metals [28]. The calculation methods of bio-concentration factors (BCF) and transport factors (TF) are as follows [Eqs. (8) and (9)]:

$$\mathrm{BCF} = \frac{P}{E} \tag{8}$$

$$\mathrm{TF} = \frac{A_s}{A_r} \tag{9}$$

where P and E are the concentration of Mo in plants (mg/kg) and the residual concentration of Mo in the soil (mg/kg), respectively. A_s and A_r are the concentration of Mo in the aerial part of the plant (mg/kg) and the concentration of Mo in the underground part of the plant (mg/kg), respectively.

As shown in Fig. 9, the BCF values of C1 and C2 groups were 0.432 and 0.247, respectively. Obviously, the addition of FeS reduced the Mo enrichment capacity of cabbage. Besides, after FeS restoration, the TF value of Mo in the plant was lower than that of the original soil, which proved that FeS can inhibit the transport of Mo from the root of cabbage to the aboveground part. As shown in Figs. 8 and 9, the high content of Mo in C1 had strong toxic effects on cabbage mustard growth, such as growth retardation, root stunting, and lower dry biomass [45]. However, because the bioavailable form of Mo in the soil is reduced, cabbage mustard growth in C2 was increased when compared to C1 growth. FeS treatment was therefore feasible for Mo-contaminated soil.

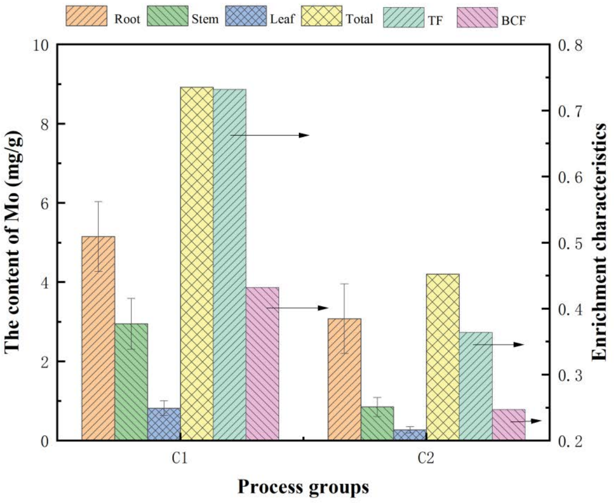


Fig. 9. Effects of different treatment methods on Mo(VI) contents and enrichment characteristics in cabbage mustard (C1: Mo-contaminated soil; C2: FeS-treated soil).

4. Conclusions

The leaching amount of Mo(VI) in soil was significantly reduced after nano-FeS remediation through adsorption and reduction. Moreover, the leaching amount of Mo(VI) gradually decreased with the increase of FeS addition and reaction time. The presence of NOM increased the content of soluble Mo in the soil and promoted the leaching of Mo(VI) in the soil. Opposite results were obtained with the presence of SO_4^{2-} and $H_2PO_4^-$. With the coexistence of NOM or inorganic salts, nano-FeS effectively improved the immobilization of soil Mo(VI) and increased the residue Mo. Additionally, for cabbage mustard seedlings, nano-FeS could effectively reduce the bioavailability and bioaccumulation of Mo. Thus, nano-FeS has the potential to be used in the field to clean up Mo(VI)-contaminated soil.

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